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Analysis of the Structure of Polyurethane Matrix in Fiber-Composites

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Summary.

The presence of fiber tissues disturbs the chemical reaction between isocyanate and alcohol or amine. The extraction by the solvent tetrahydrofurane shows that the matrix polyurethane with carbon or aramid tissues contain an abnormally high proportion of soluble macromolecules. The FT-IR analysis shows incomplete reaction with these two fibers, or by-side products present on the glass fiber surface.

Introduction.

After having studied the physical behaviour of polyurethane and polyurethane-urea by varying notably the structure of the chain extender (Y. Camberlin and al, 1982), we are now focusing our attention on the use of these polymers as soft matrix in composites.

In this paper we deal with the characterization of the polyurethane matrix and the eventual differences caused by the presence of fibers. Two techniques have been used for this : extraction, followed by Gel Permeation Chromatography (GPC) of the solvent extracts and Fourier-Transform Infra-Red Absorption (FT-IR).

The physical behaviour of these materials will be published later on.

Experimental.

We used two polyurethane formulations :

1 - Adiprene L100 (DuPont Ref.) is a polyoxytetramethylene glycol prepolymer ($\overline{Mn} \cong 1000$) reacted with toluene diisocyanate (TDI). The chain extender used with this prepolymer is the methylene 4,4' bis (o.chloroaniline) (Moca).

2 - Adiprene M400 (DuPont Ref.) a similar prepolymer ($\overline{Mn} \cong 1000$) reacted with methylene 4,4' diphenyl diisocyanate (MDI). The chain extender for this formulation is 1,4 butane diol.

The fiber tissues used as reinforcements are presented in Tab. 1.

The only difference between the two glass fiber reinforcements is the coupling agent. A1100 (Union Carbide Ref.) is a classical amino silane which we have fixed on the glass fiber tissue ; whereas P109 is a Vetrotex-Saint Gobain Ref. with amine and epoxies functions.

The reaction mixture (prepolymer and chain extender) are cast into moulds where the fiber plies have been previously laid.

Tab 1. Characteristics of tissues used as reinforcements
a) Vetrotex ref. ; b) γ amino propyl triethoxy-silane ;
c) Brochier ref.

Tissues	V-P109 a)	V-A1100 b)	G827 c)	E1950 c)
Fiber	R-glass		Carbon T300	Aramide K49
mass per area unit (kg/m^2)	0.340		0.160	0.100
density (kg/m^3)	$2.55.10^{-3}$		$1.74.10^{-3}$	$1.45.10^{-3}$
single layer theorical thickness (mm)	0.13		0.09	0.07
weft weight (%)	6.5		.15	5

In order to forme 1 mm thick sheets of composites -with a fixed fiber volume ratio we are obliged to vary the number of plies depending on the nature of fibers as shown in Tab. 2.

Tab. 2. Different composites (sheets 1 mm thick) a) per cent obtained by calcination and weight ; b) sheets 1.2 mm thick

Composite	V(glass)	C(carbon)	K(aramide)
Number of plies	4	6 8 b)	8
Volumic fraction of reinforcement (%)	52 a)	54 65 b)	49.6 b)

The reaction for the polyurethane L100 takes place at 100°C and lasts for 3 hours. In the case of M400, the reaction mixture takes place at 80°C and then annealing at 110°C lasts 15 hours.

The extractions of the tetrahydrofurane (THF) soluble fractions of the PUR are carried out at room temperature with a continous stirring during the 48 hours. The residual polymer is filtered and then vacuum dried until constant mass ; three control extractions are carried out using the same procedure. The extracts are analysed by GPC.

InfraRed Analysis is performed using a Fourier Transform InfraRed Spectrometer Nicolet MX1. For each composite, two series of analysis are carried out. The first, on the sample taken from the core of the material, and the second one on the sample obtained by scratching the interface matrix-fiber. Thus we hope to characterize the whole matrix and to observe the possible modifications at the surface of the fiber.

Absorbance spectra of fiber reinforced composites are obtained from KBr pellets containing the finely ground materials.

Results.

1) The weight losses of the composites caused by the extraction of a fraction of polyurethane matrix with THF solvent are given in Tab. 3.

Tab. 3. PUR weight loss in composites (stirred 48 h in THF). a) PUR matrix alone ; b) the number indicates the number of plies

Fiber	a)	V-P109$_{(4)}$	V-A1100$_{(4)}$	C$_{(6)}$	C$_{(8)}$	K$_{(8)}$ b)
% extract PU-L100	2.2±0.1	6.9 ± 0.1	4.9 ±0.05	17.4±1.0	24.4±1.4	96.1±3.0
% extract PU M400	2.3±0.1	5.6 ±1.0	--	--	34.4±0.6	97.1±0.5

Slight differences are observed depending either on the nature of PUR or on the number of fiber plies (6 or 8 in the case of carbon) ; but major differences result from the nature of the fiber.

The weight loss in the case of glass-fiber is quite comparable to that observed for the matrix alone. For carbon fibers these losses are much more important (20-30 %) and with Aramid we can extract nearly all the matrix.

GPC analysis of soluble fractions shows nearly always the same molecular weight distribution, which correspond in fact (in the region of the higher $\overline{Mw}$) to the limit of solubility of PUR in THF (Fig. 1).

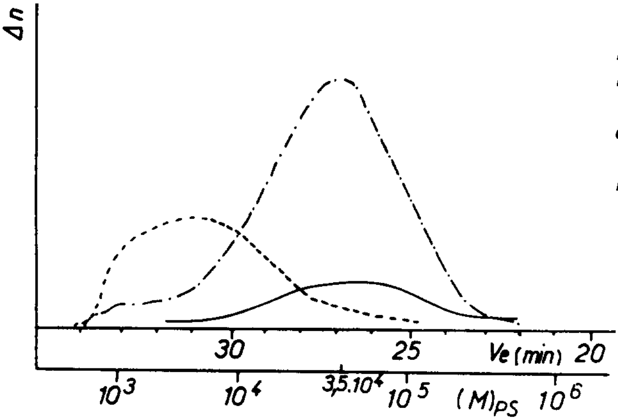


Fig. 1. Chromatograms of PUR soluble fractions in THF : (———) C$_{(6)}$-L100 and (-.-.-) C$_{(8)}$-M400 ; (----) initial L100 prepolymer

On the other hand, there are no lower Mw fractions on the chromatograms ; the THF soluble extracts do not contain any prepolymer or any diisocyanate or any chain extender which would not have reacted.

2) InfraRed Analysis of PUR has been extensively studied (Nakayama and al 1969, H. Ishihara and al 1974, V.W. Srichatrapimuk 1978). We have focused our attention on the absorbance region of 2000 - 1000 cm^{-1}, and in particular on the absorption bands of carbonyl groups $>C=O$:

1732 cm^{-1},free	$>C=O$ in urethane group
1705 cm^{-1},bonded	$>C=O$ in urethane group
1660 - 1630 cm^{-1}	$>C=O$ in urea group

The aramide-composites spectra are very difficult to handle because of the overlapping of the urethane bands due to the strong absorption of the fiber aramide group.

On the other hand, all the spectra regarding the carbone-composite present intensive diffusion.

The spectra of the core and the interface in the glass-fiber V-M400 composite are shown in Fig. 2a and Fig. 2b respectively.

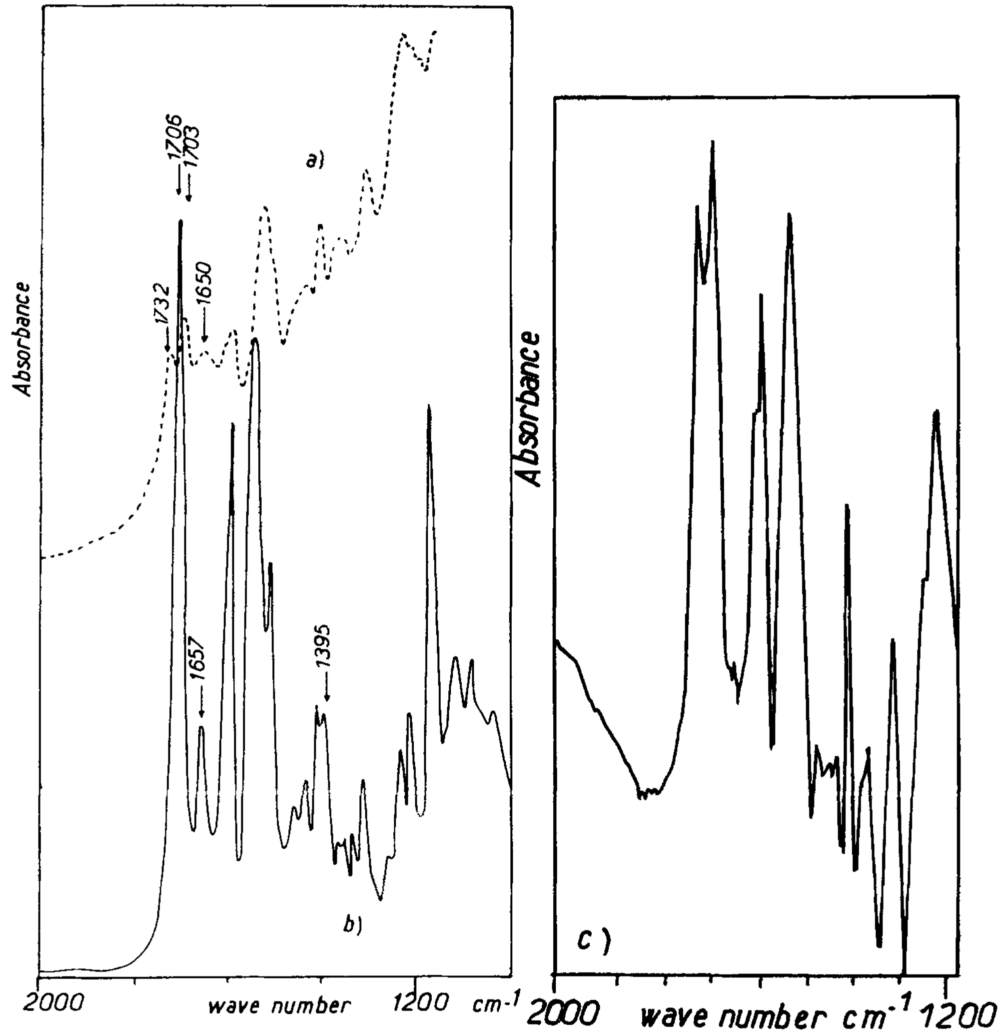


Fig. 2. IR spectra of V(P109)-M400. a) in the core ; b) at the fiber surface ; c) M400 alone

The important differences between spectrum Fig. 2a and the spectrum of the polyurethane M400 matrix is the appearence of a new band at 1650 cm^{-1} due to the carbonyl $>C = O$ in the urea group, and the increase of band intensity of the bonded $>C = O$. The spectrum of the interface (Fig. 2b) is very different from the previous one (Fig. 2a). We notice again the presence of urea groups due to the absorption band at

1650 cm^{-1} which is relatively stronger.

The thing worth noticing is the total absence of free $>C = O$ band (1732 cm^{-1}), and the band at 1706 cm^{-1} gaining in intensity. But it should be noted that a new band has appeared at 1395 cm^{-1} which is due to $>C = O$ absorption in isocyanurate rings (A.T. Dang Thi and al, 1983) and that may explain on the other hand, the increasing intensity of the absorption band at 1706 cm^{-1}, the latter being the superposition of bonded $>C = O$ in urethane and $>C = O$ in isocyanurate. Finally, the polyoxytetramethylene (POTM) bands are fine and less intense compared to those of the matrix alone (see 1080 cm^{-1} - 1100 cm^{-1}). This leads us to thinck about a certain orientation of these chain segments on the surface of fibers.

The spectra on Fig. 3 of composite C-M400 represente a large degree of diffusion. The only thing we can notice is the high proportion of bonded $>C = O$ in urethane.

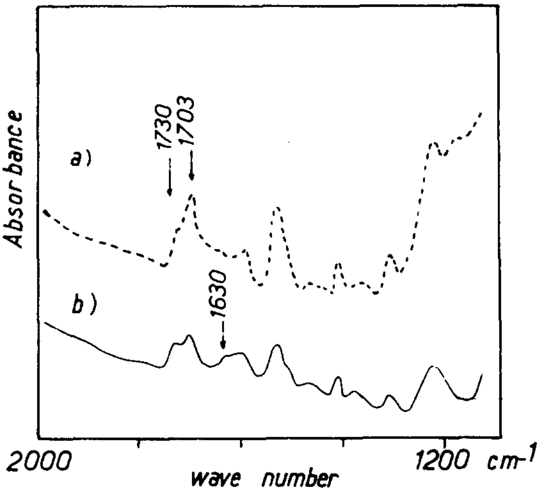


Fig. 3. IR spectra of C-M400 composite
a) in the core
b) at the fiber surface

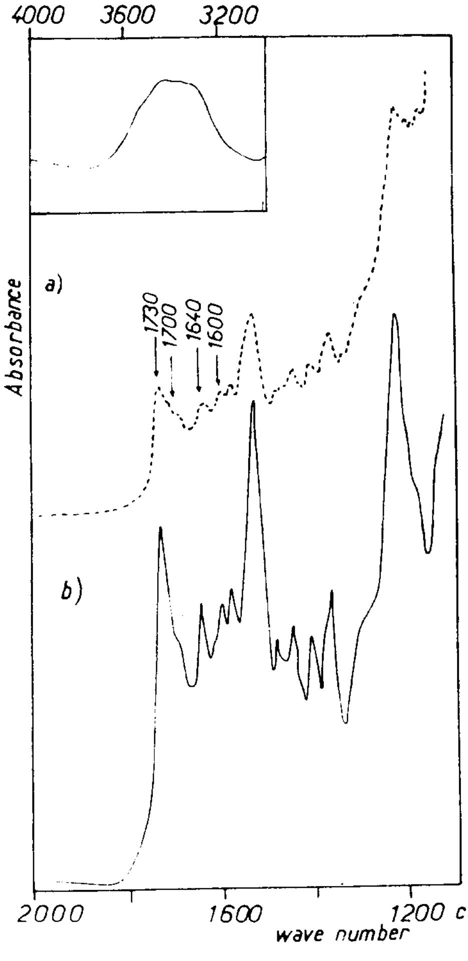
On the spectra of Fig. 4 and 5, the $>C = O$ urea bands (1640 cm^{-1}) belonging to C-L100 composite and compared to $>C = O$ in urethane, appear to be less intense than those in V-L100 composite. For the C-L100 composite, the free and bonded $>C = O$ bands are poorly separated as if there was a large zone of interference due to hydrogen-bonds. The separation is better in the case of the V-L100 composite where the bonded $>C = O$ appears at 1690 cm^{-1}. The δ_{NH} band (1530 cm^{-1}) was of equal intensity in the two cases (V-L100 and C-L100) ; but the ν_{NH} band had a sharper maximum in the case of V-L100 (3300 cm^{-1}) whereas for the C-L100 the maximum stretched from 3320 cm^{-1} to 3420 cm^{-1}.

Finally, the extracts of soluble fractions in THF were analysed. The spectra were comparable to those obtained for the matrix alone.

Discussion and Conclusion.

1) The extraction by the solvent THF shows that the matrix PUR with carbon tissue contains an abnormally high proportion of soluble macromolecules with a molecular mass of $\overline{Mn} \cong 30000$. This is confirmed by the IR spectra. For example, in the case of C-L100 composite we were able to distinguish on the IR spectrum of the polymer, the urea bonds due to the extension of the macromolecular chains of urethane group in the prepolymer. These urea bonds are in much smaller proportion than for a poly-

Fig. 4. IR spectra of V(P109)-L100 composite
a) in the core
b) at the fiber surface



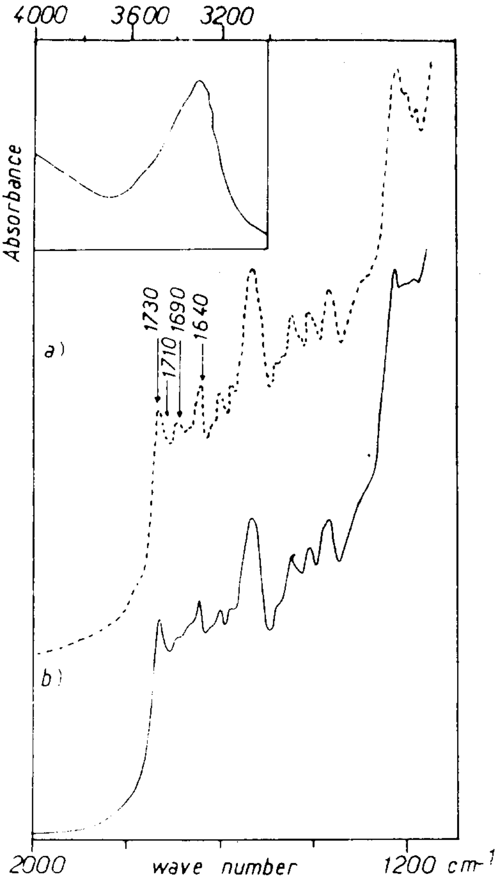
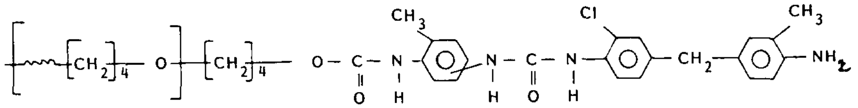


Fig. 5. IR spectra of C-L100 composite
a) in the core
b) at the fiber surface

urethane-urea (L100) prepared in the absence of tissue reinforcements. However, the ν_{NH} bond is intense and complex due certainly to the presence of the amine group (-NH$_2$) at the end of the chain :



The functional group present on the macromolecule has difficulties in reacting in the last stade of the reaction because of the presence of the fiber tissue. This would explain the weaker molecular mass distribution, the lack of urea groups and the persistance of amine when the chain extender is Moca. In the case of carbon tissue, the amount of extract increases as we pass from 6 to 8 plies.

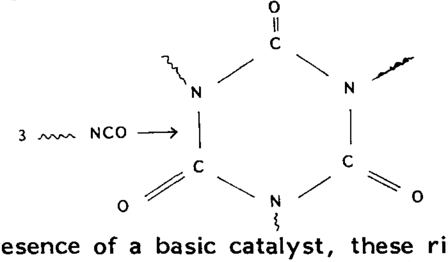
But we do not observe any noticeable difference between the structure of the matrix at the heart of the composite and on the fibre surface.

2) The presence of an aramide fiber tissue has a catastrophic effect on the reaction rate of the polycondensation. The phenomena of steric hinderance and functions dilution due to the presence of tissues is not enough to explain this result. We can evoke the polar structure of aramide molecules which may form complexes with the alcohol and isocyanate functional groups, thus slowing down the chemical reaction.

3) The glass fibers give totally different results. It is well-known that water molecules are always present on the glass surface. These molecules are not inert with respect to the isocyanate groups, they react giving amine groups capable in turn of forming urea bonds. These bonds can also be formed by the reaction with the coupling agent present on the surface of glass fibre. This explains the larger amount of urea bonds in the V-L100 composite than in the C-L100 one. This mechanism allows us to explain the presence or urea bonds in the composite V-M400 which logically should have only urethane bonds.

The urea bonds are found rather on the surface of reinforcement than in the core or the matrix.

The reactivity of the glass surface suppresses the negative effect due to the presence of the tissue layer. The composite V-M400 possesses on the other hand the particularity of having macromolecules PUR on the fibre surface very different from that found in the rest of the matrix. The basic nature of glass can explain the formation of isocyanurate rings.



In the presence of a basic catalyst, these rings are more easily obtained with MDI as diisocyanate than with TDI (A.T. Dang Thi and al, 1983). Finally, the lack of polyoxytetramethylene POTM soft segments can be explainded by a segregation of the hard segments (MDI + 1.4 Bd) on the surface of the fibers as observed on the cold walls of the mould during the manufacturing of polyurethanes by the RIM process (A.L. Chang and al, 1982). The reaction ~NCO + amine is much faster than the ~NCO + alcohol reaction, and this segregation effect will not be observed with L100 polyurethane formulations.

In conclusion, the extract by a solvent followed by GPC analysis and coupled to the FT-IR analysis give us useful indications concerning the structure of the PUR matrix and of the perturbations caused by the fibres of different nature during the chemical reaction. These observations will be very useful to understand the different stress-strain behaviour and ultimate elongations of our materials.

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