Vol. **126** (2014) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Solid State ^{13}C NMR Study of Modified Polyhydroxybutyrate

P. Vrábel[a,*], V. Hronský[a], O. Fričová[a], M. Kovaľaková[a], I. Chodák[b], P. Alexy[c]

[a]Department of Physics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia
[b]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia
[c]Institute of Polymer Materials, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovakia

Structural changes in polyhydroxybutyrate (PHB) brought about by addition of chain extender and/or plasticizer were studied using ^{13}C MAS NMR spectra, which were measured using the direct polarization technique at 30 and 98 °C. Four resonances associated with the CO, CH, CH_2 and CH_3 groups of PHB were observed in the spectra. The CH_3 resonance appearing at 98 °C shows splitting into two lines related to the crystalline and amorphous regions. Analysis of the CH_3 resonances made it possible to estimate the influence of applied modifications on crystallinity and distribution of conformations in amorphous and crystalline domains of PHB samples.

DOI: 10.12693/APhysPolA.126.419

PACS: 61.41.+e, 76.60.–k, 81.05.Lg

1. Introduction

Polyhydroxybutyrate (PHB) is a semi-crystalline material with a helical structure of macromolecules. Because of this, some of its mechanical properties are similar to those of polypropylene. PHB has been broadly studied mainly because of its biodegradability, but its industrial applications are quite limited due to its brittleness and limited stability during processing. The ultimate properties of this material change remarkably during storage due to physical aging under ambient conditions. Improved properties and better applicability have been observed in modified PHBs, some of which possess unique mechanical properties. In this research ^{13}C MAS NMR spectra were used for characterization of the changes in structure of PHB resulting from thermal treatment, modification by addition of chain extender and plasticizer triacetine (TAC).

2. Experimental

The virgin powdered PHB and PHB modified by thermal treatment (PHB-t) and addition of either chain extender (Joncryl, BASF) (PHB-J) or plasticizer TAC (PHB-T) or both plasticized and modified (PHB-TJ) were used for NMR measurements. All modifications were carried out in a twin-screw extruder at 190 °C. The PHB-T and PHB-J samples contained 10.0 and 2.0 wt.% of TAC and Joncryl respectively, while the PHB-TJ sample contained 10.0 wt.% of TAC and 2.0 wt.% of Joncryl [1].

The ^{13}C MAS NMR measurements were performed on a Varian 400 MHz NMR spectrometer. The spectra were recorded at resonance and MAS frequency of 100 MHz and 10 kHz respectively, at 30 and 98 °C. Free induction decay (FID) was recorded after a $\pi/2$ pulse of 1.9 μs duration, with high-power proton decoupling of 86.2 kHz and recycle delay of 90 s. Each spectrum was obtained using the Fourier transformation of the FID, which was an average of 300–350 scans. The chemical shifts were referenced to the TMS.

3. Results and discussion

Nuclei of PHB carbons are present in four different groups – CO, CH, CH_2 and CH_3, and for this reason their magnetic moments, when the sample is placed in the external magnetic field, experience four different magnetic fields brought about by the surrounding electrons, hence four resonances appear in ^{13}C MAS NMR spectra at 170.0, 68.5, 41.3 and 21.4 ppm respectively (Fig. 1).

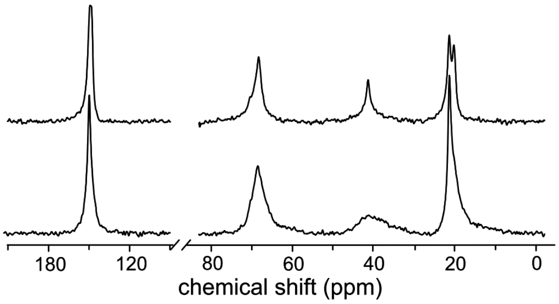

Fig. 1. ^{13}C MAS NMR spectra measured for PHB sample at 30 (bottom) and 98 °C (top).

The differences in the shapes of particular lines in the spectra can be seen in Fig. 1. While the lines assigned to the CO, CH and CH_2 groups are symmetrical, or show weak asymmetry when measured at both temperatures, the line associated with the CH_3 groups measured at 30 °C is evidently asymmetrical, and the one measured at 98 °C is split into two components which can be related to the CH_3 groups in amorphous and crystalline domains [2].

---

*corresponding author; e-mail: peter.vrabel.3@tuke.sk

The ratio of integral intensities of the lines associated with the CO, CH, CH_2 and CH_3 groups differs from the theoretical expectation 1:1:1:1. They were found to be 0.64:0.74:0.44:1.00 or 0.97:0.93:0.64:1.00 in the spectra measured at 30 and 98 °C respectively. The differences can be explained by the recycle delay which was sufficiently long to obtain an acceptable signal to noise ratio in the spectra but not sufficiently long for relaxation of the carbons in the CO, CH, CH_2 groups [3].

For this reason the modifications of the PHB will be further explored by means of analysis of the lines assigned to the CH_3 groups with the spin system completely relaxed at the used recycle delay.

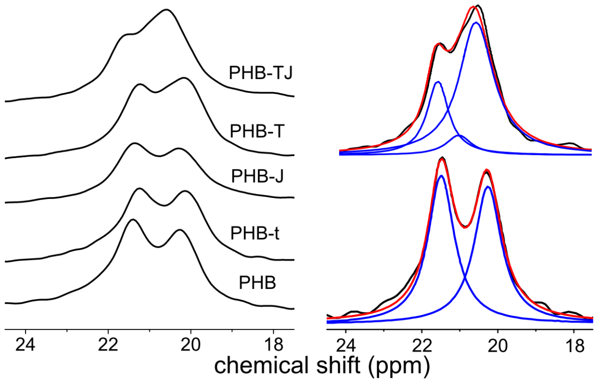

Fig. 2. CH_3 lines of ^{13}C MAS NMR spectra measured at 98 °C (left) for the samples as indicated. Deconvolutions (right) of the lines into two and three components are illustrated in the line measured for PHB (bottom) and PHB-TJ (top) respectively, at 98 °C.

Similar to the case of unmodified PHB, lines split into two components were observed at 98 °C for the modified samples and the shape of the spectra depended on the method of modification (Fig. 2). To evaluate the effect of the particular modification on the structure of polymers, deconvolutions of the spectra into two or three components were made for the lines detected at 98 °C (Fig. 2). The parameters evaluated by the deconvolutions are summarized in Table. It is reasonable to divide the samples into two groups. If the presence of 2 wt.% of Joncryl is considered as negligible concerning the polymer structure, then the first group of samples, namely PHB, PHB-t and PHB-J consists only, or nearly only of chains of pure PHB. The samples in the second group, PHB-T and PHB-TJ, contain 10 wt.% of TAC with three CH_3 groups in its molecule, which has to be taken into account in the interpretation.

The components of the CH_3 line determined by the deconvolution can be related to the CH_3 groups within crystalline ($\delta_{cr} = 21.3$–21.8 ppm) and amorphous ($\delta_{am} = 20.1$–20.6 ppm) regions [2]. The data listed in Table indicate that thermal treatment of PHB results in increase of the width of the conformation distribution within crystalline regions, as can be inferred from the widths of the peaks, and the degree of crystallinity (w_{cr}) increases. Addition of Joncryl, besides the effects mentioned above, resulted in broadening of the conformation distribution within amorphous regions. It should be stressed that all modified samples PHB-X (X = t, J, T, TJ) underwent the same preparation procedure.

TABLE

Weight fractions (w) and widths (Δf) of peaks determined by deconvolutions of the lines related to the CH_3 groups in the ^{13}C MAS NMR spectra measured at 98 °C. w_{cr}, w_{im} and w_{am} are the weight fractions determined from the areas beneath the peaks related to the crystalline, intermediate and amorphous regions. All CH_3 resonances were deconvoluted using Lorentzian lines.

Sample	w_{cr} [%]	Δf_{cr} [Hz]	w_{im} [%]	Δf_{im} [Hz]	w_{am} [%]	Δf_{am} [Hz]
PHB	52	88	-	-	48	90
PHB-t	56	101	-	-	44	90
PHB-J	57	102	-	-	43	96
PHB-T	41	85	3	32	56	100
PHB-TJ	24	72	7	84	69	116

Error of weight fractions was estimated from repeated deconvolutions and it did not exceed of 3%.

Deconvolution into three components was necessary for the CH_3 resonances of the plasticized PHB-T and PHB-TJ samples, in which a third component was found positioned between those that were attributed to the crystalline and amorphous regions. The data listed in Table indicate decrease in the crystallinity (w_{cr}) and narrowing of the conformation distribution within crystalline regions due to the plasticizing. In fact the degree of crystallinity, which is the ratio of the number of chains in the crystalline region to the total number of PHB chains, calculated assuming that TAC molecules and consequently also TAC CH_3 groups are absent in the crystalline domains, was a little higher (2–3%) than the w_{cr} values in Table.

The broadening of the conformation distribution and the presence of TAC molecules in the amorphous regions is the reason for the broadening of the amorphous peaks for the plasticized samples compared with the other studied samples.

Acknowledgments

This work was supported by the Slovak Ministry of Education under VEGA projects 1/0492/13 and 2/0185/10.

References

[1] P. Alexy, P. Bugaj, J. Feranc, M. Pavlačková, K. Tomanová, F. Benovič, R. Plavec, M. Mihalík, M. Botošová, *Chem. Listy* **105**, 241 (2011).

[2] F. Nozirov, Z. Fojud, J Klinowski, S. Jurga, *Solid State Nucl. Magn. Reson.* **21**, 197 (2002).

[3] L. Zhang, H. Tang, G. Hou, Y. Shen, F. Deng, *Polymer* **48**, 2928 (2007).