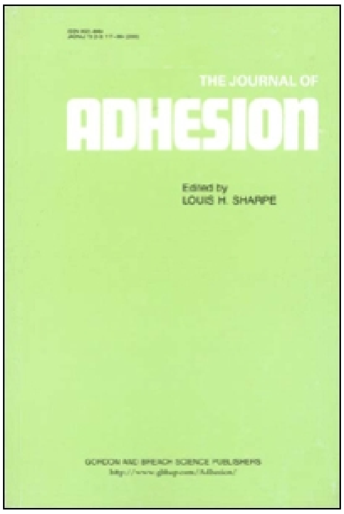

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Surface Energy and Wettability of Modified Cellulosic Fibres for Use in Composite Materials

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The surface modification of cellulosic substrates in the form of powders and sheets was carried out using nonpolar oligomeric and polymeric reagents bearing isocyanate and anhydride reactive moieties. The characterization of these surfaces by inverse gas chromatography and by dynamic and equilibrium contact angle measurements, before and after the treatments, revealed that the lower the polarity of the coupling agent, the higher the loss of hydrophilic character of the substrate. In particular, the use of styrenic copolymers of rather high molecular weight gave rise to essentially dispersive-modified surfaces which should be highly suited for the preparation of composites based on non-polar macromolecular matrices.

Keywords: Cellulosic materials; surface modification; isocyanate coupling; anhydride coupling; surface energy; polar character; dispersive character

1. INTRODUCTION

The use of cellulosic fibres as a reinforcing agent in polymeric composites has stimulated much research in recent years and numerous laboratories have become involved in the various aspects related to this topic [1–4]. This renewed interest stems from the fact

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* Corresponding author.

that a number of advantages can be gained by calling upon these natural fibres, namely: (i) their renewable character; (ii) their low density; (iii) their world-wide availability with a wide variety of compositions (e.g., with or without lignin) and aspect ratios, depending on the species and the isolation techniques; (iv) their low cost in most instances; (v) the possibility of preparing high-modulus regenerated forms by solution-coagulation spinning; and (vi) the recyclability of the entirely organic composites (as opposed, e.g., to glass-fibre counterparts) which can be burnt completely in an energy-production approach.

In order to obtain a composite material with good mechanical properties, it is essential to insure that the fibre/matrix interface displays a high degree of compatibility, based on similarity of chemical structures, and adhesion, possibly enhanced by macromolecular interpenetration. The surface treatment of glass fibres with a variety of silanes bearing specific groups is a typical example of how to adapt them to different polymeric matrices [5].

The same considerations must, of course, apply to cellulosic fibres used in composites, and the hydroxy groups sitting at the surface of these polysaccharidic materials are the obvious candidates for chemical modification. In a first approach to this problem, we considered typical non-polar polymeric matrices (e.g., polyethylene, polypropylene, polystyrene,...) and set out to modify the surface of the fibres in order to attain two goals, namely (i) the modification of its highly-polar structure into a non-polar one, and (ii) the grafting of polymeric chains which would interpenetrate into the macromolecular structure of the matrix. The aim of this investigation was indeed to fulfil both these objectives through a single chemical modification.

The study involved many different reagents, monomeric, oligomeric and polymeric, and a variety of cellulosic substrates which allowed us to examine the modified surfaces by numerous complementary techniques. The two chemical mechanisms chosen for these coupling reactions involving the surface OH groups of cellulose were esterification with an anhydride function or urethane formation using isocyanates. The details of these operations and the procedures used to prove the occurrence of grafting have been published elsewhere [6, 7].

The purpose of the present paper is to show how these modified cellulosic surfaces were characterized in terms of their novel physicochemical properties, with particular emphasis on energetic and wettability aspects.

2. EXPERIMENTAL

2.1. Materials

Two cellulosic substrates were chosen for this specific work, namely a commercial microcrystalline powder (Avicell) and a commercial uncoated tracing paper made of pure cellulose. The former was ideally suited for the Inverse Gas Chromatography (IGC) measurements, whereas the latter was more suited for contact angle determinations. Both were tested as such and after different surface modifications, which involved the following coupling agents:

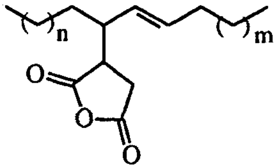
- A commercial alkenyl succinic anhydride (Accosize 18 from American Cyanamid) consisting of a mixture of oligomers of different sizes, centred around C18 (Mn = 300), bearing the general structure I.
- An oligoether monoisocyanate synthesized in our laboratory [8], with mostly propylene oxide units, as shown in structure II. Its Mn was 600 and its NCO terminal functionality was very close to unity [8].
- A commercial (Aldrich) styrene-maleic anhydride copolymer (see structure III) with Mn = 2000 and an average anhydride functionality of 7, as determined in our work [7].
- Copolymers involving 3-isopropenyl-α-α'-dimethylbenzyl isocyanate (TMI) and styrene or α-methylstyrene prepared by cationic polymerization as previously described [9]. Their general structure IV bore an average of 18 NCO functions per macromolecule of Mn = 18,000 [7].

2.2. Methods

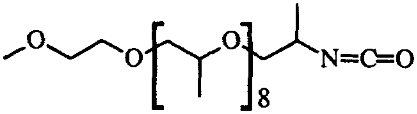
2.2.1. Functionalization

The functionalization procedures called upon a heterogeneous reaction between the surface OH groups of the cellulosic samples and specific complementary functions borne by the coupling agent

Chemical structures



Structure I



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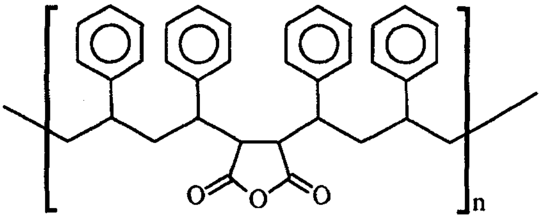
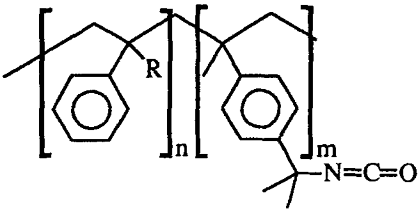


Structure III



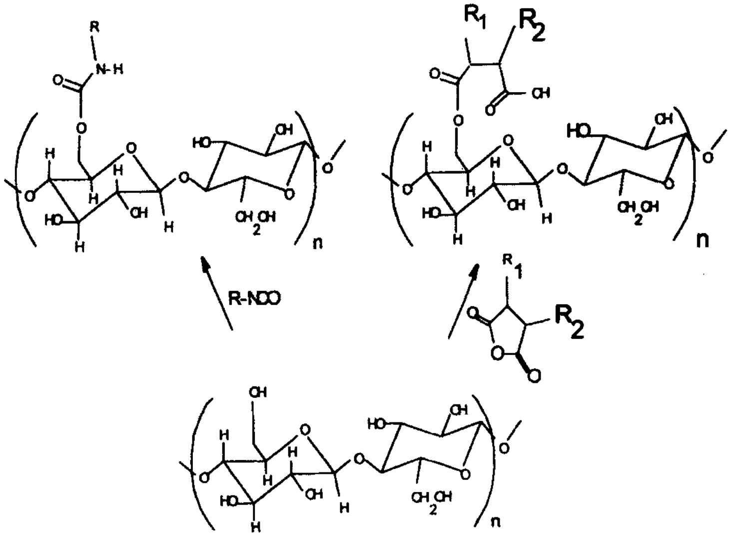
Structure IVa, R = H
Structure IVb, R = CH_3

which was dissolved in an appropriate dry medium. Scheme 1 illustrates the two condensation mechanisms involved in these grafting operations. The details of each of these syntheses have been reported previously [7]. The combined use of FTIR spectroscopy, elemental analysis, SEM and XPS gave clear evidence of the success of all these chemical modifications.

The surface characterization was carried out using the following two basic techniques:

2.2.2. Inverse Gas Chromatography (IGC) [10]

For the IGC measurements, about 1 g of material was packed into a glass tube 4 mm diameter and 280 mm long (of which only 160 cm contained the substrate, the rest being filled with silylated glass wool), previously washed with acetone and dried at 105°C. These columns were conditioned overnight at 100°C under a flow of nitrogen before starting the experiments and data collection. A Delsi 121 DFL gas chromatograph equipped with flame ionization detector (FID) was used to measure the retention times.



SCHEME 1

The relevant characteristics of the *n*-alkane homologues chosen as probes, namely, the dispersive component of their surface tension and their molecular surface areas were reported previously [11, 12]. All these substances, as well as propane, used in this study as a marker, were commercial products of the highest purity. Measurements were conducted in zero-coverage conditions. i.e., a very small amount (1 μl) of the vapor of the selected compound was introduced into the column through the injection block kept at 110°C. All measurements were carried out at a column temperature of 50°C.

Before starting the measurements, we verified that diffusion and sorption phenomena were absent in our experimental conditions. The following observations confirmed these points: (i) peaks were perfectly symmetrical and sharp, (ii) the retention times were found to be independent of the amount of injected probe in the range of 1 to 10 μl, (iii) the retention times of the probes were reproducible, and (iv) the injection of hexane at the end of each series of probes showed that its retention time remained unchanged which indicated that there had been no permanent surface contamination.

Since peaks were symmetrical, the retention times (t_r) were taken at peak maxima. From the IGC chromatograms, the following information could be obtained: (i) the retention time, t_r, of a given probe molecule, (ii) the retention time, t_0, of the marker which did not interact with the substrate, (iii) the carrier gas flow rate, F, and (iv) the inlet (P_i) and outlet (P_0) pressures of the column. These parameters were used to calculate the net retention volume, V_n, which is the key thermodynamic parameter in IGC, viz:

$$V_n = FD(t_r - t_0) \tag{1}$$

Here, D is the correction factor for gas compressibility which can be calculated from Eq. (2):

$$D = \frac{3\left[\left\langle \dfrac{P_i}{P_0} \right\rangle^2 - 1\right]}{2\left[\left\langle \dfrac{P_i}{P_0} \right\rangle^3 - 1\right]} \tag{2}$$

In this study we used two methods for the calculation of the dispersive contribution to the surface energy of the solid substrate, namely

Dorris and Gray's [13] and Schultz *et al.*'s [11] approaches. Dorris and Gray [13] proposed a method based on the increment of the free energy of adsorption or desorption per methylene group in the *n*-alkane series, defined by:

$$\gamma_S^D = \frac{\left[\mathrm{RT}\ln \frac{V_{N(\mathrm{C}_{n+1}\mathrm{H}_{2n+4})}}{V_{N(\mathrm{C}_n\mathrm{H}_{2n+2})}}\right]^2}{4\,\mathrm{N}^2(a_{\mathrm{CH}_2})^2\,\gamma_{\mathrm{CH}_2}} \tag{3}$$

where N is Avogardro's number, a_{CH_2} the cross-sectional area of a CH_2 group (equal to 6Å^2) and γ_{CH_2} is given by the following expression [14]:

$$\gamma_{\mathrm{CH}_2} = 35.6 - 0.058T(\mathrm{mJ\,m}^{-2}) \tag{4}$$

Schultz *et al.* [11] calculated the γ_S^D of the adsorbate using Eq. (5), viz.:

$$\mathrm{RT}\ \ln Vn = 2\mathrm{N}(\gamma_S^D)^{1/2}a(\gamma_L^D)^{1/2} \tag{5}$$

where a is the surface area of the probe molecule and γ_L^D is the dispersive component of the surface tension of the probe molecule in the liquid state.

The interactions of the *n*-alkane molecules with the substrates under investigation are only caused by dispersive forces and, consequently, a plot of RT ln (Vn) *vs* $a(\gamma_L^D)^{1/2}$ gives, in principle, a straight line from the slope of which γ_S^D can be obtained [11, 12].

In order to assess the acid-base properties of the cellulosic surfaces before and after modification, we used chloroform as an electron-acceptor probe and tetrahydrofuran (THF) as an electron-donor one. The free energy of adsorption of THF or chloroform onto these surfaces can be obtained [11] easily using Eq. (6):

$$\Delta G_{sp} = \mathrm{RT}[\ln V_N - \ln V_{\mathrm{Nref}}] \tag{6}$$

where V_N is the retention volume of the corresponding polar probe and V_{Nref} that derived from the *n*-alkane reference line, at the value of $a(\gamma_L^D)^{1/2}$ corresponding to the polar probe used, as shown in Figure 1.

The ratio between the free energies related to THF and chloroform gave an indication of the acid-base properties of our surfaces. This

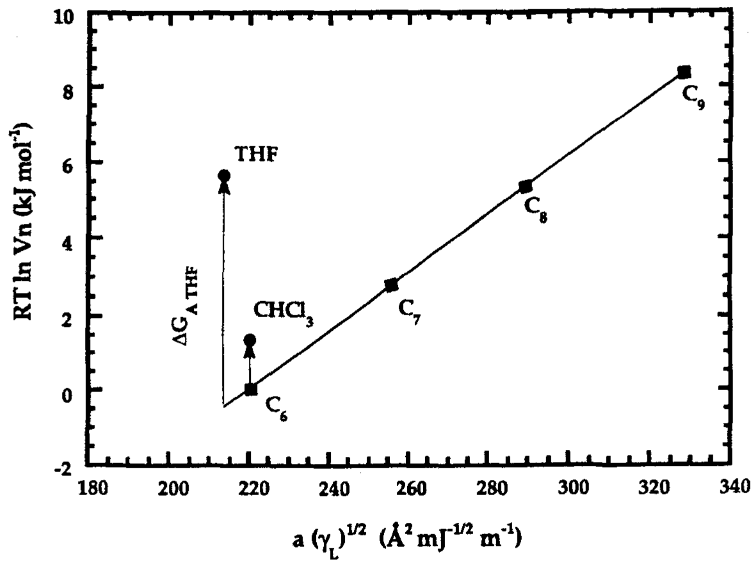


FIGURE 1 RT ln V_n *versus* a $(\gamma_L^D)^{1/2}$ plot for pristine Avicell fibres at 50°C.

parameter is close to unity for amphoteric substrates, higher than 1 for acidic ones and lower than 1 for basic surfaces. Moreover, this ratio is usually associated with the corresponding ratio between the acceptor, AN_s, and donor, DN_s, numbers of the surface under examination, following Gutmann's classical scale [15].

$$\left[\frac{\Delta G_{\mathrm{THF}}}{\Delta G_{\mathrm{CHCl_3}}}\right] = \left[\frac{AN_s}{DN_s}\right] \tag{7}$$

2.2.3. Contact Angle Measurements

Static and dynamic measurements of contact angles were carried out with various liquids. The apparatus used here was a home-made instrument which allowed both the determination of values at equilibrium with a precision of ± 1° as well as the kinetics of its evolution by taking images at frequencies as high as 200 Hz, starting within a few tens of milliseconds after the deposition of the drop [16]. From the static data with pure liquids of different polarity, namely water, formamide, ethylene glycol and diiodomethane, the dispersive and polar contributions to the surface energy were obtained using the approach proposed by Owens and Wendt [17].

3. RESULTS AND DISCUSSION

3.1. Inverse Gas Chromatography

The pristine Avicell was examined first. Figure 1 shows the response of this material to classical non-polar probes of increasing molecular size and to both acidic (chloroform) and basic (tetrahydrofuran) molecular structures. The application of both approaches to determine the dispersive contribution to the surface energy provided the values given in Table I which are in excellent agreement. The acid-base properties of this cellulosic surface, also reported in Table I, suggest a definite acidic character. Both sets of results obtained here are in tune with previous IGC studies of cellulosic substrates [12, 18, 19].

The surfaces resulting from four different types of modification, based on the use of the coupling agents chosen for this study, were then examined under the same conditions and a representative behaviour is depicted in Figure 2. The corresponding data for all analyses are shown in Table I.

The relevant features which differentiate the properties of the untreated surface from those arising from the different modifications are:

- The value of the dispersive contribution to the surface energy did not vary appreciably after the coupling reactions and was,

TABLE I γ_S^D and acid-base properties of Avicell before and after grafting with different coupling agents, as obtained from IGC measurements

		coupling agent			
	Avicell	*I*	*III*	*IVa*	*IVb*
		γ_S^D (mJ m^{-2}) according to			
Gray	42.5	40.9	37.3	37.6	39.1
Schultz	40.5	39.5	35.4	35.7	37.6
		ΔG_A (kJ mol^{-1})			
THF (AN_S)	5.5	5.8	7.3	8.3	4.2
$CHCl_3$ (DN_S)	1.2	6.8	9.8	6.0	4.1
AN_S/DN_S	4.5	0.9	0.7	1.4	1.0

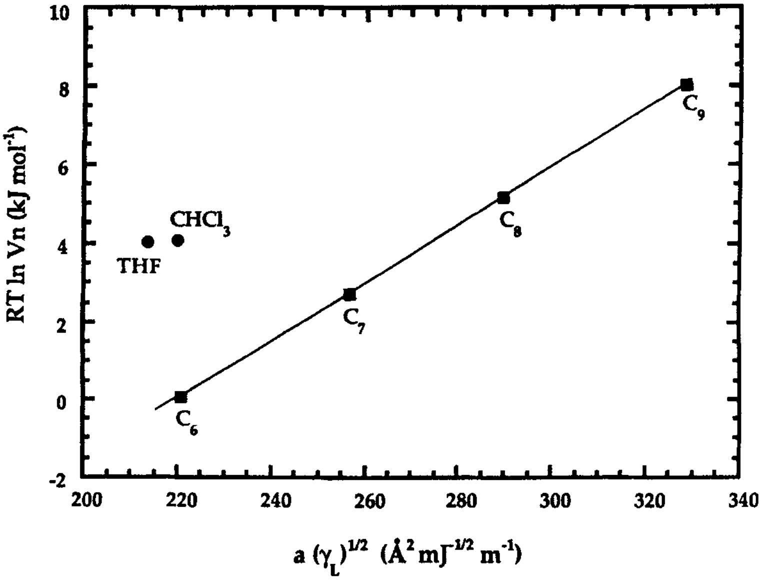


FIGURE 2 RT ln V_n *versus* a $(\gamma_L^D)^{1/2}$ plot for Avicell fibres modified with coupling agent IV b, at 50°C.

moreover, not sensitive to the type of agent. The value of γ_S^D ranges, in fact, between 35 and 40 mJ m^{-2} without a specific trend, i.e., the values were within the experimental errors associated with this technique.

- The acidic character of the surface of Avicell did not vary appreciably with all the treatments, whereas the basic character increased appreciably in every instance. This may be a reflection of the fact that, on the one hand, a large proportion of OH groups remained untouched (the grafting yields were modest [7]) and, on the other hand, the formation of urethane or ester moieties resulting from the coupling reaction introduced nucleophilic sites.

3.2. Contact Angle Measurements

A typical example of the dynamic behaviour of the contact angle as a function of the nature of the surface is shown in Figure 3. Here, drops of formamide, viz. a highly polar liquid, were placed on the

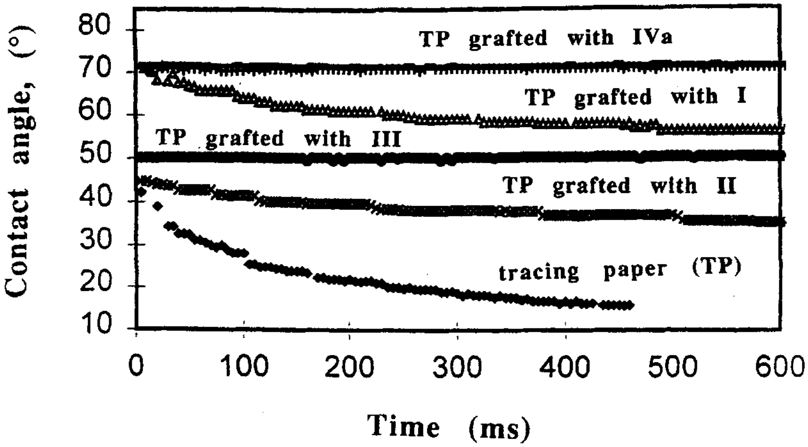


FIGURE 3 Dynamic contact angles of formamide on the surfaces of tracing paper (TP) as such and after modification with the various coupling agents.

unmodified and modified samples of tracing paper and the changes in the value of θ with time followed during the first second or so, i.e., until it became constant.

Several comments can be made from an analysis of the results presented in Figure 3, namely:

- The untreated cellulose surface is the substrate most apt to establish hydrogen bonding (high hydrophilicity), since it gives the lowest initial contact angle which, moreover, rapidly decreases to a vanishingly small value. In other words, wetting with formamide is highly favoured and rapidly complete.
- When the grafting modified the cellulosic surface by appending oligopropylene oxide chains (structure II), the modification of its polarity was modest as shown by the fact that the initial value of θ was barely higher than that obtained with pristine tracing paper. However, its decrease was less pronouned and settled at about 40°. This behaviour suggests that the short chains introduced at the surface probably did not cover it entirely and/or that their specific structure is only modestly non-polar. Indeed polypropylene oxide is hydrophobic and insoluble in water, but retains a polar character because of its ether moieties.

- The behaviour of the cellulosic surfaces treated with anhydride-containing coupling agents (structures I and III) differed in the dynamic approach, but gave similar equilibrium θ values of 50–55°. The first observation is, of course, that with hydrophobic chains such as aliphatic or oligostyrene sequences, it was to be expected that the contact angle would increase considerably with respect to both the untreated surface and that modified with an oligoether. The reasons for the very different dynamic evolution of θ between these two surfaces are less easy to rationalize, but could be ascribed to the more non-polar character of I (lower density of reactive groups) which would induce a high initial contact angle, followed, however, by a rapid decrease caused by the very modest length of its chains. In conclusion, both modifications produced a loss of polarity which was, nevertheless, modulated by the relative density of the polar COOH groups on each modified surface. These moieties, formed in the esterification reaction, were present at a higher surface concentration when the styrene-maleic anhydride copolymer III was used and, consequently, the corresponding contact angle was somewhat lower.
- The most striking change was achieved with the isocyanate-bearing styrenic copolymers IV, as shown in the specific plot in Figure 3 which shows both a high initial θ value of more than 70° and its remarkable stability with time. The surface of the cellulosic fibres was rendered permanently highly non-polar by this treatment.

All the qualitative features illustrated by Figure 3 were also found when drops of water were deposited on the same substrates. The quantitative differences are given in Table II. The dramatic change brought about by the grafting of the isocyanate-bearing styrenic copolymer IV is best visualized by the pictures in Figure 4 related to static contact angles before and after the reaction.

Table II also gives the equilibrium contact angles measured on the five substrates with the other liquids. As opposed to the common behaviour of such polar substances as water ($\gamma = 72.6\,\mathrm{mJ\,m^{-2}}$) and formamide ($\gamma = 58.2\,\mathrm{mJ\,m^{-2}}$), the use of diiodomethane, which is essentially non-polar ($\gamma = 50.8\,\mathrm{mJ\,m^{-2}}$, of which only about $2\,\mathrm{mJ\,m^{-2}}$ are attributed to polar contributions), resulted in a completely different response of the surfaces which gave practically the same value of θ, viz. 32±3°. This result is not surprising, because with such a non-polar structure only dispersive interactions are possible when an interface is created. In particular, here, diiodomethane is placed in contact with different solid polymeric structures which have similar values of the dispersive contribution to their surface energy. As a consequence, the vlaue of γ_S^D will be roughly the same for all interfaces and Young's equation predicts, therefore, the same contact angle, as indeed observed.

Table III gives the values of the dispersive and polar contribution to the surface energy of the five substrates as obtained using Owens-Wendt's formalism [17] for treating the corresponding θ values obtained with the four liquids. The untreated cellulosic substrate exhibited a polar component as high as the dispersive one, as expected from an OH-rich surface.

With the introduction of non-polar chains from anhydride-bearing coupling agent III, albeit bearing COOH and COOR functional groups resulting from the esterification coupling, the dispersive component did not change, whereas the polar one decreased considerably. Interestingly, this decrease was more substantial when I was used as the grafting agent, in accordance with the behaviour of the respective contact angles. This fact corroborates our interpretation based on the higher density of polar groups (mostly COOH) when the styrene-maleic anhydride copolymer (III) was used as surface modifier.

TABLE II Equilibrium contact angles (°) of different liquids on tracing paper before and after grafting with different coupling agents

	tracing		*coupling agent*		
liquid probes	*paper*	*I*	*II*	*III*	*IVa*
water	32 ± 3	74 ± 8	76 ± 4	65 ± 5	92 ± 3
formamide	24 ± 7	58 ± 5	36 ± 4	50 ± 3	69 ± 7
ethylene glycol	44 ± 3	59 ± 6	50 ± 6	48 ± 8	61 ± 4
diiodomethane	33 ± 2	35 ± 4	32 ± 5	29 ± 4	34 ± 2

TABLE III Dispersive and polar components of the surface energy (mJ m^{-2}) of tracing paper before and after grafting with different coupling agents

	tracing		*coupling agent*		
	paper	*I*	*II*	*III*	*IVa*
γ_S^D	29.4	27.3	36.0	28.1	34.4
γ_S^P	20.0	8.6	6.1	13.2	1.0
γ_S	49.4	35.9	42.1	41.3	35.4

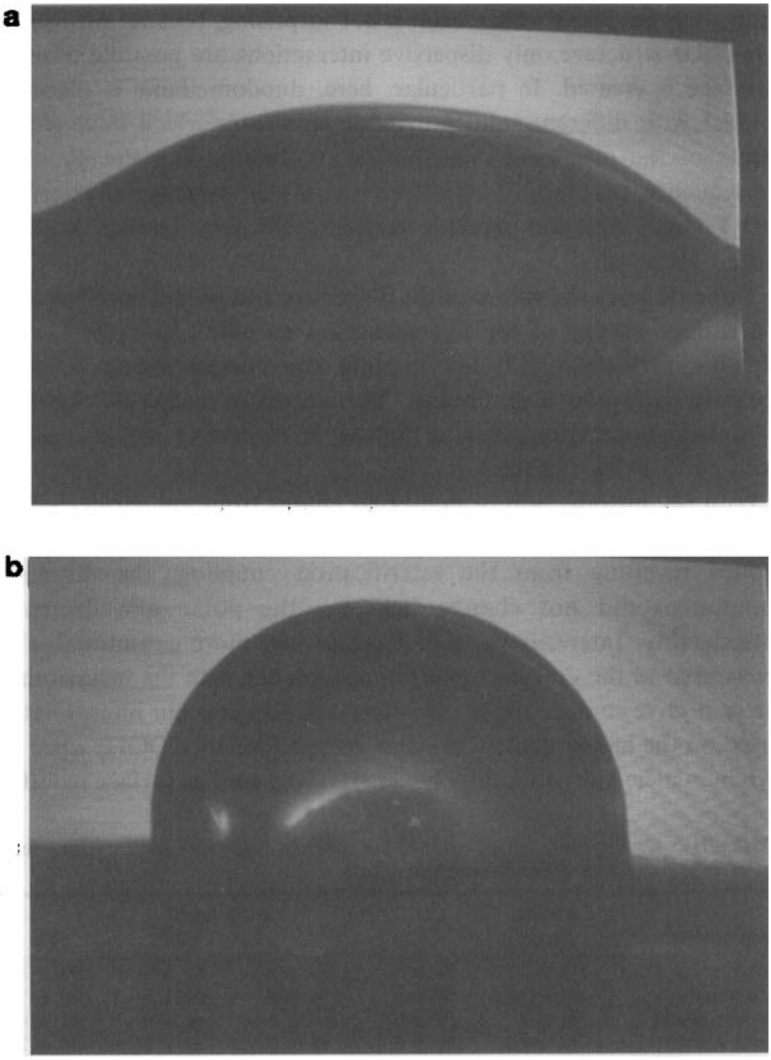


FIGURE 4 Photographs of a water drop on (a) pristine tracing paper and (b) modified with coupling agent IVb.

The grafting of the isocyanate-bearing styrene copolymer (IV) again gave rise to the least polar surface since the contact angles indicated an almost exclusively dispersive character. This result confirms all previous observations concerning this specific treatment [7] and is readily explained by the joint effect of the non-polar character of the styrene units and the high molecular weight of this coupling agent providing an efficient surface coverage. Note again that this dispersive value is close to those obtained for the other treated and untreated surfaces.

The only minor anomaly in this otherwise consistent set of features is the relatively low value of γ_S^P and the correspondingly high value of γ_S^D for the cellulosic surface treated with the oligoether isocyanate (II).

3.3. A Comparison Between the Two Sets of Data

The results obtained by IGC and contact angle measurement give different types of information owing to the specific nature of each technique. In fact, IGC provides a molecular inspection of the surface and specific moieties can, therefore, be recognized by the probes. The presence and/or formation of acidic or basic sites can, thus, be detected before and after surface treatment, quite apart from the quantitative assessment of the dispersive contribution to surface energy. The present results made use of both potentials of IGC as discussed above.

Contact angle measurements represent a less microscopic way of inspecting a solid surface and the results reported here clearly show that only the global modifications could be revealed by the deposition of liquid derops, namely a loss of the polar character of the cellulosic surface which was the larger the more efficient the coverage by the grafting agent and the higher its dispersive character.

The fact of having used different substrates for the two types of measurements is unlikely to constitute a problem becasue the charaterization of several cellulosic materials (including Avicell and tracing paper) treated with coupling agents I–IV showed that the extent of grafting did not vary appreciably as a function of the substrate, but depended instead strongly on the chemical nature and the molecular size of the reagent used [7].

4. CONCLUSION

The radical changes in surface properties induced by various chemical modifications of cellulosic surfaces were considered as very convincing evidence of the usefulness of these treatments. In particular, the introduction of non-polar polymeric chains as grafts on fibrous structures offers promise to improve considerably the quality of the interface between them and macromolecular matrices possessing a predominantly dispersive character, such as polypropylene. The elaboration of these types of composites and their mechanical testing will be discussed in a forthcoming paper.

Acknowledgements

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