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Cationic copolymerization involving NCO-bearing monomers and reaction of the ensuing materials with the superficial hydroxy groups of cellulosic fibres

José Antonio Trejo-O'Reilly [1], **Jean-Yves Cavaillé** [1], **Alessandro Gandini** [2]

[1] CERMAV-CNRS, BP 53, F-38041 Grenoble Cedex 9, France
[2] Ecole Française de Papeterie et des Industries Graphiques (INPG), BP 65, F-38402 St. Martin d'Hères, France

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Summary

This paper describes the cationic polymerization of 3-isopropenyl-α,α'-dimethylbenzyl isocyanate (TMI) and its copolymerization with isopropenylbenzene (IPB) in order to synthesize materials with varying amounts of NCO side groups. These polymers were characterized by FTIR, ^{1}H-NMR, elemental analysis and DSC. Their structure showed an essentially random incorporation of TMI. Preliminary reactions of the copolymers with cellulosic fibers are also reported.

Introduction

Composite materials involving a polymeric matrix and cellulosic fibres have been the object of a recent upsurge of research activity (1-2) because the replacement of traditional reinforcing agents like glass fibres with these natural counterparts can provide good mechanical properties, lower densities, easier recycling and economic advantages. One of the standing problems is to achieve adequate compatibilization of the interface because one deals in general with non-polar matrices and highly polar surfaces associated with the OH groups of the cellulose chains. Among the solutions sought are specific treatments of the fibres, such as corona discharge (3), their chemical grafting by free-radical reactions (4) and the use of copolymers in which the main structure is that of the required matrix but with small amounts of reactive comonomer units like maleic anhydride (5). The use of isocyanates to modify the surface of cellulosic fibres has also been described (6).

It seemed interesting to investigate a novel way of attacking this problem, by (i) either preparing a copolymer with varying amounts of NCO groups which could provide points of chemical attachment to the fibres' surface and therefore an improved compatibility with bulk homopolymers with similar structures; or (ii) condensing NCO-bearing alkenyl monomers onto the fibres and thereafter polymerizing a conventional monomer in the presence of these alkenyl-modified fibres in order to obtain copolymers again possessing covalent bondings to the surface. In both instances the matrix and the fibres would therefore be chemically connected and provide a very compatible interface. The present communication reports preliminary results concerning the former approach.

Experimental

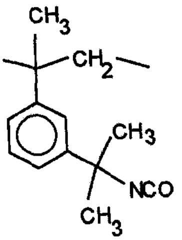
Commercial IPB (Aldrich) was vacuum-distilled over calcium hydride and stored at -2 °C. Commercial TMI (Aldrich) was used as received. The initiator was $TiCl_4$ used as a commercial 1M solution in dichloromethane (Aldrich). Commercial dichloromethane (SDS) was stored over activated 50 nm molecular sieves. Polymerizations were conducted for 30 min at -75 °C under nitrogen and stopped by adding an excess of monoisopropylamine which neutralized the acidic medium but also reacted with the NCO groups in the polymer. In the systems involving the reaction of the NCO-bearing polymers with the surface OH groups of cellulosic fibres (commercial AVICEL microcrystalline cellulose or TENCEL (lyocel) regenerated cellulose fibres), the polymerization media were neutralized with triethylamine, allowed to reach room temperature, diluted by a factor of three with dichloromethane before adding the dry cellulose sample.

The polymers neutralized with monoisopropylamine were isolated by precipitating in excess methanol, filtering and vacuum-drying to constant weight. Their structural characterization called upon elemental analysis, IR and ^{1}H-NMR spectroscopy. Their thermal properties were probed by DSC. The polymers grafted onto cellulosic fibres were isolated by filtration, washed several times with dichloromethane to remove any ungrafted material, vacuum-dried to constant weight and characterized by IR spectroscopy.

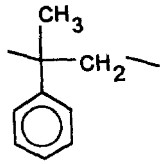
Results and discussion

It has been reported (7) that although the radical homopolymerization of TMI in solution is not feasable, its copolymerizations with acrylic and styrenic monomers occur with a good degree of incorporation of the isocyanate comonomer (7,8). It has also been briefly mentioned (7) that TMI is sensitive to cationic activation. Interestingly, there is very little published information on the role of isocyanates in cationic polymerization. One of us (A.G.) recently found that the presence of aromatic or aliphatic isocyanates in systems involving the cationic polymerization of isobutene did not alter their kinetic features even at high concentrations, i.e. their presence did not seem to interfere with the normal course of the reaction. This feature is not surprising since isocyanates have an electrophilic character. We confirmed that TMI homopolymerizes under the action of $TiCl_4$ with water cocatalysis at low temperature. This prompted us to study the cationic copolymerization of IPB with TMI.

The two comonomers were found to display similar reactivities because the copolymer compositions at low conversion were close to the initial monomer feeds. We are presently establishing a more quantitative assessment of the reactivity ratios. Figures 1 and 2 give respectively the FTIR and ^{1}H-NMR spectra of a copolymer with about 80% IPB and 20% TMI units (calculated from the values of the elemental analysis: C 85.65%, H 8.67%, N 3.28% and O 2.09%) obtained according to the isolation procedure described above. The structures of the two monomer units before neutralization are therefore:



TMI



IPB

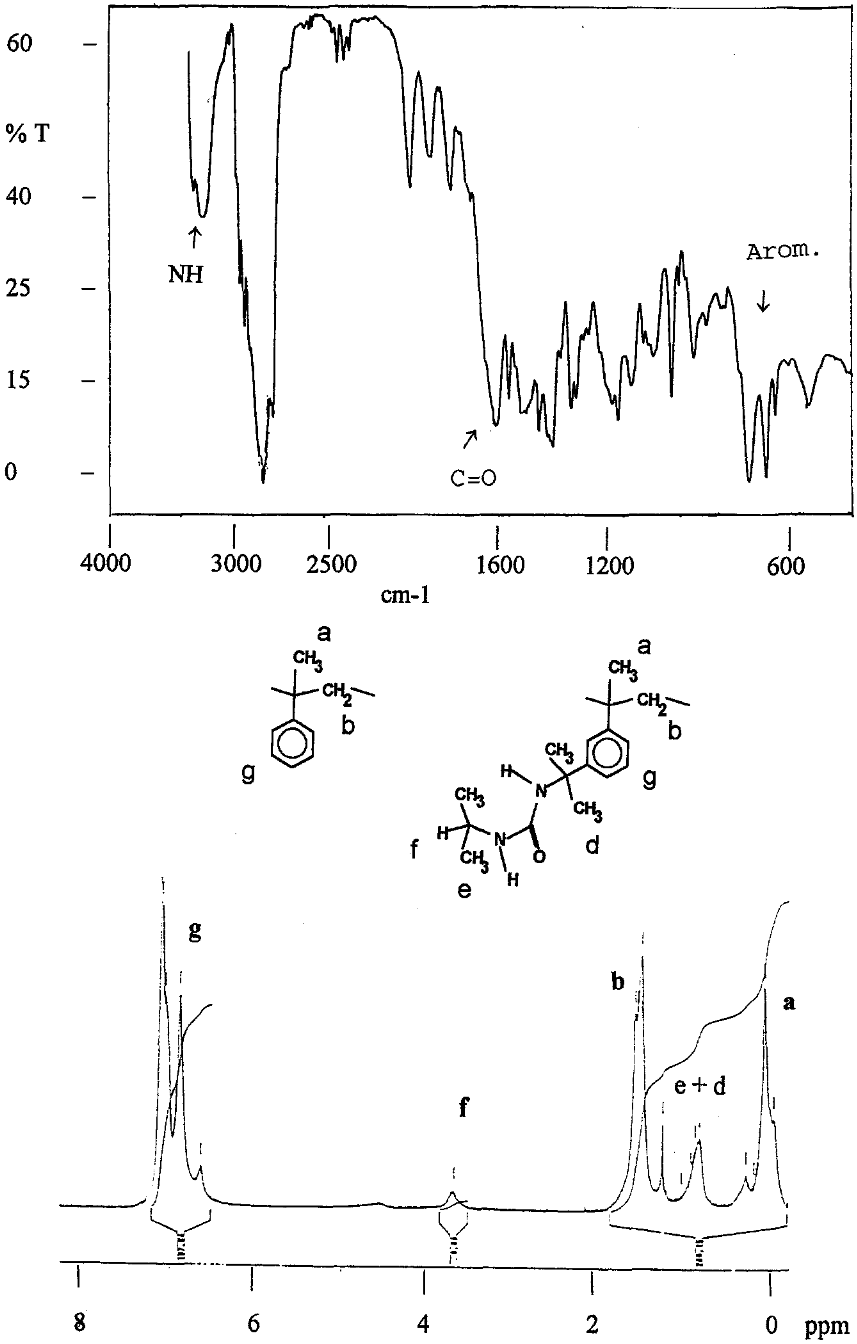


Figure 1 and 2 FTIR and ^{1}H-NMR spectra of the 80/20 copolymer.

The relevant features in the IR spectrum (Fig. 1) corresponding to the modified TMI units are the carbonyl peak at 1656 cm^{-1} for the urea group and the corresponding NH peak at 3350 cm^{-1}. The NMR spectrum (Fig. 2) shows the aromatic protons arising from both types of monomer units and the resonances of the various aliphatic moieties, among which the singlet at 3.7 ppm is attributed to the methyne protons of the modified TMI units. The urethane N-H protons are bearly visible around 4.5 ppm because of their lability which promotes important exchanges and thus a very broad resonance. The peak at 0.8 ppm reflects the resonance of the 12 isopropyl protons in the modified TMI units. The relative intensities of all peaks are in good agreement with the structure of each monomer unit and with the composition calculated from elemental analysis data, viz. 80% of IPB units and 20% of modified TMI units, probably distributed in a random fashion.

The DSC thermograms of the IPB-TMI copolymers were typical of amorphous macromolecular materials with a single discontinuity attributed to their glass transition. The Tg of the copolymer described above was 162°C, i.e. a decrease of some 8 degrees caused by the presence of 20% of modified TMI units, with respect to the Tg of the IPB homopolymer which was 170°C, in good concordance with the literature.

Having established the possibility of synthesizing random copolymers of IPB and TMI by cationic initation, we proceeded to examine their reactivity towards the surface OH groups of cellulose in view of applying this approach to the compatibilization of cellulosic fibres with non-polar polymeric matrices. Therefore, instead of neutralizing the copolymer solution at the end of the reaction with isopropylamine, a tertiary amine was used in order to preserve the NCO functions borne by the copolymer. An excess of triethylamine was added not only to neutralize the acidity due to $TiCl_4/H_2O$, but also to provide a good catalytic medium for the subsequent reaction between the NCO of the copolymer and the OH from the cellulose surface. The amount of cellulose added was calculated so as to have an excess of surface OH groups with respect to the available NCO from the copolymer, i.e. to insure the complete consumption of the latter groups.

As an example, to a CH_2Cl_2/triethylamine solution containing 2.6 g of the 80/20 IPB/TMI copolymer were added 7.8 g of AVICEL cellulose. The resulting suspension was stirred at room temperature for four days before filtering, washing the solid with CH_2Cl_2, drying and weighing it. In this way 10.3 g of product were recovered, which indicated a very high grafting efficiency, since only about 0.1 g of copolymer was left in solution. The FTIR spectra of the AVICEL cellulose before and after grafting are shown in Fig.3. The most important differences are related to (i) the appearance of two peaks in the carbonyl region around 1740 and 1610 cm^{-1} attributed to the urethane functions; (ii) the appearance of two peaks around 705 and 780 cm^{-1} arising from the aromatic rings and occurring at the same frequencies as those of the corresponding IPB/TMI copolymer (see Fig. 1); (iii) the substantial decrease in the relative intensity of the OH band around 3400 cm^{-1}.

The fact that the sample recovered weighed considerably more than the added cellulose and that this weight increase corresponded closely to the amount of copolymer formed, were strong indications of a good coupling efficiency between the superficial cellulosic OH groups and the NCO moieties of the copolymer in solution. The IR spectra clearly confirmed this conclusion. Fig. 4 illustrates both a specific moiety created by the condensation reactions between NCO and primary OH groups and the ensuing interchain assembly at the surface of the cellulose. Since the copolymer contained

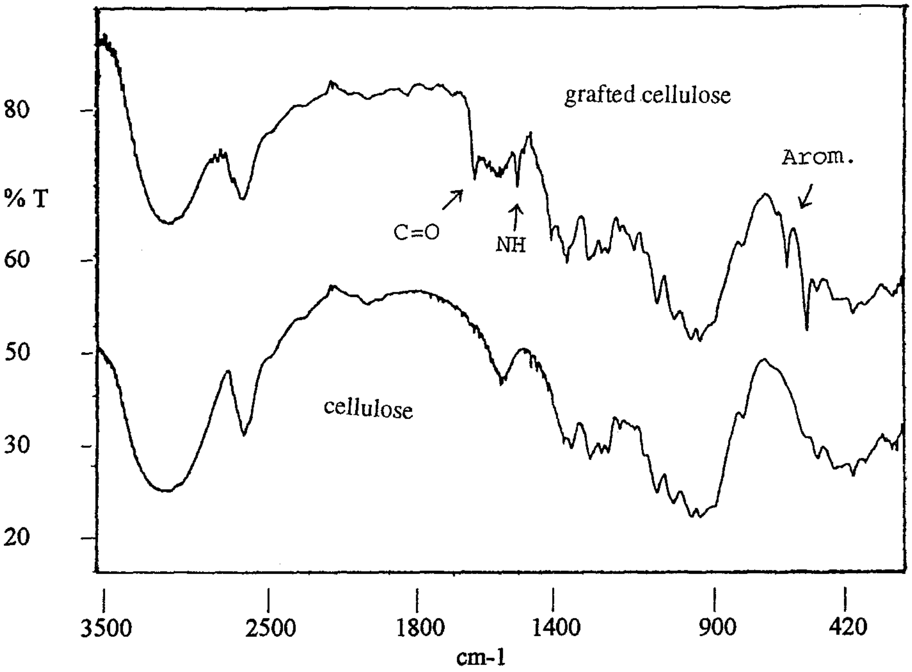


Figure 3 FTIR spectra of cellulose samples before and after modification.

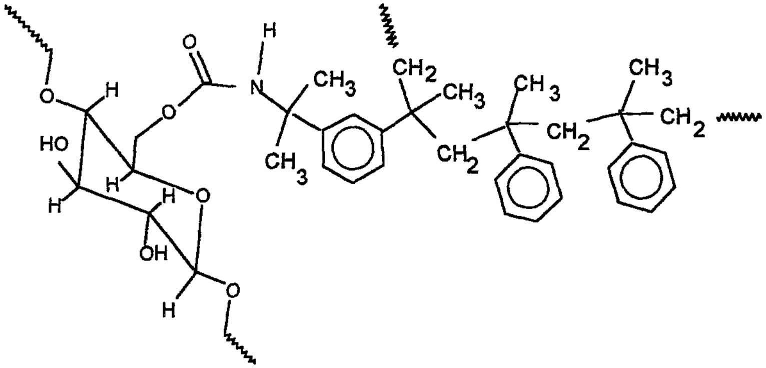


Figure 4a

Figure 4b

several NCO function per macromolecule, its condensation onto the cellulose surface produces ribbon-like configurations (Fig. 4b). Of course secondary OH functions can also intervene in these coupling reactions, albeit with lower kinetic probability.

Much remains to be done to fully characterize these new "surface copolymers", in terms of chemical and physical properties. We are presently extending the range of materials prepared on the basis of this idea and studying their surface composition and energy. We are also preparing composite materials from cellulosic fibres treated according to this procedure and different matrices in order to test their mechanical properties and see whether the chemical modification of the cellulosic surface has improved the quality of the interface.

Finally, work is also in progress concerning the second approach to this problem, namely the reaction of TMI with the superficial OH groups of cellulose followed by the activation of a common monomer in the presence of these modified natural fibres in view to induce its copolymerization with the pendant alkenyl groups from the grafted TMI.

Conclusion

Cellulosic surfaces can be made to react efficiently with copolymers bearing isocyanate functions thus obtaining major changes in their chemical nature which in turn should result in a corresponding change in the surface characteristics. In principle this method ought to work with a variety of reactive surfaces (e.g. other polysaccharides, polyvinyl alcohol, polyethyleneimine,...) as well as with different copolymers based on TMI, but also on other NCO-bearing monomers, and various comonomers. The implication of this general methodology applied to the improvement of the mechanical properties of polymeric composites containing cellulosic fibres seems quite promising.

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