

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polypropylene/Cellulosic Fiber Composites Chemical Treatment of the Cellulose Assuming Compatibilization Between the Two Materials

C. Joly^a; M. Kofman^a; R. Gauthier^a

^a Laboratoire d'Etudes des Matériaux Plastiques et Biomatériaux URA CNRS 507, Université Claude Bernard Lyon, Villeurbanne, Cedex, France

To cite this Article Joly, C. , Kofman, M. and Gauthier, R.(1996) 'Polypropylene/Cellulosic Fiber Composites Chemical Treatment of the Cellulose Assuming Compatibilization Between the Two Materials', Journal of Macromolecular Science, Part A, 33: 12, 1981 – 1996

To link to this Article: DOI: 10.1080/10601329608011023

URL: <http://dx.doi.org/10.1080/10601329608011023>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYPROPYLENE/CELLULOSIC FIBER COMPOSITES: CHEMICAL TREATMENT OF THE CELLULOSE ASSUMING COMPATIBILIZATION BETWEEN THE TWO MATERIALS

C. JOLY, M. KOFMAN, and R. GAUTHIER*

Laboratoire d'Études des Matériaux Plastiques et Biomatériaux
URA CNRS 507
Université Claude Bernard Lyon I
43 Boulevard du 11 Novembre 1918, F-69622 Villeurbanne Cedex,
France

ABSTRACT

The present work deals with the realization of composites with a polypropylene (PP) matrix and cellulosic fibers as reinforcement. In order to achieve a good adhesion with the PP matrix, the modification of different cellulosic fibers has been performed with various chemical functions: carboxylic anhydrides, isocyanates, vinylsulfone, and chlorotriazine systems. All these compatibilizing agents carry an alkyl chain or a PP chain. Grafting is evidenced by infrared and ESCA spectroscopies, and the grafting rates for the different chemicals are determined by microweighing measurements. Modification of the surface characteristics is followed by wettability tests and inverse gas chromatography. Determination of the water sorption isotherm for the treated fibers shows an important decrease in water regain in the case of isocyanate treatments in swelling medium. Enhancement of adhesion between fibers and the matrix is demonstrated by mechanical tests: the interfacial shear stress obtained by the microbond test increases by 70% for cellulosic fibers treated with maleated PP. This may be the result of entanglements

between PP chains, but for macrocomposites the effect is much more limited due to the predominance of external factors during development of the composite.

INTRODUCTION

Composite systems consist in an association of a matrix and a reinforcement or filler such as short fibers, continuous fibers, powders, spherical balls, etc. The result is a synergetic effect on the global mechanical properties of the system. For instance, spherical balls of elastomer dispersed in a thermoset allow impact damping. For matrices reinforced with fibers, the stresses applied to the whole composite are transferred to the fibers, taking advantage of their high modulus. A good adhesion between matrix and fibers is necessary for this transfer.

These composites are widely used in packaging, construction, transportation, etc. At the end of their useful lives, these products are concentrated in waste areas and present environmental problems: storage, only partial combustibility, a source of pollution, etc. All aspects which were favorable during their period of use (stability, resistance, durability) now operate against their destruction.

In the automotive industry, new requirements in economic and environmental concepts are used in the manufacture of all parts:

- Use of cheap and light materials

- Use of fewer materials to make the selection of recycling or destruction easier

- No production of pollutants by combustion

With these imperatives, a good candidate for a matrix is thermoplastic polypropylene due to its low price, its chemical innocuity, and its ease to processing, but it has to be reinforced with fibers in order to reach the expected mechanical properties.

For fiber/matrix composites, the man-made fibers generally used are glass, carbon, steel, polyesters, polyamides, and polyaramides. Some of them have the very high performances (and are priced accordingly) required. Replacing synthetic materials by natural ones has many advantages:

- The use of renewable and worldwide available products, saving those based on petroleum

- The diminution of pollution because of their biodegradability and combustibility

As for polyesters matrices, glass fibers, which have also been used for the reinforcement of polypropylene, present many inconveniences. Vegetal fibers with cellulose as their major component are now being tested to replace glass fibers, and they may afford many advantages:

- A density about half that of glass fibers

- No abrasion of the processing machines

- As single filaments, their modulus is almost as high as that of aramides

- They can withstand the processing temperature of polypropylene ($\approx 200^{\circ}\text{C}$)

Their use in such a new field of applications may also represent a good opportunity for the enhancement of agricultural by-products

Composites made of cellulosic fibers and polypropylene are 100% combustible, without the production of noxious gases nor solid residues

But if we look at the chemical formulas of both components (Scheme 1), there is evidence of a problem in associating hydrophilic cellulosic fibers with a hydrophobic matrix. The answer to this poor adhesion lies in a chemical treatment of the fibers with compatibilizing agents. These compounds possess:

A function able to react with the hydroxylic groups of cellulose

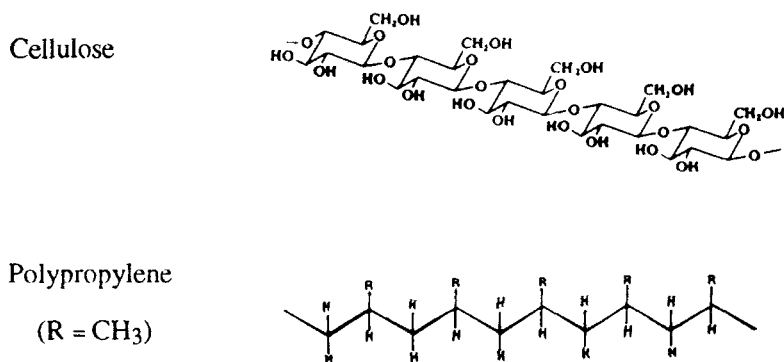
A more or less long alkyl chain, even a polypropylene chain, which decreases the hydrophilicity of the fiber and at the same time makes its surface more convenient for good adhesion to the matrix.

With these principles in mind, much work has been done in the past 15 years with different vegetal sources (Table 1). Except for some exotic materials, cellulose and wood fibers are the most often used.

Cellulosic fibers are located in the wall of cells of different organs: *bast fibers* in the stems and stalks (flax, jute, ramie, . . .), *leaf fibers* (sisal, banana, . . .), and *seed fibers* (cotton, kapok, . . .). The raw material containing these fibers has to be processed to isolate the "pure" fibers from the so-called "natural composite" where the technical fibers are bound together by pectic cements. Steam explosion with pretreatment by sodium hydroxide solution allows for the separation of these fibers by dissolution of the cements [32, 33].

Wood fibers contain mainly cellulose, hemicellulose, and lignin. Paper pulp is often used because its handling is standardized and gives rise to constant properties (thermomechanical or chemothermomechanical pulp). These wood fibers are primarily studied in countries where paper pulp is of economical importance (Canada, Sweden, . . .).

Cellulosic fibers/polypropylene composites are presently used in the automotive industry for dashboards, rear window shelves, and roof and doors upholstery.



SCHEME 1. Structures of cellulose and polypropylene.

TABLE 1. Composites Made of Vegetal Material and Thermoplastic

Matrix	Vegetal material	Literature
Polyethylene (PE)	Cellulose	1-3
	Wood fibers	4-8
	Wood flour	9
	Sugar cane bagasse	10
	Nut shell flour	11, 12
	Sisal fibers	13, 14
Polypropylene (PP)	Cellulose	15, 16
	Wood fibers	4, 17-20
	Wood flour	21-24
	Flax or ramie fibers	25, 26
PE/PP	Jute	27
Polystyrene	Wood fibers	28, 29
Polyester	Jute	30
Polyepoxide	Bamboo cane	31

CHEMICAL TREATMENTS OF CELLULOSIC FIBERS

Materials

The chemical grafting in this work was performed by different compatibilizing agents bearing different functions (Scheme 2):

Carboxylic anhydrides: maleic anhydride (MA) grafted onto a polypropylene (PP) chain to give the widely used PP-*graft*-MAs. Octadecyl succinic anhydride C18-SA is also used as a model compound

Alkyl isocyanates, R-NCO, with small alkyl chains having 3 to 18 carbon atoms

Two particular systems, both bearing an octadecyl chain, and either a vinyl sulfone function or a dichlorotriazine ring. These two functions are commonly used as binding systems in the synthesis of reactive dyes for the dyeing of cotton. Their interest lies in the possibility of operating with textile techniques for ennoblement and in an aqueous medium (solution or emulsion). The compounds C18-VS and C18-T were synthesized in the laboratory

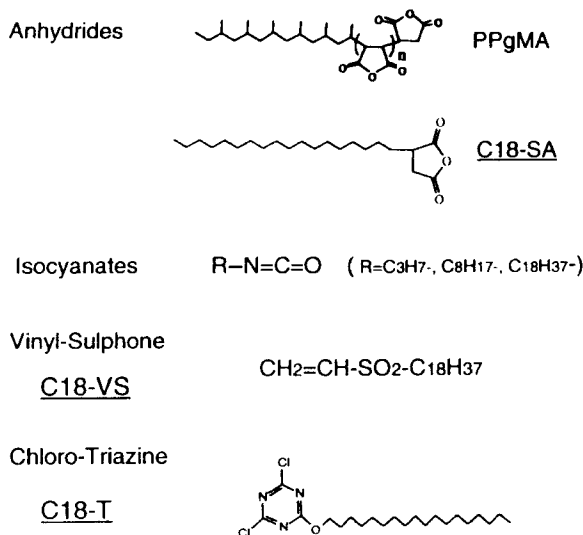
Three cellulosic samples were tested:

Macroscopic composites made with flax fibers (*Linum usitatissimum*)

Pure cellulose powder (Sigma) for modeling chemical reactions

Ramie fiber is specifically suited for microbond tests because it presents a constant diameter over a great length without defaults

As a matrix, PP with a melt flow index of 40 and M_w/M_n values of 160,000/46,000 was used in form of fibers to allow for processing as a textile.



SCHEME 2. Chemical structures of the compatibilizing agents.

Treatment

Treatment consists of soaking the fibers in a solution or emulsion of the compatibilizing agent and heating for a few hours. The fibers are then Soxhlet extracted so that all the molecules of a reagent not chemically linked to the fibers are eliminated. Swelling of the fiber may occur with some solvents, such as pyridine for isocyanate treatment.

Characterization

Evidence of the effective bonding of the agent onto the fiber after grafting is obtained by a quantitative determination of the grafting rates. This is difficult because of the very low rates, but by using compressed pellets of cellulose fibers and microweighing measurements we obtained the grafting rates shown in Table 2. The fibers have to be correctly desorbed of all water and solvent they contain under high vacuum before all measurements.

Grafting rates in the second column of Table 2 are weight percentages. The results for three successive treatments with C18-T show the good reproducibility of the method for the determination of grafting rates. As the different reagents possess very different molecular weights, the molar percentage of grafting is more significant (third column) but is no interest for very large molecules like *PP-graft-MA*. In the fourth column the fraction of hydroxyl groups reacted is given:

With nonswelling solvents and macromolecules as grafts (*PP-graft-MA*), one OH group out of 19,000 to 45,000 reacts. It is clear that the grafting occurs only at the surface of the fiber

With pyridine as solvent and small grafts such as isocyanates, one OH group out of 100 to 250 reacts. Grafting now takes place also in the bulk of the fiber

TABLE 2. Grafting Rates on Cellulose Powder

Reagents	Grafting rates on cellulose powder		
	Weight %	Molar %	1 OH reacted out of
Isocyanates:			
C3-NCO	1.8	3.5	1/86
C8-NCO	1.2	1.2	1/250
C18-NCO	2.2	1.2	1/250
C18-T:			
(1x)	0.19	0.08	1/3750
(2x)	0.38	0.16	1/1875
(3x)	0.55	0.23	1/1300
C18-VS	0.6		
C18-SA	0.37	0.17	1/1760
PPgMA:			
Epolene 43	0.30		1/19.000
Hercoprime G	0.52		1/33.000
Hostaprime HC5	0.23		1/45.000

When grafting rates are high enough, the new formed linkages can be visualized by infrared spectroscopy. Figure 1 shows the urethane bond for cellulose treated with octadecylisocyanate.

ESCA analysis is also suitable for detecting the grafted alkyl chain. Figure 2 shows the deconvolution of the C_{1s} peak for cellulose treated by C18-T into three contributions. The increase of the peak at 286.5 eV corresponds to the octadecyl chain grafted on the cellulose fiber by the chlorotriazine ring intermediate. This allows us to estimate that in the "skin" analyzed by this technique, the reagent represents 35% by weight.

Control of the thermal stability of these new linkages is also indispensable. For instance, cellulose and flax fibers treated with octylisocyanate can support a temperature of 190°C for 1 hour without degradation of the urethane linkage (Fig. 3).

EFFECTS OF TREATMENT ON THE PROPERTIES OF FIBER

The grafting consists of replacing some hydrogen atoms of the hydroxylic groups by the function F' and an alkyl chain (Scheme 3). As these OH groups are at the origin of the hydrophilicity of the cellulosic fiber, the grafting may be responsible for modification 1) of the hydrophilic character of the fiber's surface and 2) of the water sorption in the bulk of the fiber. Both are expected to decrease.

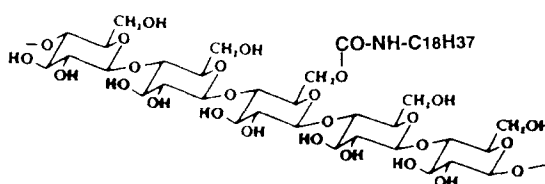
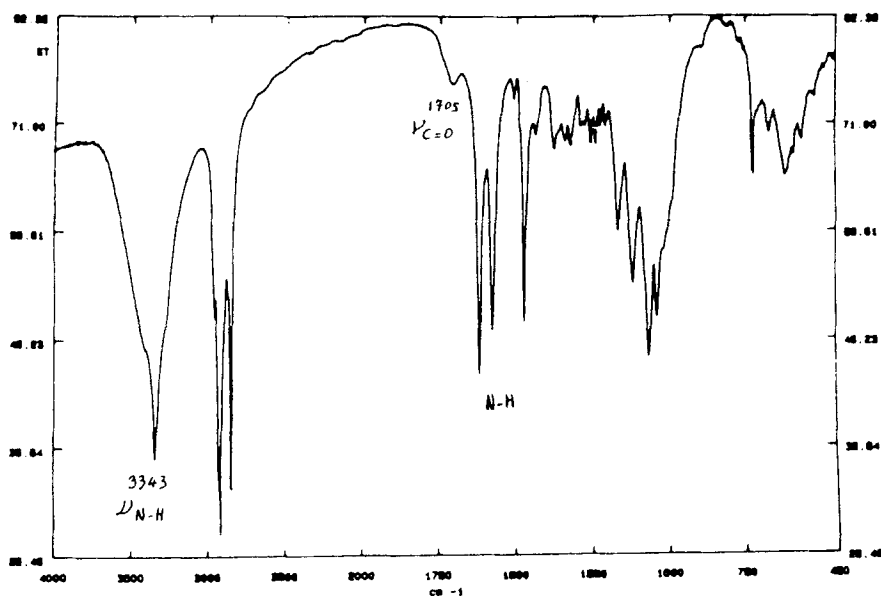


FIG. 1. IR spectrum of cellulose treated with octadecylisocyanate (C18-NCO).

Surface Modification

For the surface properties, two tests show the relative hydrophobic character of the treated fibers:

When a water droplet is deposited on a nontreated rayon fabric, it is immediately absorbed into the filaments. But if the fabric has been treated, the droplet remains unchanged at the surface for about 20–30 minutes.

For the Takase test [16], cellulosic fibers are shaken in a biphasic mixture of water and ether. When not treated, the fibers sediment at the bottom of the tube; when treated, their partial hydrophobic character allows them to remain at the interface (Fig. 4).

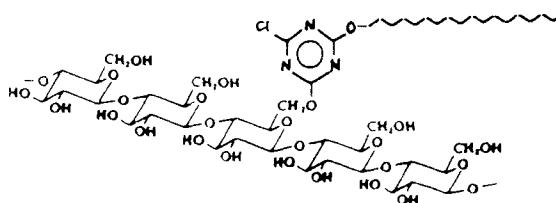
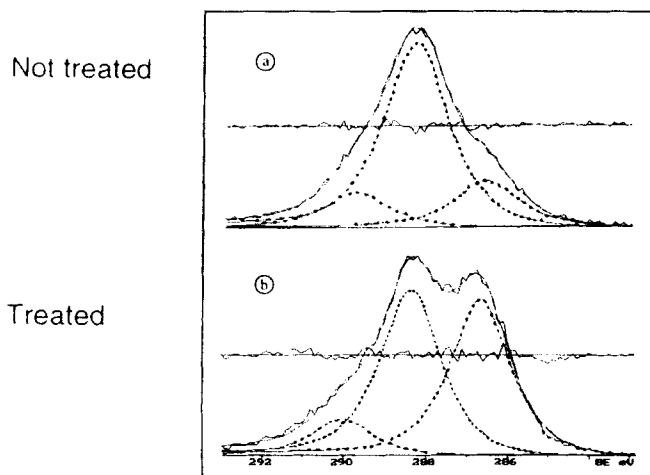


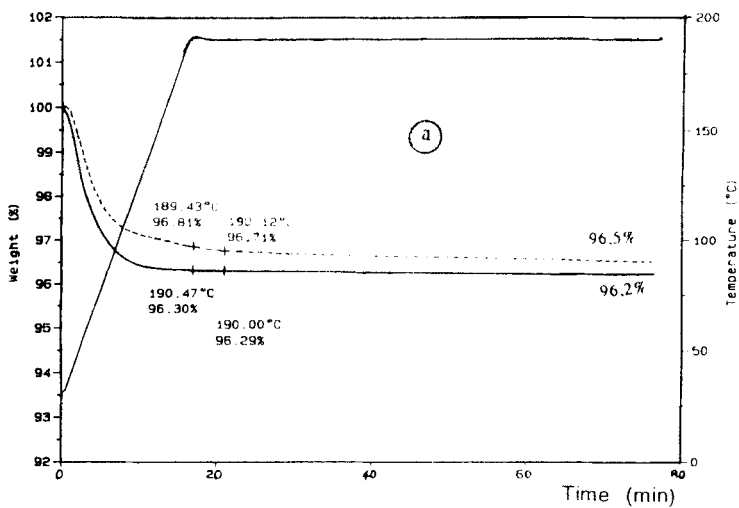
FIG. 2. ESCA analysis of cellulose: deconvolution of the C_{1s} peak. (A) Before treatment and (B) after treatment with C18-T.

Another way to characterize this modification is to determine the surface parameters using inverse gas chromatography [34]. Columns are fitted with treated or nontreated fibers, and pure probe molecules are injected. Their retention time after a large number of adsorption/desorption cycles depends on interactions with active sites at the surface (Fig. 5).

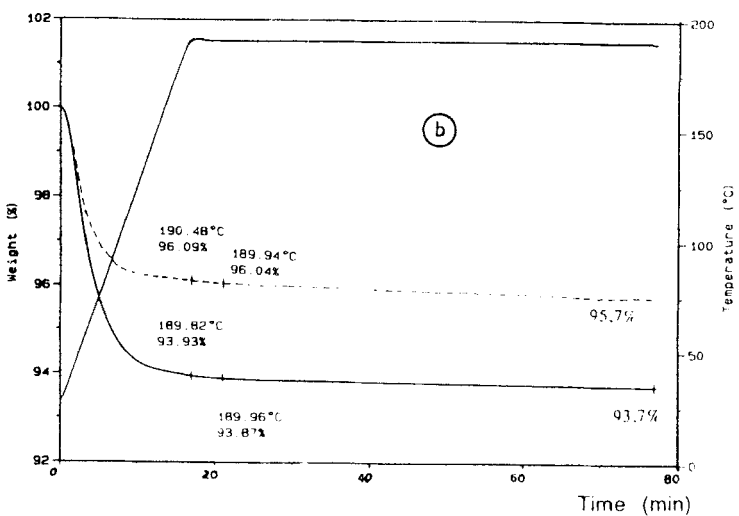
With nonpolar molecules such as alkanes, the technique gives the dispersive component of surface energy γ_S^D . Treatment by C18-T increases γ_S^D , which is explained by better hydrocarbon/alkyl chain interaction (Fig. 6A).

With polar molecules which have a basic character, like tetrahydrofuran, the technique gives the specific component of free energy of adsorption ΔG_{sp} . Here, the same treatment decreases ΔG_{sp} due to the disappearance of some acidic hydrogen atoms at the surface (Fig. 6B).

Cellulose

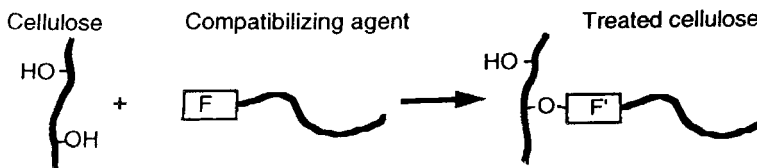


Flax



Not treated ——— C8-NCO treated - - - - -

FIG. 3. Thermogravimetric analysis of (a) cellulose and (b) flax before and after treatment with octylisocyanate (C8-NCO).



SCHEME 3. Chemical modification due to grafting.

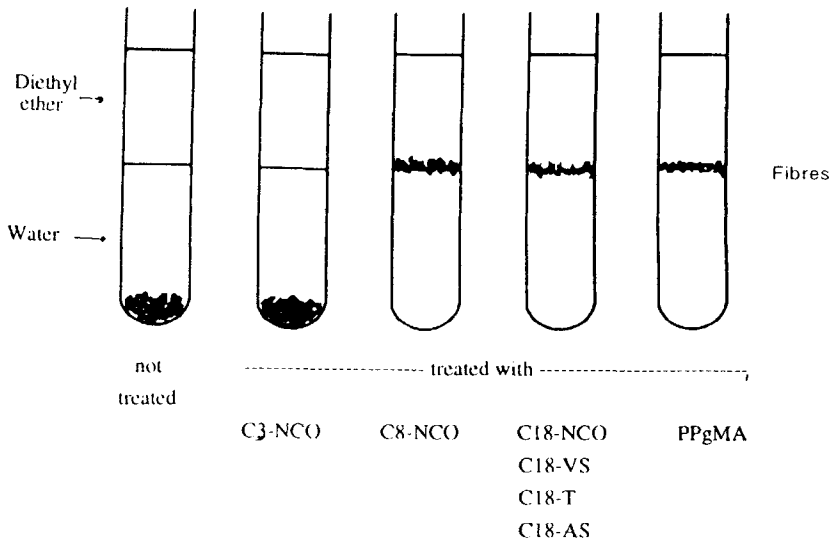


FIG. 4. Schematization of the test of Takase.

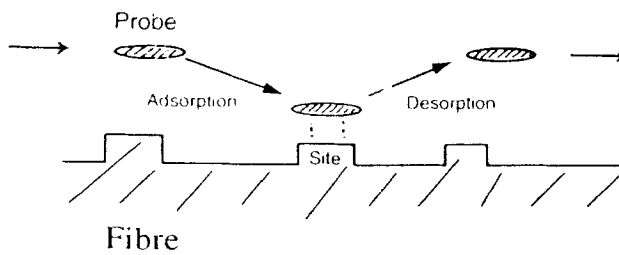
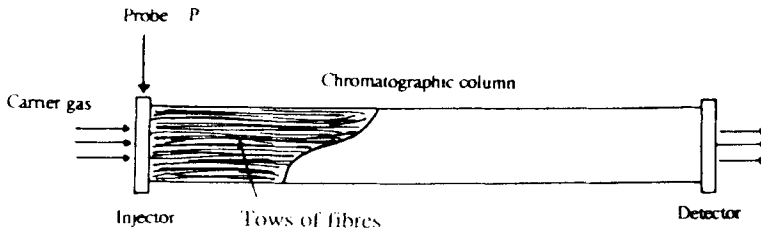


FIG. 5. Inverse gas chromatography: interactions of probe molecules with active sites of a solid surface.

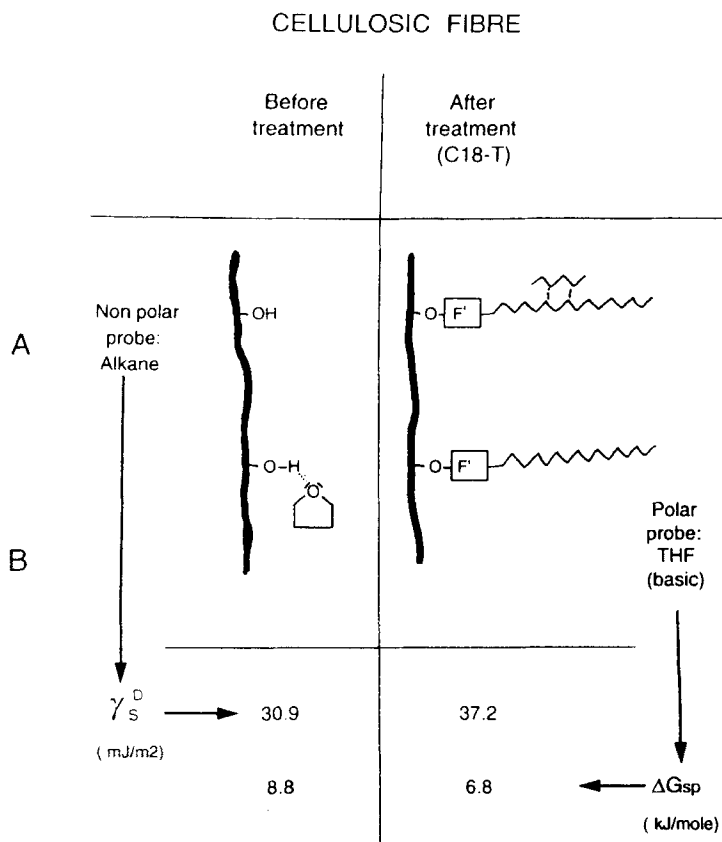


FIG. 6. Interactions of cellulose surface with nonpolar molecules leading to γ_s^D (A) and polar molecules leading to ΔG_{sp} (B).

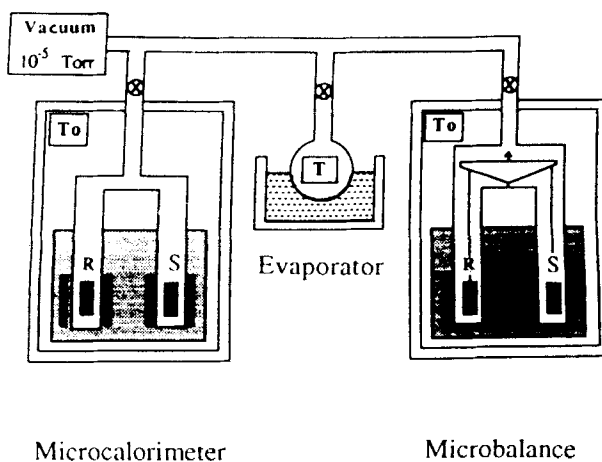


FIG. 7. Microcalorimeter and microbalance coupled for sorption measurements. S = samples. R = reference. T = temperature.

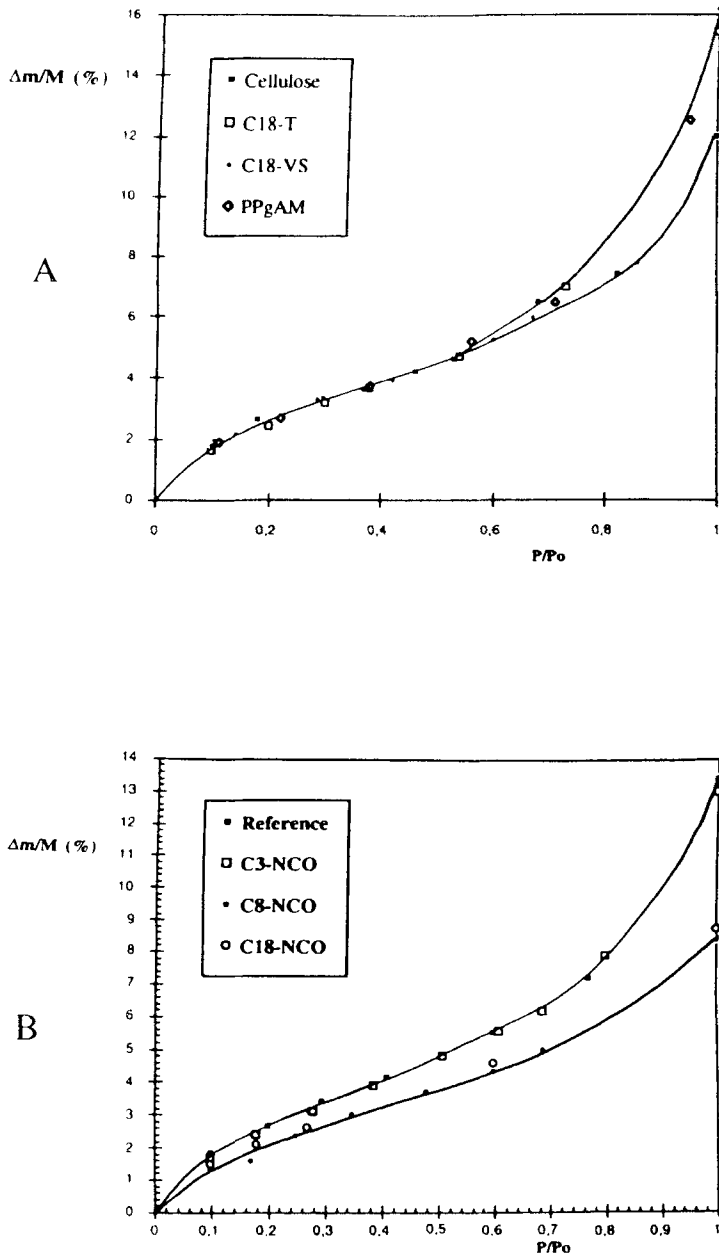


FIG. 8. Water sorption isotherms for cellulose treated with (A) PPgMA, C18-T, or C18-VS, or with (B) isocyanates.

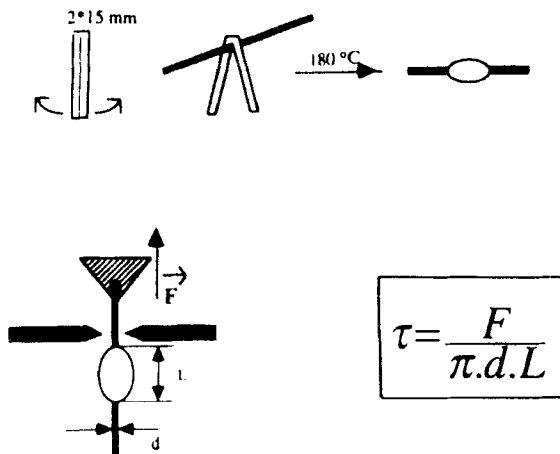


FIG. 9. Microbond test used for the determination of the interfacial shear stress τ .

TABLE 3. Interfacial Shear Stresses τ Determined by the Microbond Test

Fibers	Not treated	Treated with	
		C8-NCO	PPgMA
$\bar{\tau}^a$ (MPa)	9.6	9.2	16.3

^aMean value for 30-50 experiments.

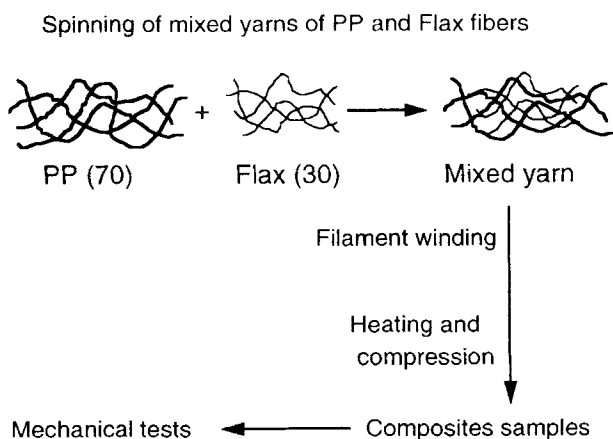


FIG. 10. Realization of macroscopic polypropylene/flax composites.

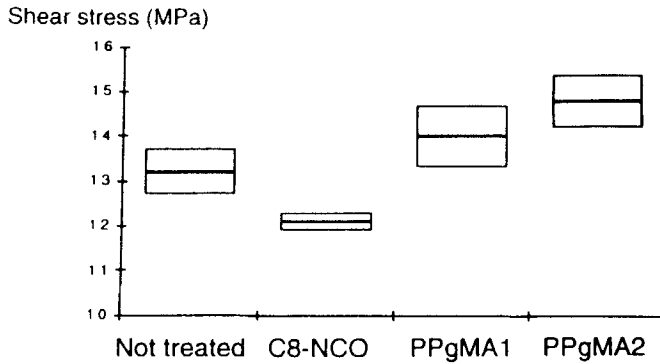


FIG. 11. Effect of treatments on the interfacial shear stress τ in macroscopic composites.

Bulk Modification

Modifications due to grafting also occur in the bulk of the cellulosic fiber and have consequences on water sorption by the fiber.

The apparatus used for the determination of the water sorption isotherm [35] is made of a microbalance and a microcalorimeter in connection with a high vacuum system (Fig. 7). Samples of fibers are placed in each part of the apparatus and totally desorbed of water and solvent molecules. The partial pressure of water vapor in the system is established. The value of this pressure is regulated by the temperature T of the evaporator. Following the mass gain in the microbalance versus the partial pressure gives the sorption isotherm. The thermic effects associated with this sorption are measured in the microcalorimeter to give the sorption enthalpy. If these values are followed over time, kinetic information is obtained.

In a nonswelling or low swelling medium, fibers treated by PP-graft-MA, C18-T, or C18-VS give the same isotherms as nontreated fibers (Fig. 8A). Grafting rates are too small and grafts are located at the surface, so that there is no perceptible effect on water sorption.

For fibers treated in a swelling solvent (pyridine for isocyanates), C8-NCO and C18-NCO treatments show (Fig. 8B) a notable diminution of water sorption in comparison with nontreated fibers or fibers treated with a small alkyl chain (C3-NCO). The diminution is important (about 25% over the total range of partial pressure) for low grafting rates (1.2 to 2.2%, or one OH group reacted out of 250).

EFFECTS OF TREATMENT ON THE MECHANICAL PROPERTIES OF COMPOSITES

Treatments were performed with the aim of enhancing adhesion between the fibers and the matrix. Mechanical tests were conducted on microcomposites and on unidirectional macrocomposites.

The microbond test [36] is used with a ramie monofilament on which a drop of polypropylene is deposited. The interfacial shear stress τ (Fig. 9) allows the

measured debonding force to be calculated. The results show a better adherence with PP-*graft*-MA-treated fibers: τ increases by about 70% (Table 3).

Macroscopic composites are prepared by spinning mixed yarns (PP/flax: 70/30 by weight), filament winding, heating, and compression (Fig. 10). The composites specimens are then mechanically tested. Shear stresses increase with PP-*graft*-MA treatment, but with isocyanate treatment the lower dispersion in the results indicates that the interface is more controlled (Fig. 11).

CONCLUSIONS

Cellulosic fibers may be incorporated as a reinforcement in a polypropylene matrix. Chemical treatment is necessary for good compatibilization between two components.

Treatment with small molecules in a swelling medium reduces the water sorption of a fiber due to a reaction in the bulk of the fiber, but the chain is not long enough for high adhesion at the interface

Treatment with large molecules like PP-*graft*-MA occurs only at the surface and so enhances adhesion. The hydrophilicity of treated fibers is not reduced in comparison with nontreated ones

Other questions are under investigation: influence of the nature and length of the alkyl chain, water sorption by the composites, aging in a moist environment, use of wood fibers, etc.

REFERENCES

- [1] R. G. Raj and B. V. Kokta, *Polym. Eng. Sci.*, **31**, 1358 (1991).
- [2] C. M. G. Carlsson and G. Ström, *Surf. Interface Anal.*, **17**, 511 (1991).
- [3] Y. H. Zang and S. Sapiaha, *Polymer*, **32**, 489 (1991).
- [4] C. Klason, J. Kubat, and H. E. Strömvall, *Int. J. Polym. Mater.*, **10**, 159 (1984).
- [5] S. Sapiaha, P. Allard, and Y. H. Zang, *J. Appl. Polym. Sci.*, **41**, 2039 (1990).
- [6] S. Sapiaha, J. P. Pupo, and H. P. Schreiber, *Ibid.*, **37**, 233 (1989).
- [7] R. G. Raj, B. V. Kokta, D. Maldas, and C. Daneault, *Polym. Comp.*, **9**, 404 (1988).
- [8] R. G. Raj, B. V. Kokta, G. Groleau, and C. Daneault, *Plast. Rubber Proc. Appl.*, **11**, 215 (1989).
- [9] S. N. Maiti and K. Singh, *J. Appl. Polym. Sci.*, **32**, 4285 (1986).
- [10] R. G. Raj and B. V. Kokta, *Eur. Polym. J.*, **27**, 1121 (1991).
- [11] J. M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609 (1991).
- [12] R. G. Raj, B. V. Kokta, F. Dembele, and B. Sanschagrín, *Ibid.*, **38**, 1987 (1989).
- [13] R. G. Raj, B. V. Kokta, and C. Daneault, *Int. J. Polym. Mater.*, **12**, 239 (1989).
- [14] R. T. Woodhams, G. Thomas, and D. K. Rodgers, *Polym. Eng. Sci.*, **24**, 15 (1984).

- [15] M. Xanthos, *Plast. Rubber Process. Appl.*, **3**, 223 (1983).
- [16] S. Takase and N. Shiraishi, *J. Appl. Polym. Sci.*, **37**, 645 (1989).
- [17] G. E. Myers, C. Gonzales, I. S. Chahyadi, C. A. Coberly, and D. S. Ermer, *Int. J. Polym. Mater.*, **15**, 171 (1991).
- [18] H. Dalväg, C. Klason, and H. E. Strömvall, *Ibid.*, **11**, 9 (1985).
- [19] S. N. Maiti and R. Subbarao, *Ibid.*, **15**, 1 (1991).
- [20] G. E. Myers, I. S. Chahyadi, C. A. Coberly, and D. S. Ermer, *Ibid.*, **15**, 21 (1991).
- [21] K. P. Mieck, A. Nechwatal, and C. Knobelsdorf, *TechTextil Symposium 93*, Frankfurt, June 1993, 3.11.
- [22] J. Colijn, *Ibid.*, 3.12.
- [23] D. Maldas and B. V. Kokta, *J. Appl. Polym. Sci.*, **41**, 185 (1990).
- [24] D. N. S. Hon and W. Y. Chao, *Ibid.*, **50**, 7 (1993).
- [25] R. G. Raj, B. V. Kokta, and J. D. Nizio, *Ibid.*, **45**, 91 (1992).
- [26] R. G. Raj, B. V. Kokta, and J. D. Nizio, *Plast. Rubber Process. Appl.*, p. 75 (1992).
- [27] A. C. Karmaker and G. Hinrichsen, *Polym.-Plast. Technol. Eng.*, **30**, 609 (1991).
- [28] J. Kuruvilla, T. Sabu, C. Pavithran, and M. Brahmakumar, *J. Appl. Polym. Sci.*, **47**, 1731 (1993).
- [29] J. Kuruvilla, T. Sabu, and C. Pavithran, *Mater. Lett.*, **15**, 224 (1992); *J. Reinforc. Plast. Comp.*, **12**, 139 (1993).
- [30] P. J. Roe and M. P. Ansell, *J. Mater. Sci.*, **20**, 4015 (1985).
- [31] S. Jain, R. Kumar, and U. C. Jindal, *Ibid.*, **27**, 4598 (1992).
- [32] M. Sotton and M. Ferrari, *SET 88*, Milan, October 1988.
- [33] B. Focher, A. Marzetti, G. Conio, E. Marsano, A. Cosani, and M. Terbojevich, *J. Appl. Polym. Sci.*, **51**, 583 (1994).
- [34] D. R. Lloyd, T. C. Ward, and H. P. Schreiber, *Inverse Gas Chromatography* (ACS Symp. Ser. 391), American Chemical Society, Washington, D.C., 1989.
- [35] M. Escoubes, M. Pineri, E. Eisenberg, and S. Gauthier, *J. Appl. Polym. Sci.*, **29**, 1249 (1984).
- [36] B. Miller, P. Muri, and L. Rebenfeld, *Compos. Sci. Technol.*, **28**, 17 (1987).