Surface Modification of Cellulose Fibers. I. Spectroscopic Characterization of Surface-Modified Cellulose Fibers and Their Copolymerization with Styrene

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Synopsis

Two coupling agents based on trichloro-s-triazine with different terminal unsaturated groups were synthesized in order to improve the bonding between cellulose fibers and an unsaturated polyester matrix. The products of the reactions between hydroxyl groups of cellulose and reactive species of coupling agents were analysed by Fourier-transform infrared spectroscopy (FTIR) and by elemental microanalyses. ESCA was used for surface characterization of treated fibers. The coupling agents were found to be concentrated on the fiber surface. Polymerization of styrene was carried out in the presence of treated fibers. That the unsaturated groups of the treated fibers were able to copolymrize with styrene was shown by FTIR. Further evidence of the presence of grafted polystyrene on the surfaces of the cellulose fibers was provided by ESCA measurements.

INTRODUCTION

The concept of coupling agents is well known in the field of reinforced and filled plastics. Their main function is to overcome incompatibility between two phases. A coupling agent, usually a bifunctional molecule, is capable of forming covalent bonds with both the organic polymer matrix and the fiber or filler. The bonds across the interface between the polymer matrix and the reinforcement achieved via the coupling agent provide good adhesion even under high humidity. This is required to obtain satisfactory long-term properties of composite materials.[1]

In a recent study of cellulose-fiber-reinforced polyesters,[2] we considered the failure under wet conditions to be due to lack of adhesion between the cellulose fibers and the polyester matrix. Adhesion can be improved by better contact through wetting and by covalent bonding between fiber and matrix.[3] One way to obtain wetting and bonding between fibers and matrix is to modify the surface of cellulose fibers. Since curing of the polyester resin has the nature of a radical polymerization, the introduction of double bonds onto the fibers should make it possible to achieve covalent bonding between fiber and matrix. For this reason one of the objectives of this work has been to obtain cellulose fibers with polymerizable double bonds on the surface.

The grafting of vinyl polymers onto cellulose has been extensively reviewed.[4,5] However, procedures involving introduction of polymerizable

groups onto cellulose have only been mentioned in a few publications.[6,7] In this work, dichloro-*s*-triazine derivatives with double bonds (methacrylic and allylic) were synthesized and used for fiber treatment.

The chemical reaction of cellulose with trichloro-*s*-triazine has been under investigation for several years. Thus *s*-triazine derivatives are widely used in the field of textile dye chemistry as one of the major types of fiber reactive dyes.[8] The mechanism of the reaction between trichloro-*s*-triazines and the hydroxyl groups of the polysacharides proceeds via an oxyanion (Fig. 1) and is considered to be of an SN2 type.[9]

The present paper describes the syntheses of 4,6-dichloro-*s*-triazines with unsaturated substituents, suitable for use as coupling agents in cellulose–polyester composites. Their reactions with cellulose were studied by analyzing the products with elemental microanalyses and FTIR. Polymerization of styrene was carried out in the presence of modified fibers.

The surface composition of cellulose fibers and wood fibers has been determined using ESCA.[10,11] Since ESCA has an information depth of 10–50 Å, it is a very useful tool for examining only the outer layers or surfaces of fibers. In this work ESCA is used to determine whether the coupling agent is present on the surface or uniformly distributed throughout the fibers.

EXPERIMENTAL

Materials

The cellulose fibers used in this study were bleached softwood kraft paper with a surface weight of 115 g/m^2, obtained from Klippans Finpappersbruk AB, Sweden. All solvents were dried and distilled before use.
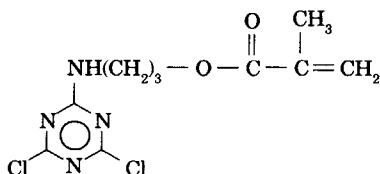
Synthesis of Coupling Agents

Two derivatives of dichloro-*s*-triazine with double bond activity were synthesized. Their formulas are shown below and henceforth referred as compounds A and B.

Compound A: 2-diallylamino 4,6-dichloro-s-triazine:

$$N-(CH_2-CH=CH_2)_2$$
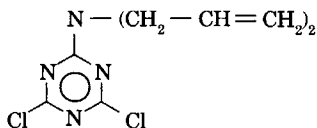
Compound B: Methacrylic acid, 3-((4,6-dichloro-s-tiazine-2-yl)amino) propyl ester:

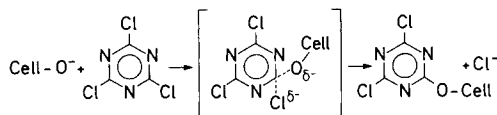$$NH(CH_2)_3-O-\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2$$

Fig. 1. Chemical reaction of trichloro-s-triazine with cellulose.

Compound A (mp 42°C) was synthesized using the Thurston method[12] from trichloro-s-triazine and diallylamine. Compound B (mp 93°C) was prepared with the same method from trichloro-s-triazine and 3-aminopropyl methacrylate-HCl.

Fiber Treatment

Cellulose fibers in the form of sheets of paper were impregnated in an acetone solution with various concentrations of the dichloro-s-triazine derivatives for 3 min. The wet pickup was 100%. After drying for 15 min at 30°C in an oven with air circulation the paper was impregnated in an aqueous solution of sodium hydroxide (0.1M) for 3 min. The wet pickup was 300%. The paper was then thermally treated for 1 h in 93°C in a nitrogen atmosphere, and then rinsed several times with distilled water and acetone. Finally, the paper was Soxhlet-extracted with acetone for 20 h to remove compounds not covalently bonded to the fibers.

Elemental Microanalyses

The nitrogen content was determined with a Carlo Erba ANA 1400 Automatic Analyzer.

Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared absorption spectra of treated and untreated cellulose fibers were obtained with the KBr technique[13] on a FTIR spectrophotometer Nicolet 10-MX at a resolution of 2 cm^{-1} with coaddition of 400 scans.

ESCA

The cellulose fiber surfaces were analysed with a Hewlett-Packard 5950A ESCA spectrometer with a monochromatized Al(Kα) X-ray source in an ultra-high vacuum (background pressure < 10^{-9} torr) and the energy and spectrum of photoelectrons was recorded. The energy resolution of the ESCA was 0.9 eV. The analyzed area was 1 × 5 mm with an information depth of about 30 Å. The spectrometer was operated in a computer-controlled scanning mode. A graphics terminal was used for peak separation. The buildup of a positive charge (about 5 eV) on paper surfaces was not neutralized by electrons. To check that the charging was constant over time, repeated spectra were recorded.

Grafting of Styrene onto Cellulose Fibers

A mixture of cellulose fibers (1 g), styrene (5 g), toluene (5 g), and AIBN (0.05 g) was placed in a sealed tube. Graft copolymerization was carried out
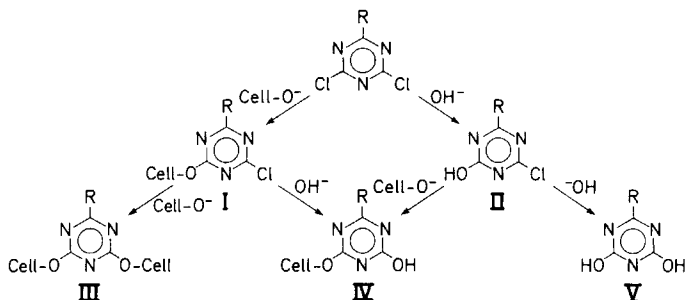
Fig. 2. Chemical reactions between cellulose and 2-substituted -4,6-dichloro-s-triazine.

at 60°C under nitrogen. After 5 h the reaction was quenched by addition of methanol. The cellulose fibers were then rinsed with acetone. The ungrafted polymers were removed by Soxhlet-extraction with acetone for 24 h. Finally, the samples were dried in a vacuum.

RESULTS AND DISCUSSION

Fiber Treatment

The aim of this part of our work was to determine the optimum conditions for the reaction of dichloro-s-triazine derivatives with cellulose, with retention of the fibrous form. Analyses for nitrogen and chlorine were made in order to determine the effects of changing the reaction conditions on the efficiency of treatment. The fiber treatment described under "experimental" is a two-step process, where the first step involves the deposition of the reagent on the fibers and the second step induces the transfer of cellulose hydroxyl groups to oxyanions by alkali and the chemical reaction between these oxyanions and the chlorine bearing carbon atoms of dichloro-s-triazines derivatives. Some possible structures occuring during the treatment are summarized in Figure 2. Compounds II and V are removed during washing and extraction of the fibers. Determination of the chlorine to nitrogen ratio of the treated fibers shows that there is one chlorine atom per s-triazine ring. This indicates that the treatment leads to a derivative according to structure I shown in Figure 2.

TABLE I
Treatment Efficiency of Cellulose Fibers with Dichloro-s-Triazine Derivative

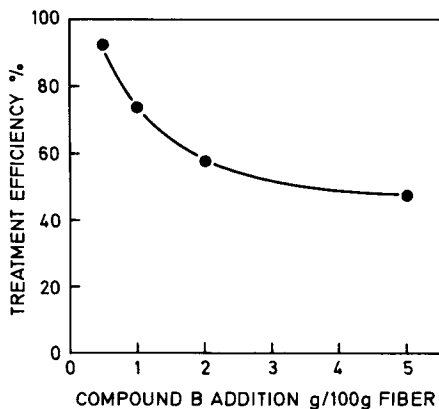| Compound B addition (g/100 g fibers)	Initial nitrogen content (%)	Nitrogen content of fibers (%)	Efficiency of treatment (%)	Compound B bonded to fibers (%)
0.5	0.096	0.089	92.7	0.46
1.0	0.190	0.140	73.7	0.74
2.0	0.380	0.220	57.9	1.16
5.0	0.950	0.450	47.0	2.35

Fig. 3. Efficiency of the reaction of compound B with cellulose fibers.

Effect of Reagent Concentration

Table I and Figure 3 show the effect of compound B concentration on the fiber treatment efficiency. The shape of the curve shown in Figure 3 is similar to the curve which has been reported on the receptivity of cellulose fibers to reactive dyes on repetitive dyeing.[14] The high efficiency at low concentration can be ascribed to the reaction of the disordered hydroxyl groups on the surfaces of the elementary fibrils.[14]
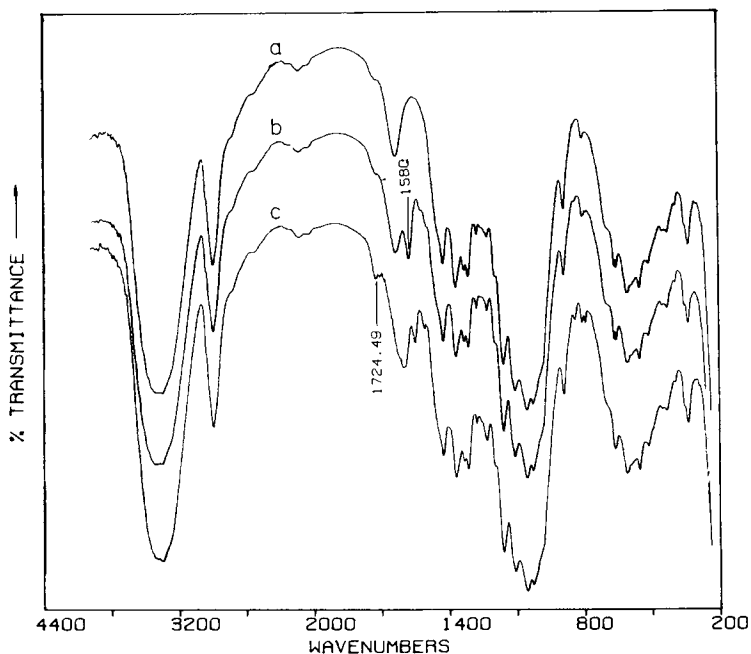

Fig. 4. FTIR spectra of (a) untreated cellulose fibers, (b) cellulose fibers treated with compound A, (c) cellulose fibers treated with compound B.
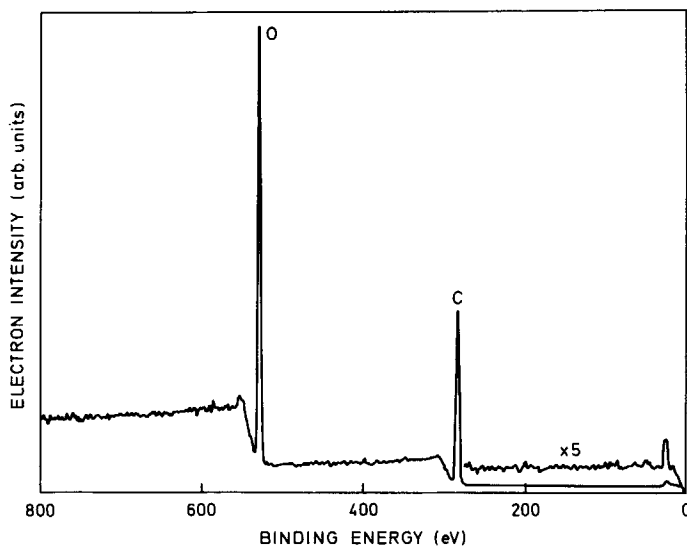
Fig. 5. Photoelectron spectrum of untreated cellulose fibers shown over a binding energy range of 0–800 eV.

Following the Reaction with FTIR

Figure 4 shows IR spectra of untreated fibers, fibers treated with 5% of compound A, and fibers treated with 5% of compound B. In the spectrum of treated fibers we can see a new absorption band at 1580 cm^{-1} which is characteristic for the triazine ring.[15] In addition to the triazine band, the spectrum of fibers treated with compound B contains a band at 1724 cm,$^{-1}$ which is assigned to the carbonyl in the methacrylic group.

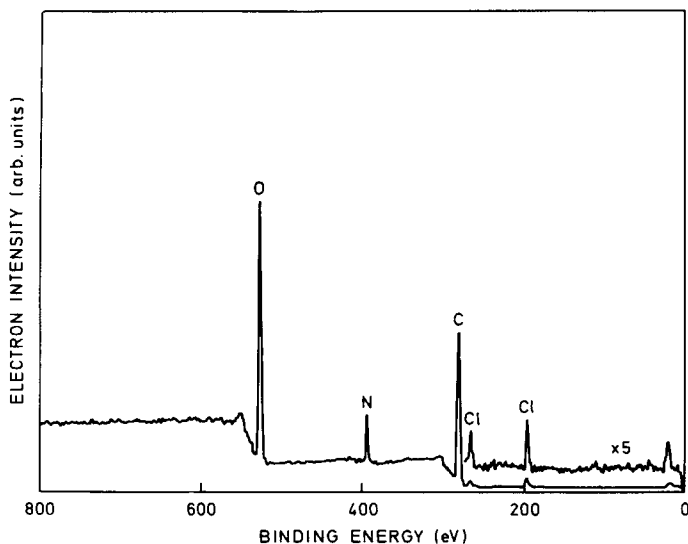Since all fibers were Soxhlet-extracted before the FTIR analyses, we could

Fig. 6. Photoelectron spectrum of cellulose fibers treated with compound A shown over a binding energy range of 0–800 eV.
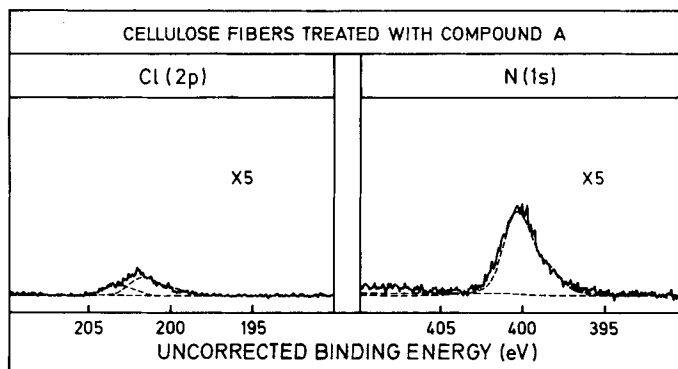
Fig. 7.   ESCA spectra of cellulose fibers treated with compound A.

confirm that the *s*-triazine derivatives are chemically bonded to the cellulose fibers.

Characterization of Cellulose Fibers Surfaces by ESCA

The surfaces of treated and untreated paper were characterized by ESCA. To ensure that the results only apply to the compound which is covalently bonded to the fibers, the cellulose fibers were Soxhlet-extracted with acetone for 24 h and dried in a vacuum for 1 week. A mass spectrometer in the ESCA vacuum chamber only showed traces of water leaving the sample.

The ESCA spectrum of untreated cellulose paper (Fig. 5) shows the carbon (1s) and oxygen (1s) peaks. In addition to carbon (1s) and oxygen (1s) peaks, the ESCA spectrum of paper treated with compound A (Fig. 6) also shows nitrogen (1s) and chlorine (2s,2p) peaks. The latter belong to the triazine derivative molecule.

In a high resolution spectrum the elemental composition of the surface can be determined from the area under the ESCA peaks. The high resolution spectra of nitrogen (1s) and chlorine (2p) can be seen in Figure 7, while the spectra of oxygen (1s) and carbon (1s) are shown in Figure 10. Table II summarizes the ESCA peak areas of the treated and untreated fibers. The area under the O (1s) peak for treated fibers can be used for calculation of the cellulose content of the surface because compound A contains no oxygen. Thus the treatment makes no contribution to the O (1s) peak area. The concentration of compound A on the surface of treated cellulose fibers was calculated from the area under the N (1s) peak. The area ratio O (1s)/N (1s) was 5.39. The atomic ratios was calculated by dividing the area ratio

TABLE II
Results from ESCA Spectra

Sample	Area under ESCA peaks			
	O	C	N	Cl
Untreated fibers	8.352	4.126	0	0
Fibers treated with compound A	5.610	4.163	1.040	0.303

by the coefficient 1.62.[16] The atomic ratio of O/N on the surface was found to be 3.32.

Elemental microanalyses gave a nitrogen content of 0.4% for the same sample, which gives an O/N of 108. When comparing the results from ESCA with results from elemental microanalyses, it becomes evident that compound A is concentrated on the surfaces of cellulose fibers by a factor of about 32 times.

Grafting of Styrene onto the Treated Fibers

Finally, to show that cellulose fibers with unsaturated activity can copolymerize with styrene, the polymerization of styrene was carried out in the presence of treated fibers. Nongrafted homopolymer was removed from cellulose during solvent extraction with acetone, which is a good solvent for polystyrene.[17] Confirmation of grafting was obtained from FTIR. Figure 8 shows the difference spectrum between the spectrum of cellulose fibers treated with compound A and grafted with styrene and that of fibers just treated with compound A. The absorption band at 698 cm^{-1} is characteristic of polystyrene.[18] This band was also found in the corresponding difference spectrum of cellulose fibers treated with compound B and grafted in the same way (Fig. 9). Untreated fibers were subjected to the same polymerization and extraction procedure and was analysed by FTIR. No evidence of polystyrene was found in those fibers.

Characterization of Grafted Fibers by ESCA

Figure 10 shows the ESCA spectra of untreated cellulose fibers [10(a)], fibers treated with compound A [10(b)], and fibers both treated with compound A and grafted with styrene [10(c)]. The shape of the carbon C (1s) peak is clearly distinctive in all three cases. The carbon C (1s) peak can be resolved into three main components C_1, C_2, and C_3 situated at 285.6, 287.4, and 288.8 eV.[10] They have been assigned in the following manner: C_1 carbon atoms are only bonded to carbon or hydrogen, C_2 carbon atoms are bonded to a single nonketonic oxygen atom, and C_3 carbon atoms are bonded to
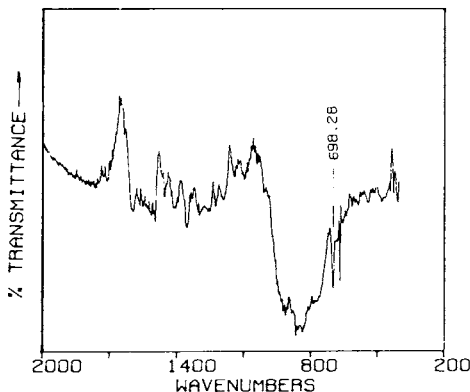

Fig. 8.   FTIR difference spectrum between the spectrum of fibers treated with compound A and grafted with styrene and the spectrum (b) in Figure 4.
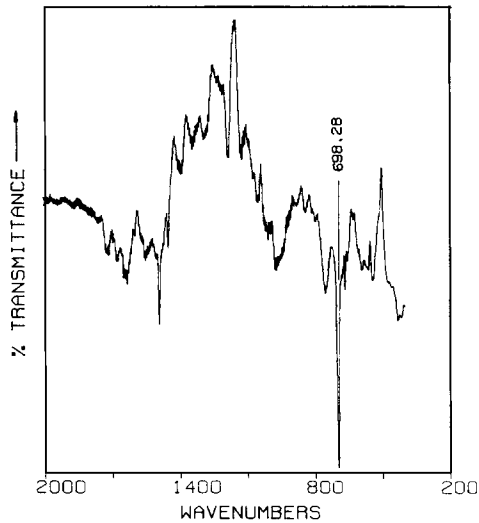
Fig. 9. FTIR difference spectrum between the spectrum of fibers treated with compound B and grafted with styrene and the spectrum (c) in Figure 4.
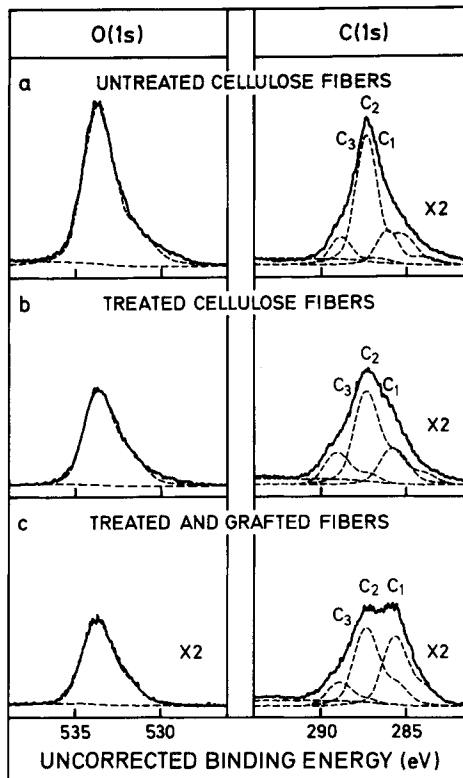

Fig. 10. ESCA spectra of (a) untreated cellulose fibers, (b) cellulose fibers treated with compound A, (c) cellulose fibers treated with compound A and grafted with styrene.

TABLE III
Scofield Yield Factors[16] Used for Calculation of Surface Composition

Element		Y
C	1s	1.00
O	1s	2.93
N	1s	1.80
Cl	2p	2.29

two nonketonic oxygen atoms or to a single ketonic oxygen atom. In the case of treated fibers there was an increased intensity in the C_1 and C_3 regions, which is in agreement with the chemical structure of compound A.[19] Fibers grafted with styrene gave a different shape of carbon (1s) peak in the ESCA spectrum (11c). The C_1 peak had increased most compared to peaks of the treated fibers. It can be concluded that a considerable amount of grafted polystyrene is present on the surface of cellulose fibers.

CONCLUSIONS

Dichloro-s-triazine derivatives with substituents containing double bonds were used for the modification of cellulose fibers. Using a two-step treatment process over 50% treatment efficiency was obtained, for the addition of the reagent below 5%.

The dichloro-s-triazine derivatives were concentrated on the surface of the cellulose fibers as detected by ESCA.

When polymerization of styrene was carried out in the presence of treated fibers, and the fibers extracted, polystyrene on the fibers was detected by FTIR. The ESCA measurements showed that a considerable amount of polystyrene was present on the surface of the fibers, which provided the further evidence of the ability of modified fibers to copolymerize with styrene.

Since dichloro-s-triazine derivatives were able to react with cellulose fibers and to form covalent bonds with polystyrene during polymerization of styrene, they seem suitable for use as coupling agents in order to improve adhesion in cellulose–polyester composites.

TABLE IV
Elemental Composition in Mole Fractions of Cellulose Fiber Surfaces

Sample	Mole fractions of element			
	O	C	N	Cl
Untreated fibers	0.41	0.59	0	0
Fiber treated with compound A	0.282	0.614	0.086	0.019

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