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Modified Cellulose Fibers as Reinforcing Fillers for Macromolecular Matrices

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Summary: Various cellulose substrates were submitted to different surface OH chemical modifications in non-swelling media and then fully characterised by FTIR, XPS, contact angle measurements and elemental analysis. The alternative procedures adopted were:

(i) simple grafting with monomeric or oligomeric agents which bore one or several reactive functions, either as a single terminal moiety or as numerous moieties placed along the chain;
(ii) grafting with polymerisable molecules, which involved the use of reagents of small molecular size, but bearing two functions, one able of reacting with the surface cellulose OH groups and the other used as a source of subsequent covalent linkage with the matrix;
(iii) the use of planar stiff molecular configurations bearing two identical reactive functions, calling upon the working hypothesis that only one function will react with a cellulose OH group, whereas the other will be left to copolymerise with the matrix;
(iv) coupling with siloxanes using the same strategy as in (ii), except for the fact that this specific approach involves molecules already commonly used in glass fibres treatment;
(v) grafting with organometallics such as triethyl aluminium following the same working hypothesis as in (iii) but with a second reaction involving monomeric or polymeric alcohols or amines.

Keywords: cellulose; chemical grafting; surface characterisation; surface treatment

Introduction

The chemical modification of the surface of lignocellulosic fibres has attracted considerable attention in recent years because of the growing interest in the use of these natural filaments as reinforcing agents in macromolecular composite materials[1]. The main driving force of this

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research activity resides in the possibility of recycling such composites at the end of their life cycle, in contrast with glass-fibre-based counterparts. Additional advantages related to the use of lignocellulosic fibres include their renewable character, and the fact that they are available ubiquitously at modest costs, albeit from different sources like annual plants and wood species.

The quality of the fibre-matrix interface in composite materials plays a fundamental role on their mechanical properties and often requires the surface modification of the fibres to achieve maximum compatibility and therefore good adhesion. The functions exploited for these coupling reactions applied to cellulose include isocyanates, anhydrides, oxiranes and siloxanes, i.e. moieties capable of reacting with the surface hydroxyl groups of the fibres. Additionally, the modification should provide an efficient hydrophobic barrier for the cellulose fibres in order to avoid moisture uptake and the consequent loss of mechanical properties, in the event of spurious contacts with ambient air (e.g. from the open end of a sectioned piece of the composite material). Our laboratory has been actively involved in all these strategies[2-10], as well as in a more "physical" alternative, which calls upon the construction of a sleeve of polymer around the fibres by admicellar polymerisation[11]. The purpose of this paper is to provide a broad outlook of these different chemical approaches, as applied in our laboratory, with particular emphasis on recent advances.

Experimental

Several types of cellulose substrates were used for these modifications, including a semi-crystalline powder (Avicell), a home-made additive-free tracing paper (NMMO-regenerated continuous fibres with a regular diameter of about 30 μm (NMMO = N-Methyl-Morpholine) and Whatman filter papers. This allowed the various techniques of characterisation described below to be applied to the appropriate corresponding morphology. All reactions were carried out heterogeneously with the fibres suspended in the organic solution of an excess of the grafting reagent. The temperature and duration of the modifications depended on the specific context and varied between room temperature and 80°C and between a few hours and a few days, respectively. The characterisation of the modified fibres always followed the removal of the unreacted agent, by a Soxhlet extraction with the appropriate solvent. FTIR in different modes (Transmission, ATR, DRIFT) and XPS spectroscopy, elemental analysis, dynamic and static contact angle measurements, inverse gas chromatography and scanning electron microscopy (SEM) were the essential tools utilised to assess the occurrence and the extent of the modification.

Results and Discussion

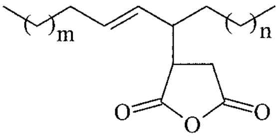
The different strategies and the corresponding results are discussed separately below, before drawing comparisons about their efficiency and potential applications. References are given to studies which have already been published for the reader who would wish to have more detailed information.

Simple grafting [2-4]

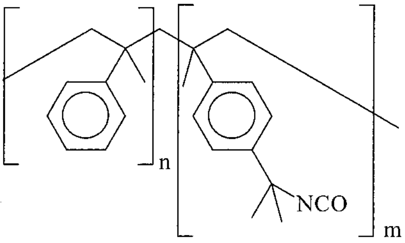
The fibres were treated with a variety of reagents bearing one or several functional groups (NCO, anhydride,...) in a cellulose non-swelling medium, e.g. methylene chloride or tetrahydrofuran (THF). Some of these agents were oligomeric structures which bore one reactive function, either as a terminal moiety (so that the coupling would give rise to "hairs" on the fibres), or as a central moiety along the oligomer (so that "umbrellas" would be clipped on the fibre surface). The modification took place successfully, albeit in modest amounts, as expected by the fact that only the surface OH groups could react in these conditions. A typical example of this approach is the reaction of a commercial alkyl succinic anhydride (ASA, structure 1), currently used as sizing agent in papermaking, viz. a mixture of C10 to C14 homologues bearing one cyclic carboxylic anhydride function pending from the middle of each molecule (umbrellas). After extraction of the excess of ASA, the fibres displayed a strong water repellence and the polar contribution to their surface energy decreased considerably, compared with that of the starting fibres.

Another type of reagent used here consisted of copolymers containing both conventional and reactive monomer units, so that the multiple coupling reactions between the cellulose OH groups and at least some of the functional groups of each macromolecule would append bridge-like structures at the surface of the fibres. As an example, a random poly(α-methyl-styrene-*co*-3-isopropenyl-α,α'-dimethylbenzyl isocyanate) (structure 2) was synthesised by cationic initiation. The ensuing NCO-modified styrene-like copolymer was carefully characterised in terms of structure and molecular weights by Vapour Pressure Osmometry and was found to have a DP of

~200 and contained some 20 NCO function per copolymer molecule[12, 13]. Its reaction with the cellulose fibres was monitored, after extraction of the unreacted copolymer, by elemental analysis (nitrogen content), FTIR (typical peaks for the urethane C=O and the aromatic moieties), XPS (presence of nitrogen and modification of the oxygen peaks of cellulose).



Structure 1



Structure 2

However, the most significant changes appeared in the fibre surface properties, as shown by contact angle measurements, which led to the calculation of the dispersive (34 mJ m^{-2}, as with polystyrene) and polar (only 1 mJ m^{-2}, compared with ~25 mJ m^{-2} for the starting cellulose) contributions to the surface energy, and by the observation of the polymer film covalently attached to the fibres by electron microscopy. Figure 1 shows an example of the contact angle of drop of water before and after grafting with polymer 2. The contact angle on the untreated paper rapidly decreased by spreading and absorption, whereas that related to the modified surface remained unchanged for hours.

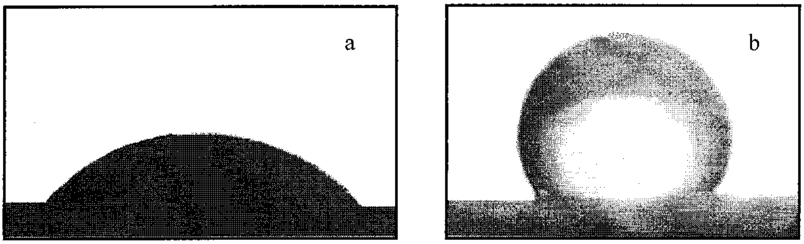


Figure 1. Instantaneous contact angle of a drop of water on tracing paper samples (a) before, and (b) after grafting with polymer 2.

Figure 2 gives the SEM microphotographs of NMMO cellulose fibres before and after modification with that coupling agent. Table 1 summarises the surface energy of cellulose before and after grafting with different agents, including those mentioned in this section.

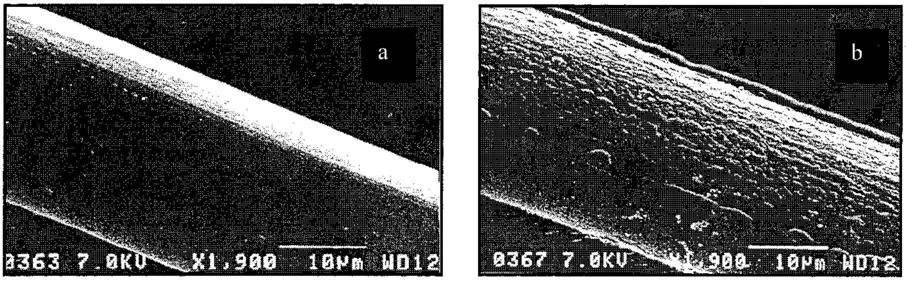
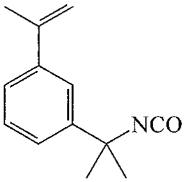


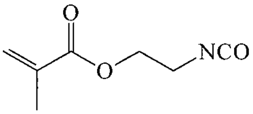
Figure 2. SEM micrographs of a NMMO cellulose fibre (a) before, and (b) after grafting with polymer 2.

Grafting with polymerisable molecules [2,3,5]

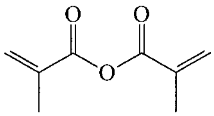
The next step in this saga called upon a different approach, which involved the use of reagents of small molecular size, but bearing both a function capable of reacting with the surface cellulose OH groups and one to be used as a source of covalent linkage with the matrix. Structures 3 to 6 illustrate this point:



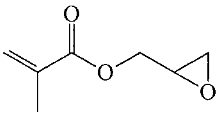
Structure 3



Structure 4



Structure 5



Structure 6

The procedure adopted with these reagents consisted in (i) carrying out the grafting with the fibres suspended in the monomer which was chosen as the source of the macromolecular matrix and thereafter (ii) induce the polymerisation of the medium. The polymerisable styrenic or acrylic moieties, attached to the surface of the fibres following the first grafting reaction, were supposed to participate in the polymerisation of the bulk monomer as co-monomer units and thus provide a continuity of covalent bonds between the substrate and the matrix. This was confirmed by extracting the entire unbound polymer and characterising the modified fibres. Their weight gain was as high as 10-15% (to compare with 1-2% when simple coupling with large molecules described in previous section) and the presence of covalently anchored polymer was readily detected by FTIR spectroscopy.

Thus FTIR spectroscopy was used to ascertain the occurrence of the grafting at each step and Figure 3 give a comparison of the FTIR spectra of microcrystalline cellulose (avicel) before, after treatment with **4,** and after copolymerisation with methyl methacrylate (MMA) and then extracted to remove all unbound polymer. This figure gave clear-cut evidence about the occurrence of the first step of grafting, by the presence of two main bands, namely at 1715 and 1642 cm^{-1} associated with the formation of ester moiety and the C=C of **4**, respectively (Figure 3b). Further evidence on the occurrence of the second step of grafting (copolymerisation between the growing MMA macroradicals and the unsaturation of **4**) can be shown examining Figure 3c. In this FTIR spectrum one can observe the increase of the band at 1726 cm^{-1}, attributed to carbonyl groups, which moreover shifted to higher frequencies. This is a clear indication of the presence of polyMMA chains bounds to the cellulose surface. The appearance of a shoulder at 2955 cm^{-1} associated to methyl groups of polyMMA confirms the above given hypothesis.

As expected, the surface properties of the fibres modified by this approach, determined by contact angle measurements applying the classical Owens-Wendt equation, resembled very closely those of the polymer which had been bound around them (Table 1). Apart from the actual success of the desired modification, the additional interest of this operating procedure is the fact that no solvent is needed, since the one-pot operation provides both the grafting of the fibres and the composite manufacture. The excess of reagent used in the first step is also utilised, since it polymerises with the matrix monomer during the second and final stage. It is important to emphasise that the presence of continuous covalent links between the fibres and the matrix represents the best way to optimise the quality of the adhesion at the interface between the two components of the composite. Examples of the composite materials prepared following this strategy include matrices made of polystyrene and different acrylic polymers.

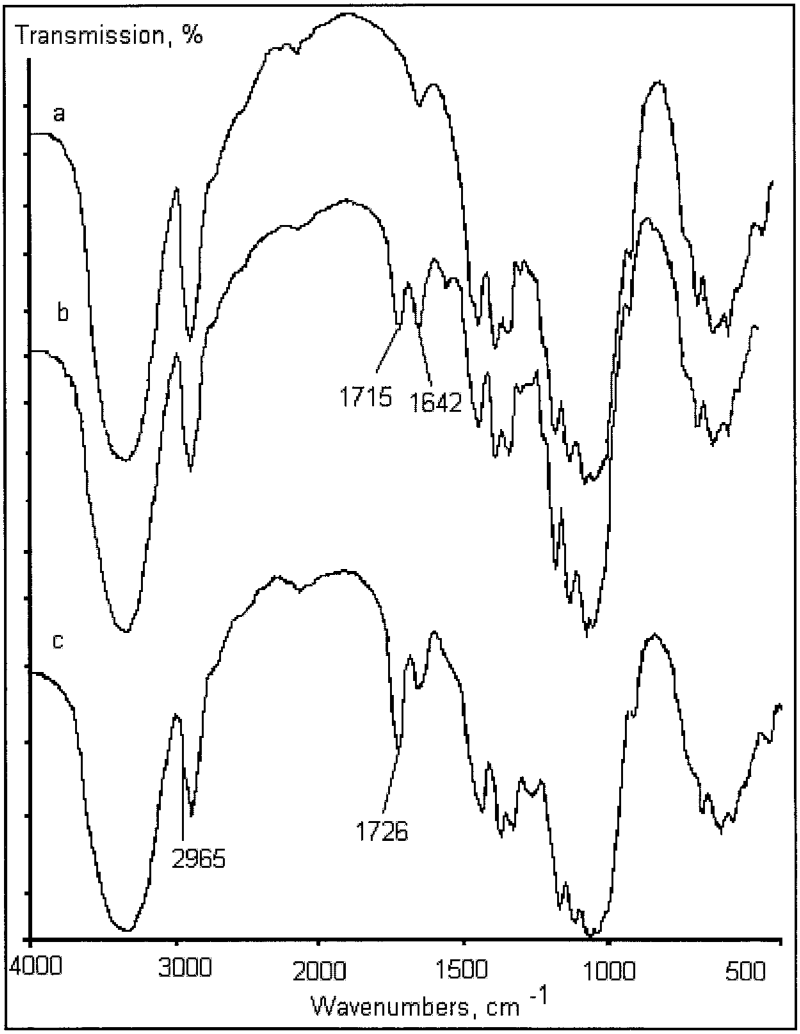


Figure 3. Transmission FTIR spectra of avicel before (a), after treatment with 4 (b), and after copolymerisation with methyl methacrylate (c).

Table 1. Surface energies of un-sized additive-free tracing paper before and after different treatments.

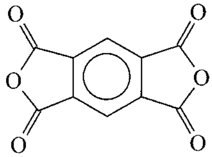
Grafting		Surface energy, mJ/m^2			Reference
First	Second	γ^D	γ^P	γ^T	
None	None	29.4	20.0	49.4	[4]
structure 1	None	27.3	8.6	35.9	[4]
structure 2	None	34.4	1.0	35.4	[4]
structure 3	None	42.7	0.3	43.0	[5]
structure 4	None	36.7	0.8	38.5	[5]
structure 3	Styrene	30.9	0.8	31.7	[5]
structure 3	MMA	44.6	0.1	44.7	[5]
structure 4	Styrene	30.9	0.8	31.7	[5]
structure 4	MMA	39.1	0.1	39.2	[5]
structure 9	None	46.9	0.1	47.0	[9]
structure 9	MMA	24.9	1.3	26.2	[9]
structure 9	Styrene	36.6	0.1	36.7	[9]
structure 10	None	33.3	9.2	43.5	[9]
structure 10	Epoxy	37.9	0.8	38.7	[9]
structure 12	None	30.5	6.3	36.8	[9]
structure 13	None	32.0	4.0	36.0	[9]
structure 13	Styrene	40.3	2.3	42.6	[9]
structure 13	None	43.5	0.8	44.3	[9]
BEt_3	1-heptanol	29.0	8.1	37.1	[10]
BEt_3	4-ABN	31.0	15.5	46.5	[10]
BEt_3	PFPEO	21.0	7.5	28.5	[10]
$AlEt_3$	PFPEO	5.8	1.5	7.3	[10]

MMA: methyl methacrylate, ABN: aminobenzonitrile, PFPEO: α-hydroxy-perfluorated polyethylene oxide.

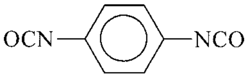
The use of reagents with two identical reactive functions [6]

Whereas in the preceding section the structure of the grafting molecules involved two specific moieties, one for each step in the processing of the composite, here the working hypothesis was inspired by the use of molecules bearing two identical reactive moieties. These structures were chosen on the basis of specific considerations which called upon planar rigid configurations with the two functions in "opposite" directions, as shown in structures 7 and 8.

It was thought that, given the heterogeneous character of the reactions between the cellulose surface OH groups (solid) and the complementary moieties borne by these reagents (in the liquid phase), only one of the two moieties would be able to couple with the fibre, leaving the other available for further exploitation. This hypothesis was confirmed experimentally, when cellulose was treated with either of the above reagents in a dry non-swelling medium, sine the recovered fibres showed, after extraction of the excess coupling agent, the clear presence of the relevant infrared bands arising from the NCO or anhydride carbonyl groups, as shown in Figure 4 in the case of the former. In fact, the intense band at 2270 cm^{-1} denotes the presence of NCO groups attached to the substrate (see Figure 4). In other words, the use of these specific molecules provided a simple and convenient means to prepare cellulose fibres bearing highly reactive groups bound at their surface.



Structure 7



Structure 8

The exploitation of this type of modification consisted in carrying out, once more, the processing of the composite material through a one-pot double operation, viz. (i) the modification of the surface of the fibres followed by (ii) polycondensation reactions in which the unreacted function could participate and thus give rise to continuous covalent links between fibres and matrix. Examples of these procedures included the successful preparation of composites with polyester (with anhydride-bearing fibres) and polyurethane (with NCO-bearing fibres) matrices. Following the extraction of the polymer which had not "copolymerised" with the cellulose reactive groups, the modified fibres showed weight gains of up to 200% and were thoroughly embedded in the corresponding polymer, which was chemically bound to them.

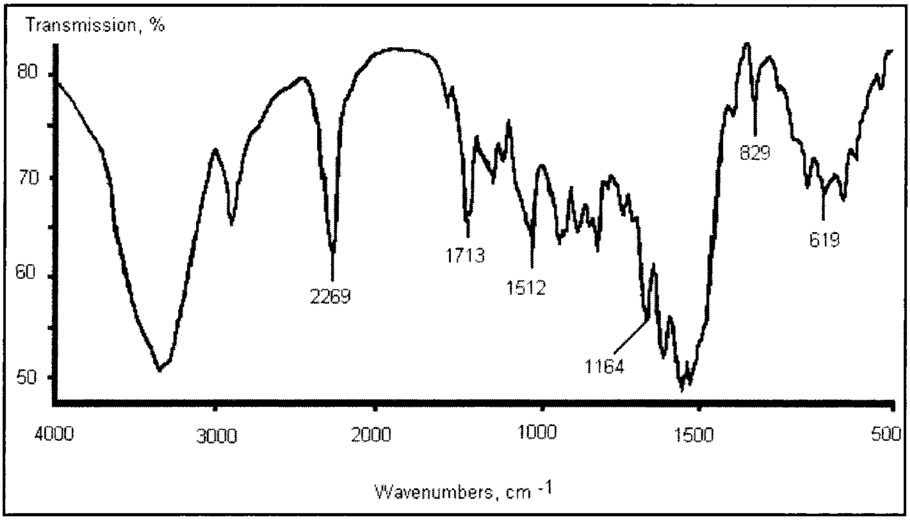


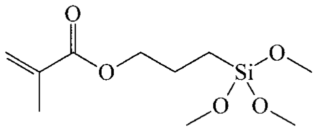
Figure 4. ATR-FTIR spectrum of cellulose grafted by 1,4-phenylene diisocyanate (structure 8) after extraction with dry methylene chloride.

Coupling with siloxanes [7-9]

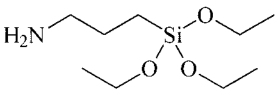
Whereas the reaction of siloxanes with glass fibres is very well documented, the same cannot be said of the corresponding coupling with cellulose fibres, because claims to the actual occurrence of these grafting reactions are often unsubstantiated by convincing experimental evidence. To the best of our knowledge, the only study which approached this problem in a thorough fashion was published by Herrera-Franco *et al.* [14]. The issue at stake here is double, namely the actual reactivity of the cellulose hydroxy groups with either the ≡Si-OR or the ≡Si-OH moieties, the first being associated with unhydrolysed siloxanes and the second with their hydrolysed oligomers. Herrera-Franco *et al.* were the first to give a clear answer to the second aspect: the reaction ≡Si-OH + ≡C-OH (solid cellulose) only takes place at reasonable rates if the temperature is higher than about 70°C.

Our recent work has extended that study in various directions and can be summarised as follows: (i) if triethoxysilanes are prehydrolysed to give essentially ≡Si-OH-bearing oligomers, strong hydrogen-bond interactions take place with the surface hydroxy groups of cellulose at room temperature, but the silanol oligomers can be removed by washing with alcohol; (ii) if the same system is heated above 100°C, a condensation reaction takes place to give ≡Si-O-C≡ bonds; (iii) if monomeric siloxanes are placed in contact with cellulose fibres in a dry solvent (e.g. toluene), no reaction takes place, even at high temperature, unless moisture is introduced in the medium. It can therefore be concluded that the chemical modification of cellulose fibres by siloxanes must be mediated by their preliminary (partial) hydrolysis and even then it will only occur to a measurable extent if the temperature is raised.

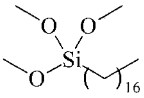
A selection of trialkoxy-silanes (structures 9-14) bearing different functions on the fourth substituent (including C=C unsaturations) were examined quantitatively in terms of adsorption isotherms and coupling reactions with cellulose fibres. The fibres modified with siloxanes possessing a copolymerisable function were shown to give covalent connections with a macromolecular matrix when the latter was prepared *in situ* from the polymerisation of its monomer. Table 1 gives the surface energies of a selection of silane-treated celluloses as well as silane-treated and copolymerised fibres. Figure 5 shows the evolution of the contact angle values with short times of a drop of water placed on the cellulose surface modified by different silanes.



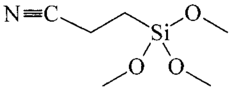
Structure 9



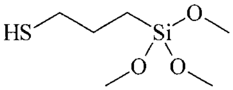
Structure 10



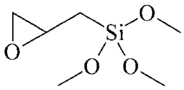
Structure 11



Structure 12



Structure 13



Structure 14

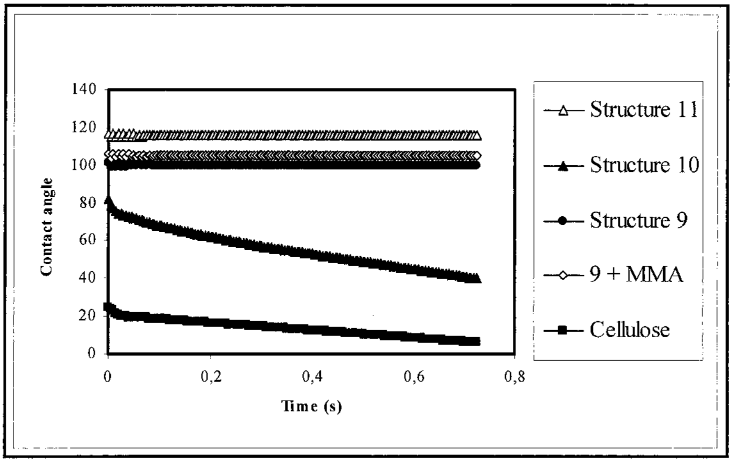


Figure 5. Contact angle kinetics of a drop of water placed on the surface of cellulose modified by different silanes.

Grafting with organometallics [3,10]

Among our most recent investigations in the context of the present topic, we tackled the reaction of cellulose fibres with organometallic derivatives of aluminium and boron. To the best of our knowledge, no study of this nature had been published previously. The fibres were treated with triethyl aluminium (Et_3Al) or triethyl boron (Et_3B) in a dry heptane medium at room temperature under a nitrogen atmosphere. After filtering off the excess reagent and washing in situ with a dry solvent, a second reaction was carried out, involving the addition of one of several alcohols or amines. If one or two of the metal-to-carbon bonds had previously reacted with the cellulose surface OH groups (but not all three, for steric reasons), then the remaining functionality would couple with the OH or NH_2 group of the second reagent and provide a permanent modification of the fibre surface. This strategy was successful, particularly with Et_3Al, which turned out to be much more reactive toward cellulose than Et_3B. The proofs for the validity of the approach were obtained by XPS spectroscopy and by surface energy analysis through contact angle measurements. Figure 6 shows the XPS spectrum of $AlEt_3$-treated cellulose followed by a second grafting with dicyanoamide which exhibits the characteristic peak related to aluminium and nitrogen atoms.

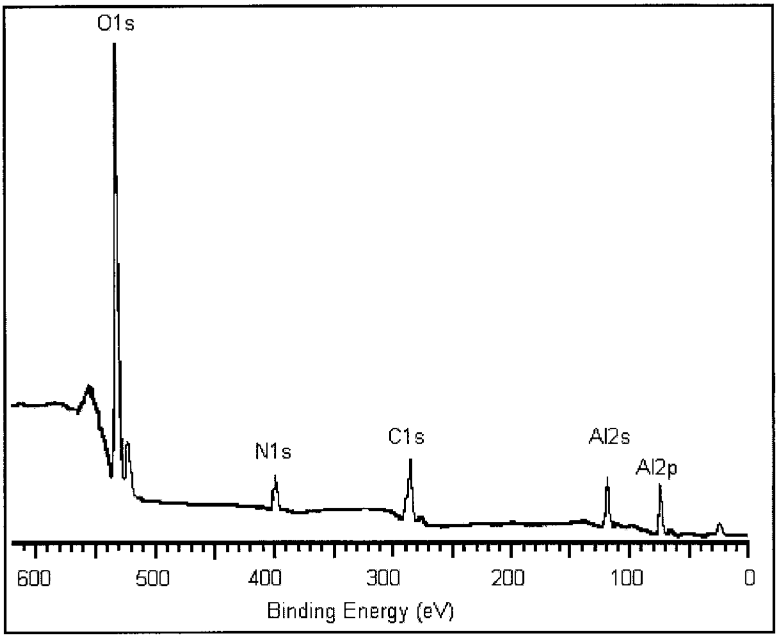


Figure 6. XPS spectrum of $AlEt_3$-treated cellulose followed by grafting with dicyanoamide in the second reaction. A Soxhlet extraction was carried out after each stage.

Conclusions

The chemical modification of the surface of cellulose fibres can be carried out following a variety of procedures and leads to interesting possibilities in terms of the type of moieties that can be appended on them. The most promising approach seems to be that giving rise to continuous covalent bonds between the cellulose surface and the matrix. Recently, we looked into a different strategy [11], which does not involve a chemical modification, but rather the formation of a physical sleeve of polymer around the fibres. This can be achieved by generating admicellar layers on the cellulose substrate with a cationic surfactant and filling it with a monomer, which is then polymerised. This type of water-based "coating" is thus a novel means of facilitating the marriage of the matrix polymer with the surface of the fibres, albeit without covalent connexion.

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