Structural features and some physico-chemical properties of materials prepared from non-aqueous solutions of cellulose-synthetic polymer blends

2. High resolution $^{13}$C-NMR study of cellulose-synthetic polymer blends in the solid phase$^1$)


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By high resolution $^{13}$C-NMR-spectroscopy the blends of cellulose with poly(methyl methacrylate), poly(acrylonitrile), poly(vinyl acetate), poly(vinyl alcohol), and poly(dimethyl siloxane) are investigated at different cellulose : polymer ratios.

*Strukturelle Besonderheiten und einige physikalisch-chemische Eigenschaften von aus nichtwäbrigen Lösungen erhaltenen Mischungen von Cellulose und synthetischen Polymeren. 2. Hochauflösende $^{13}$C-NMR von Mischungen aus Cellulose und synthetischen Polymeren im festen Zustand*

Mit Hilfe der hochauflösenden $^{13}$C-NMR-Spektroskopie wurden Mischungen von Cellulose mit Polymethylmethacrylat, Polycynrlnitril, Polyvinylacetat, Polyvinylalkohol und Polydimethylsiloxan mit unterschiedlicher quantitativer Zusammensetzung untersucht.
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1. Introduction

High resolution solid phase $^{13}$C-NMR spectroscopy is a new efficient method applied to the investigation of fine structural features of cellulose, its derivatives and other polymers [1–4]. The main advantage of this method lies in obtaining signals from separate carbon atoms of an elementary link depending on conformations of pyranose cycles, side-groups and their mutual arrangement [5, 6].

The present paper describes the first application of the method to the investigation of wood cellulose and its blends with poly(methyl methacrylate) (PMMA), poly(acrylonitrile) (PAN), poly(vinyl acetate) (PVAC), poly(vinyl alcohol) (PVA), and poly(dimethyl siloxane) (PDMS) obtained in the form of powders by deposition from non-aqueous solutions.

2. Experimental

Blends of dimethylformamide or ethylacetate with dinitrogen tetroxide were used as a common solvent of cellulose and the synthetic polymer. The blends were precipitated from the solutions by use of water and ethyl alcohol. The prepared powders were carefully washed to remove the residual solvent and dried in the air. The cellulose : synthetic polymer ratio amounted to 20 : 80, 40 : 60, 50 : 50, 60 : 40, 80 : 20 (mass%).

The high resolution solid phase $^{13}$C-NMR spectra were taken on the spectrometer “Bruker CXP-200” with the revolution of the sample at magic angle. The working frequency according to $^{13}$C amounted to 50.03 MHz, magnetic field 5.7 T, temperature 25°C and revolution frequency 3 kHz. 2500 accumulations were carried out for every spectrum.

3. Results and discussion

Fig. 1 presents the spectra of the initial and precipitated cellulose from solutions of dimethylformamide and ethylacetate with dinitrogen tetroxide. As compared to the initial material the spectra of precipitated cellulose have all the distinguishing features of a polymer with a less ordered physical structure, which is characterized by disappearance of the C₄ signals at 89 ppm and fine structure signals from Cₓ, Cᵧ, C₅ in the range of 71 to 75 ppm. A shift of the Cₓ signal from 65.3 to 62.5 ppm which corresponds to a change in conformation of the oxymethyl group also occurs in the spectra. A considerable broadening of the signals from separate carbon atoms is indicative of the formation of a practically completely disordered structure after the precipitation of cellulose from non-aqueous solutions. There are no substantial differences in the spectra of the precipitated cellulosates though a less ordered structure is specific to cellulose regenerated from the solution of dimethylformamide with dinitrogen tetroxide, which is confirmed by broader signals, especially from Cₓ.

The spectra of the blends of cellulose with different synthetic polymers are given in Figures 2 to 6. In most cases it was very difficult to analyse these spectra in detail due to overlapping of the regions of chemical shifts of signals from carbon atoms of elementary links of the cellulose and of the synthetic polymers. In view of prac-


Fig. 1. High resolution $^{13}$C-NMR spectra of cellulose in the solid phase. a) initial; b) precipitated from solution in ethylacetate-NaOH; c) in dimethylformamide-NaOH

Fig. 2. High resolution $^{13}$C-NMR spectra of cellulose-PDMS blends in the solid phase
conservation of a great part of ordered regions in the cellulose precipitated from non-aqueous solution in combination with PDMS as compared with the cellulose precipitated from a pure cellulose solution. The coincidence of conformations of cellulose and of a synthetic polymer with those of the individual products precipitated from solutions shows that in the process of precipitation a new system of polymers is formed on a level of molecular aggregates rather than on the molecular level, that is which determines a peculiar conformational independence of the components and permits one to consider the studied powders as structural mixed compositions.

It follows from the spectra shown in Fig. 2 that in the case of blends with the ratio 50:50 the signals from the C₁ and C₄ carbon atoms are missing. However, in this case, i.e. at equal mass concentrations of cellulose and polymer in the blend, a marked broadening of cellulose bands from all carbon atoms is observed in the spectrum (Fig. 2b). It is indicative of a higher structural disordering in the cellulose. However, the possibility of similar concentration selectivity of structural transformations of cellulose is not ruled out for compositions of cellulose with the other polymers. It is evident that at equal mass concentrations of cellulose and polymer less favourable conditions for the formation of sufficiently extended sections of every component exist. Moreover, the dispersity degree increases, and a structure of a lower degree of ordering is formed as compared to other cellulose: synthetic polymer ratios.

On the basis of the data obtained one can derive a correlation between the properties of cellulose-synthetic polymer blends in a solution and in solid phase. The solutions of blends as two-phase systems have the lowest kinetic stability at the cellulose: polymer ratio 50:50 [7] which corresponds, due to the data of ¹³C-NMR spectroscopy, to the highest structural disordering of cellulose and polymer. No doubt, that the latter circumstance specifies also low values of mechanical strength of fibres.
and films formed from non-aqueous solutions of blends at an equal content of cellulose and a polymer [8]. Thus, the high resolution solid phase $^{13}$C-NMR study showed that at precipitation from non-aqueous solutions the miscibility of cellulose with synthetic polymers is realized at the level of aggregates of macromolecules.

References


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