DETERMINATION OF LIQUID FRACTIONS IN FLAX COMPOUNDS USING LOW RESOLUTION NUCLEAR MAGNETIC RESONANCE*

J. Sobottka[1], I. Ritter[1], V. V. Drach[2]

[1]Institut Nachwachsende Rohstoffe e. V. i. G., Hausvogteiplatz 5-7, D 10117 Berlin, Germany
[2]ECCO-Gleittechnik Seeshaupt, Germany

A b s t r a c t. The liquid fractions in flax compounds are essentially caused by organic fluids but not by water.

K e y w o r d s: nuclear magnetic resonance, compounds with denatured flax, brake lining, hardening of resins

INTRODUCTION

For industrial use of flax fibres the BMFT (now BML) sponsors projects which deal with the application of native or denaturated flax fibres in clutch and brake linings. There is a growing industrial interest in the use of flax as re-inforcement or as process fibres also for other fields of application, e.g., for construction materials, plastics, sealing, etc.

Low resolution nuclear magnetic resonance (NMR) is a suitable method for measuring the liquid water content or/and the fraction of other liquids without chemically or physically changing the material. The investigated samples are compounds, which also include water and organic liquids. It is in principle complicated to distinguish the NMR-signal of water from that of other organic liquids.

EXPERIMENTS

The samples were measured in their original i.e., granulated or flaky - form in 10 mm-diameter ampoules using a NMR device Minispec PC 120/125/10 VTS-GRA from the BRUKER Co. Karlsruhe. The examples of original signals (Figs 1 and 2) we got from an OXFORD OP 20 NMR device. Both devices are desk top devices with a permanent magnet, working with a magnetic induction of $B_o=0.47$ T and a related resonance frequency of the protons of $f_o=20$ MHz. The measuring temperature amounts to 40 °C.

We use the free induction decay (FID) for the NMR-measurement. In this case the signal voltage U1 at the time $t=0$ is proportional to the total number of protons in the sample. The signal voltage U2 at the time $t=60$ μs is proportional to the number of protons in the liquid fraction. After the correction of device-produced measuring errors we get the correct signal voltages U1 and U2. The ratio U1/U2 is the correct amount for the molar liquid fraction of the samples. The zero lines of the signals where shifted for better presentation in the figures. An electronical analytical balance of the typ PC WS 120S of the SARTORIUS Co. was used to compare the NMR-fractions and the mass fractions after tempering at 150 °C.

RESULTS

Ten samples named Flax C 01-10 were measured. The molar liquid fractions obtained are presented in Table 1. The original names of the producer are also given in Table 1 for reference.

T a b l e 1. LR-NMR-measured liquid fractions of flax compounds

Sample name	Code name (Setralit)	Liquid fraction by NMR (%)
Flax C 01	FC /001 -4 SA	4.5
Flax C 02	FNT/108-8 SG	5.5
Flax C 03	FNT/116-4 SG	9.8
Flax C 04	FT/ 075 -4 SG	10.3
Flax C 05	FNT/111-4 SA	10.9
Flax C 06	FG /008-4SG	13.0
Flax C 07	FG /003-4 SG	26.7
Flax C 08	FG /002-4 SG	28.5
Flax C 09	FNT/119-8 SG	47.5
Flax C 10	FNT/143-4 SG	51.7

Two aspects shall be discussed here:

a) NMR-line shape of weak liquid signals

The signals of Fig. 1 show a significant relative minimum at the time $t = 20\,\mu s$ which cannot be interpreted by a superposition of monotonic decreasing exponential functions.

b) Tempering effects in samples with intensive liquid signals

Intensive liquid signals have been observed in the samples Flax C 09 and Flax C 10, whose source is not clear. To find the origin of the critical signals it was necessary to measure before and after tempering at 150 °C. Therefore the difference of the NMR-signals and the mass difference was measured. In the Table 2 the mass losses and the decrease of NMR liquid signals are compared for both samples. The expected mass loss was not observed.

DISCUSSION

a) NMR-line shape of weak liquid signals

The minima at $t = 20\,\mu s$ in the NMR signals are of methodical interest (cf. Fig. 1).
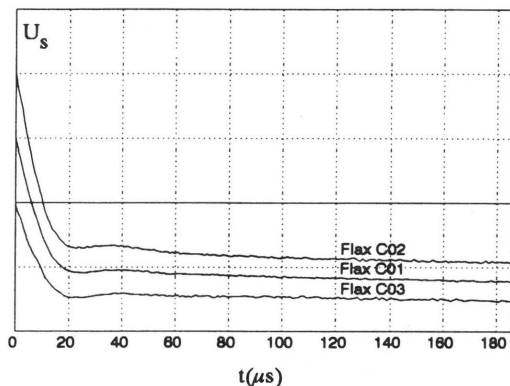

Fig. 1. LR-NMR-signals of flax compounds with low liquid fraction.

Such minima are caused by the solid state protons. The NMR-spectra of so-called solid pairs of protons have a sinus-modulated shape and are described by an ABRAGAM-function [1] $U_S(t)$:

$$U_S(t) = \frac{\sin \omega_A t}{\omega_A t} \exp\left\{-\omega_B^2 t^2\right\} \qquad (1)$$

In principle the line shape of the solid spectra in Fig. 2 is also sinus-modulated (Eq. (1)). However, the pure exponential
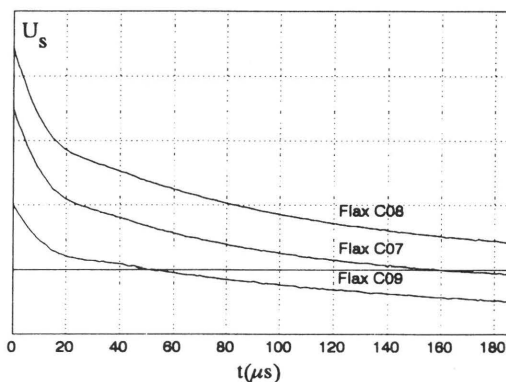

Fig. 2. LR-NMR-signals of flax compounds with high liquid fraction.

liquid signal is very intensive and covers the weak solid spectrum. Therefore the NMR-signals in Fig. 2 show a monotonic slope. The dead time in the order of 8 μs is not considered on the time axis in Figs 1 and 2. In the dead time the nuclear magnetization is relaxing undisturbed, but an observation is impossible. Further investigations are necessary in order to extrapolate the regular NMR-signal in the vicinity of the time origin.

b) Tempering effects in samples with intensive liquid signals

In the Table 2 some liquid fraction parameters of the samples Flax C 09 and C 10 are compared before respectively after tempering at the temperature $T = 150\,^\circ$C.

NMR liquid signal. In this case the two samples show a different behaviour:
- In the sample Flax C 09 the NMR liquid signal strongly decreases after tempering without a significant loss of mass for long tempering times.
- In the sample Flax C 10 the NMR liquid signal is constant during the process of tempering without significant loss of mass.

INTERPRETATION ATTEMPT

Sample Flax C 09 and C 10 obtain non-volatile fluid components in high concentration. The fluid components, e.g. resins in sample C 09 are hardened in the process of tempering in presence of oxygen from the surrounding air. The fluid components of sample C 10 do not harden.

T a b l e 2. LR-NMR of Flax C 09 and 10 - Compounds (High liquid fraction)

Liquid fraction LR-NMR:α_0(mol %) untreated	Tempering treatment at 150°C	Liquid loss	
		Δ m/m (Mass %)	NMR $\alpha_0 - \alpha_{temp}$ (mol %)
	Flax C 09		
46.7±0.6	0.5 h within the tube	4.3	3.1
46.7±0.6	0.5 h within the tube 0.5 h within the tube	4.6	32.6
47.8±0.6	1 h within the tube	2.5	6.6
48.5±0.6	3 h within the tube	0.8	39.1
50.2±0.6	3 h within the tube	1.2	35.8
49.4±0.6	1 h within the tube	-1.1	41.0
48.4±0.6	1 h within the tube	-1.4	39.0
	Flax C 10		
49.2±0.6	0.5 h within the tube	5.6	1.1
49.2±0.6	0.5 h within the tube 0.5 h within the tube	5.3	1.8
48.2±0.6	1 h within the tube	4.5	2.3
49.6±0.6	3 h within the tube	4.7	1.2
50.2±0.6	3 h within the tube	4.8	2.0
49.5±0.6	1 h within the tube	3.3	2.4
49.8±0.6	1 h within the tube	3.1	3.2

The first column presents the molar liquid fraction α_0 obtained by NMR. In the second column the tempering procedures are described. In the third column the mass loss is compared with the decrease of the

CONCLUSIONS

1. The liquid fractions referred to in Table 1 are essentially caused by organic fluids but not by water.

2. Between volatile and non-volatile fluids the distinction is possible by sample tem-

pering at $t=150$ °C.

3. In samples containing volatile organic fluis and water the NMR liquid signals and the mass are decreased after tempering.

4. In samples containing polymerizable fluids the NMR liquid signals are decreased after tempering, but the mass is approximately constant.

5. In the process of tempering the sample Flax C 09 is hardened up.

REFERENCES

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