

# SOLID STATE $^{13}\text{C}$ NMR STUDY OF MODIFIED POLY(3-HYDROXYBUTYRATE)

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## 1. Introduction

The increase in environmental pollution with synthetic plastics has become an ecological problem which has to be solved. However, processes such as combustion or recycling require sorting of garbage, which is a real problem even in developed countries. This is the reason why interest in those synthetic plastics which are known to undergo biodegradation is continuously increasing.

Poly(3-hydroxybutyrate) (PHB) is an optically pure linear polyester which is completely biodegradable into carbon dioxide and water [1]. This nontoxic biologically synthesized semi-crystalline material has a helical structure of macromolecules, which is the reason that some of its mechanical properties are similar to those of polypropylene. The material has low molecular weight and crystalline PHB has lamellar morphology with polymer chains oriented perpendicular to the crystallographic c-axis [2]. It has become highly studied thanks to its biodegradability, but its industrial applications are quite limited because of its brittleness and limited range of processing possibilities. The properties of this material change markedly during physical aging under ambient conditions. So far reported research results indicate that the brittleness of PHB can be caused by its high degree of crystallinity [3, 4], although it can be also attributed to the constraint imposed on the amorphous chains by the amorphous- crystalline interface [5]. Improved properties and better applicability have been observed in modified PHBs, some of which possess unique mechanical properties. The modifications can be accompanied by structural changes which can be studied using solid state  $^{13}\text{C}$  NMR. In this paper the changes in structure as a consequence of thermal treatment and plastification of PHB will be inferred from the  $^{13}\text{C}$  MAS NMR spectra.

## 2. Experimental

The pure unmodified powdered sample denoted as PHB and the samples modified by thermal treatment (PHB-A), blending with Joncryl (PHB-J), plastification with triacetine (PHB-T), and plastification and blending (PHB-TJ) were used for the NMR measurements. All modifications were processed with the use of the twin-screw extruder. The glass transition and melting temperatures and the degree of crystallinity of PHB were found with DSC to be 277 K, 458 K and 63.3 % respectively. The PHB-T and PHB-J samples contained 10.0 and 2.0 wt. % of triacetine and Joncryl respectively, and the PHB – TJ sample contained 10.0 wt% of triacetine and 2.0 wt. % of Joncryl.

The high-resolution solid-state  $^{13}\text{C}$  NMR measurements were performed on a Varian 400 MHz NMR spectrometer (Palo Alto, CA, USA). The samples were sliced into small pieces, placed in a zirconium dioxide rotor with a diameter of 4 mm, closed with a vespel

drive cap and teflon spacers and spun at the magic angle at 10 kHz during measurements. The NMR spectra were obtained at ambient temperature and at 370 K. Free induction decay (FID) was recorded after a radio-frequency  $\pi/2$  pulse of 1.9  $\mu$ s duration, with high power proton decoupling of 86.2 kHz and recycle delay of 240 s. The  $^{13}\text{C}$  MAS NMR spectrum was obtained using the Fourier transformation of the FID, which is an average of 300 – 350 scans. The chemical shifts were referenced to the tetramethylsilane using adamantane as an external standard, and they were determined with accuracy better than 0.02 ppm. All deconvolutions were carried out with the use of MestReNova software.

### 3. Results and discussion

PHB contains  $^{13}\text{C}$  carbon nuclei in four different groups, CO, CH,  $\text{CH}_2$  and  $\text{CH}_3$ , and for this reason their magnetic moments when placed in an external magnetic field experience four different internal magnetic fields and produce four signals in  $^{13}\text{C}$  MAS NMR spectra at 170.0, 68.5, 41.3 and 21.4 ppm associated with the mentioned groups respectively, at ambient temperature. The  $^{13}\text{C}$  MAS NMR spectra measured for the powdered sample of the pure unmodified PHB at ambient temperature and at 370 K are depicted in Fig. 1.

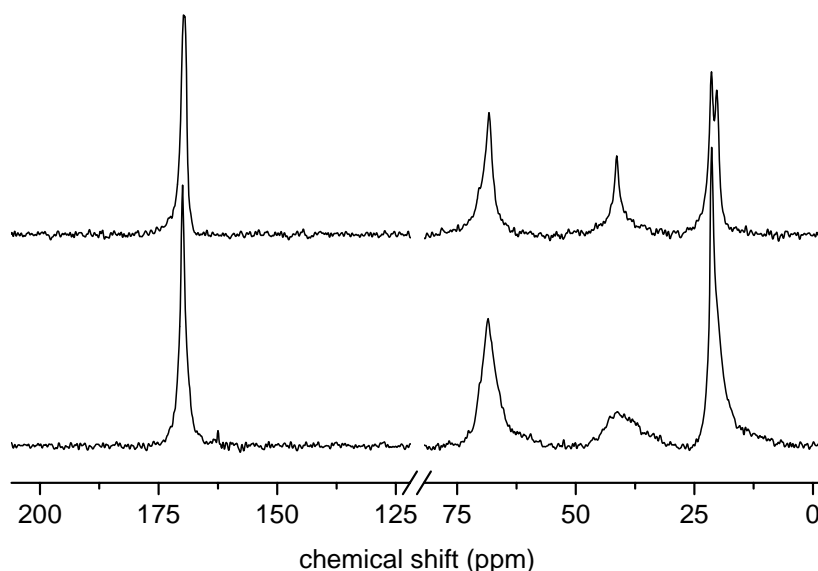


Fig. 1:  $^{13}\text{C}$  MAS NMR spectra measured for PHB sample at ambient temperature (bottom) and 370 K (top).

The ratios of integral intensities of the lines associated with the CO, CH,  $\text{CH}_2$  and  $\text{CH}_3$  groups differed from the theoretically expected 1:1:1:1. They were found to be 0.64 : 0.74 : 0.44 : 1.00 respectively, for the spectrum measured at the ambient temperature, and in the ratios 0.97 : 0.93 : 0.64 : 1.00 for the spectrum measured at 370 K. The difference can be explained by not sufficient delay time used in our experiments, which has to be at least  $5T_1(^{13}\text{C})$  and should be set in the measurements according to the longest relaxation time  $T_1(^{13}\text{C})$ . The lines of the different PHB groups do not show identical intensities even though the delay time as long as 240 s was used in these measurements. It is known that  $\text{CH}_3$  groups in PHB relax with the shortest relaxation time and so the integral intensity related to these groups corresponds with the number of carbons within them. Evidently, the applied delay time was short for the carbons in other groups, which is the reason for the lower integral intensities associated with those groups. Increase in temperature results in changes in  $T_1(^{13}\text{C})$  relaxation times, and so the ratios of the integral intensities were changed at 370 K. The ratios

of the integral intensities mentioned above indicate that those associated with CO and CH groups are about the same as that associated with CH<sub>3</sub> groups.

Differences can be found in the shapes of the particular lines in the spectra shown in Fig. 1. In contrast to the lines associated with the CO, CH and CH<sub>2</sub> groups measured at both temperatures, which are symmetrical or show weak asymmetry, the line associated with the CH<sub>3</sub> groups measured at ambient temperature is evidently asymmetrical, and that measured at 370 K is split into two components. In the following section, the modification of PHB will be explored by means of analysis of the lines associated with the CH<sub>3</sub> groups.

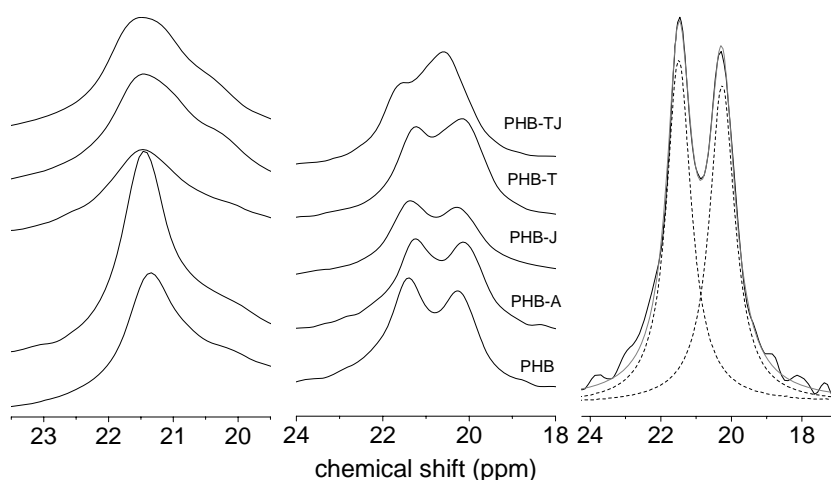


Fig. 2: CH<sub>3</sub> lines of <sup>13</sup>C MAS NMR spectra measured at ambient temperature (left) and 370 K (middle) for the samples as indicated in the figure. Deconvolution of the line into two components is illustrated in the line measured for PHB at 370 K (right).

As well as in the case of unmodified PHB, the asymmetrical shape of the lines measured at ambient temperature and the split lines into two components measured at 370 K for the modified samples can be seen in Fig. 2. It can be seen there that the shape of the spectra depends on the method of modification. To evaluate the effect of the particular modifications on the sample morphology, deconvolution of the spectra into two components was carried out for the lines detected at 370 K. Deconvolution of the line measured for PHB is depicted in Fig. 2, and the parameters revealed by the deconvolution are summarized in Tab. 1. It is reasonable to divide the samples into two groups. If we consider that 2 wt. % of Joncryl is a minute amount in terms of the polymer structure, then the first group of samples consist only of the chains of pure PHB (PHB, PHB-A, PHB-J), while the samples in the second group (PHB-T, PHB-TJ) include 10 wt. % of triacetine with three methyl groups in the molecule, which has to be taken into account in the calculations.

Tab. 1: Positions and widths of peaks determined by deconvolutions of the lines related to CH<sub>3</sub> groups in the <sup>13</sup>C MAS NMR spectra measured at 370 K. X<sub>c</sub> is the degree of crystallinity determined from the areas beneath the peaks.

Sample	Position [ppm]	Width [Hz]	Position [ppm]	Width [Hz]	X <sub>c</sub> [%]
PHB	21.47	85	20.25	87	51
PHB-A	21.33	104	20.13	83	58
PHB-J	21.49	102	20.28	108	54
PHB-T	21.35	84	20.24	115	37
PHB-TJ	21.69	93	20.66	110	33

The components of the CH<sub>3</sub> line determined by deconvolution can be related to the CH<sub>3</sub> groups within crystalline (21.3 – 21.7 ppm) and amorphous (20.1-20.7 ppm) regions [6]. It can be concluded from the data in Tab. 1 that annealing of the sample results in increased crystallinity, but modification with Joncryl restrains the forming of the crystalline domains. It could be stressed that all modified samples PHB-X (X = A, J, T, TJ) passed through the same preparation technique. According to the data in Tab. 1, the plasticized PHB-T shows a lower number of CH<sub>3</sub> groups within the crystalline domains (37%) as compared with that of PHB-A (58%). Actually, the number of PHB chains within the crystalline domains as compared with the total number of the PHB chains in PHB-T is higher (about 42 %), on account of the CH<sub>3</sub> groups of triacetine being localized within amorphous regions. The strong decrease in the degree of crystallinity was observed due to double modification by triacetine and Joncryl.

It can be noticed that modifications result in changes in distributions of conformations, which follows from the widths of the particular lines.

#### 4. Conclusions

The study of the structural changes of polyhydroxybutyrate (PHB) brought about by several modifications was done using solid state <sup>13</sup>C NMR. The <sup>13</sup>C MAS NMR spectra were measured using the direct polarisation technique at ambient temperature and 370 K. Four resonance lines appeared at 170.0, 68.5, 41.3 and 21.4 ppm associated with the CO, CH, CH<sub>2</sub> and CH<sub>3</sub> groups respectively, in the <sup>13</sup>C MAS NMR spectrum measured at the ambient temperature. The CH<sub>3</sub> resonance showed splitting into two lines related to the crystalline and amorphous regions at the increased temperature. Deconvolutions of these resonances made it possible to estimate crystallinities of the modified PHB samples.

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