CHARACTERIZATION OF POLY(3-HYDROXYBUTYRATE) AND ITS MODIFICATIONS USING ^{1}H NMR

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1. Introduction

Poly(3-hydroxybutyrate) (PHB)(Fig. 1) is a linear, isotactic, semicrystalline polyester. It is synthesized by various bacteria and it can also be produced from renewable resources via a classical biotechnological process. It is biocompatible and fully biodegradable, thus, it is an attractive material formedicine and packaging. Its physical and mechanical properties are similar to those of isotactic polypropylene. However, its commercial application is rather limited owing to its brittleness, poor thermal stability and degradation of its mechanical properties by secondary crystallisation. A possible way to overcome these drawbacks is blending of PHB with other polymers or low molecular weight agents [1,2].The incorporation of chain extending/branching agents improves thermal stability of polymers by increasing their molecular weight [3]. The improvement of physical and mechanical properties and also thermal stability of polymers can be achieved by plasticization which leads to higher mobility of polymer chains [4].Plasticizers are also used for preparation of polymer blends with desired properties [3,4].

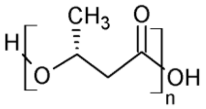

Fig. 1: *Chemical structure of PHB*

PHB has a relatively high melting temperature (in the range of 168 - 182 °C) and glass transition temperature in the range of 5 - 15 °C. Its crystallinity is 55 – 85 %.The crystalline cell of PHB is orthorhombic with two antiparallel helical chains. The thickness of PHB lamellar crystals is extremely low (between 4-7 nm) [1].Above glass transition temperature molecular dynamics of chains in crystalline domains differ from that in amorphous domains of semicrystalline polymer since segmental mobility of chains in amorphous domains markedly increases with temperature.

Single-pulse solid-state ^{1}H NMR is a powerful tool for obtaining information on segmental mobility in the studied polymer sample, as the width of lines in the ^{1}H NMR spectra narrows with increasing mobility of particular hydrogen nuclei. Hence, analysis of the spectra enables distinguishing between rigid (crystalline) and less rigid (amorphous) regions which differ in mobility of hydrogen nuclei in respective polymer chains [5,6]. Deconvolution of broad-line (BL)^{1}H NMR spectra of PHB confirmed the existence of regions with three different types of chain mobility – crystalline region with rigid chains and noncrystalline regions with rigid and mobile chains. The content of chains with different mobility was temperature dependent [5].

The aim of this study is to evaluate the crystallinity of PHB samples with and without chain extender and plasticizer and to get information on the changes in chain mobility caused by these agents in different regions of the studied semicrystalline polymer.

2. Experimental

The powdered PHB and PHB modified by thermal processing (PHB-Q) and addition of 2 wt. % of chain extender Joncryl (BASF) (PHB+J) and 10 wt. % of plasticizer triacetine (PHB+T) were studied using^{1}H NMR.All PHB modifications were carried out in a twin-screw extruder at 190°C. All samples were stored at room temperature for three years.

The broad-line (BL) ^{1}H NMR spectra were recorded on a Varian 400 MHz NMR spectrometer (Palo Alto, CA, USA) at the resonance frequency of approximately 400 MHz using a procedure suppressing the probe head background proposed by Chen [7]. The free induction decay (FID) was recorded with a recycle delay of 10 s after radio-frequency pulses with durations of 1.5 and 3 μs corresponding to $\pi/4$ and $\pi/2$ pulse, respectively. The spectral width was 100 kHz and the acquisition time was modified according to the duration of the FID signal varying with the temperature from 20 to 80 ms. Each spectrum was an average of 16 scans. Spectra were measured at room temperature and 100°C.

The temperature of the sample was stabilized for 20 minutes before NMR measurement. The chemical shifts were referenced to tetramethylsilane using adamantane as an external standard. Deconvolutions and processing of the spectra were carried out with the use of MestReNova software.

3. Results and Discussion

The BL ^{1}H NMR spectra of all studied samples measured at room temperature display one rather broad line with the centre at approximately 2 ppm which is in the case of PHB-Q and PHB+T samples overlapped with a narrow line giving a sharp peak (Fig. 1 left). The spectra measured at 100 °C display remarkable line narrowing which reflects increased mobility of hydrogen nuclei at this temperature (Fig. 1 right).

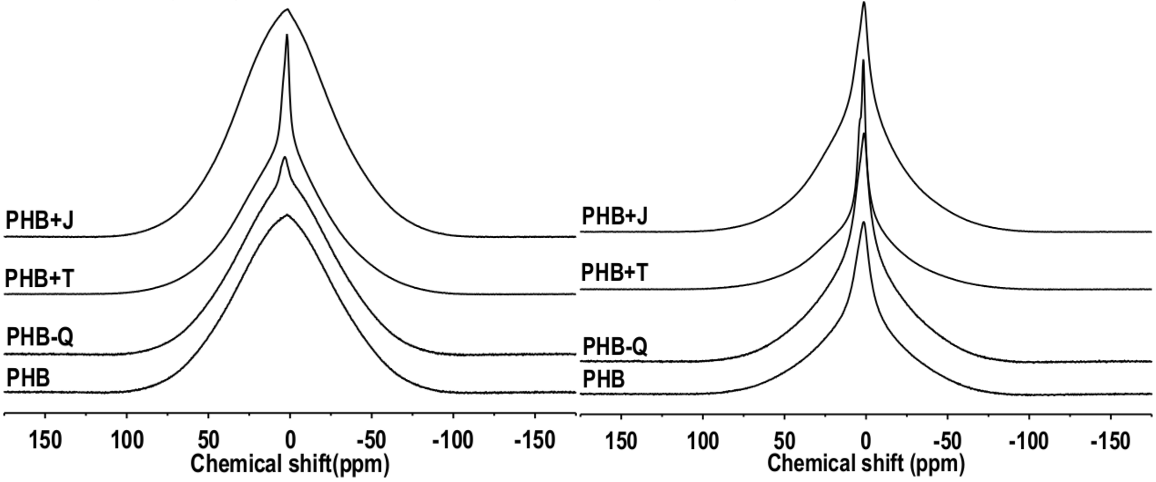

Fig.1:*^{1}H NMR spectra of PHB samples measured at room temperature (left) and 100 °C (right).*

As was mentioned above PHB is semicrystalline polymer with glass transition temperature in the range of 5 - 15 °C which means that at room temperature polymer chains in amorphous domains of PHB samples perform only slow segmental motion while the chains in crystalline domains are rigid, temperature increase to 100 °C which is well below melting temperature results in more intense chain motion only in amorphous domains while the mobility of chains in crystalline domains increases only slightly.

Deconvolutions of the spectra of all studied samples required three lines C1, C2 and C3 (Fig. 2). The line C1 with generalized Lorentzian shape which is very broad and its percentages for PHB, PHB-Q and PHB+J samples are approximately the same at RT and 100 °C (Tab. 1) can be assigned to hydrogen nuclei in crystalline domains. The width of this line decreases only slightly when samples are heated to 100 °C. The line C2 with Gaussian shape at RT and Lorentzian shape at 100 °C can be assigned to hydrogen nuclei in chains with restricted mobility within amorphous domains. Mobility of these polymer chains increases markedly at 100 °C which can be inferred not only from the change of the lineshape but also from a large decrease in linewidths (Tab. 1). The narrow C3 line can be assigned to hydrogen nuclei in mobile chains within amorphous domains. Mobility of these chains increases with temperature as can be deduced from their linewidths decrease (Tab.1). The fraction of mobile chains increases at the expense of chains with restricted mobility within amorphous domains which is reflectedin the changes in the respective line intensities (Tab. 1).

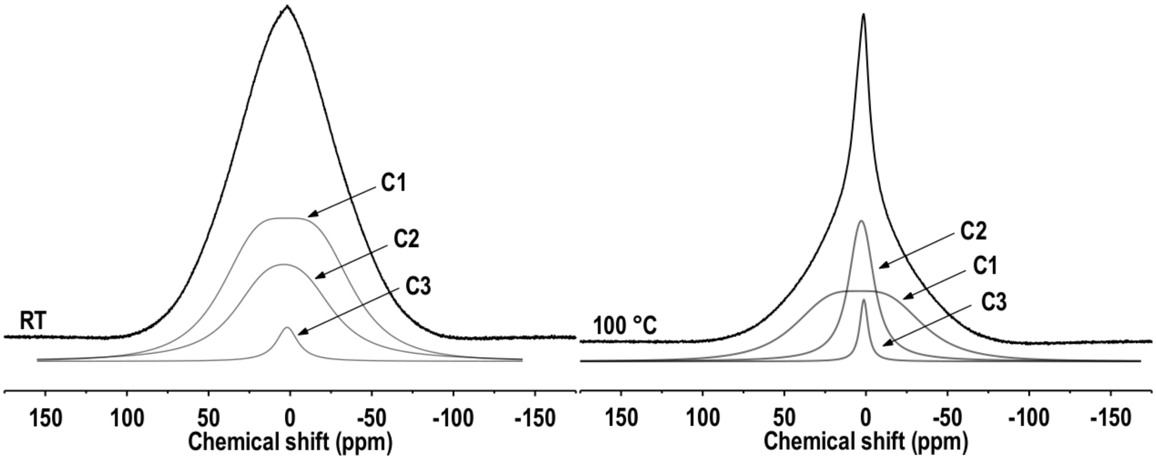

Fig.2:*Deconvolutions of ^{1}H NMR spectra of PHB powder measured at room temperature (RT) and 100 °C.*

It is known that PHB ages after thermal processing, storing at temperatures close above the glass transition temperature results in deterioration of its mechanical properties and material becomes more brittle.This is explained by extremely slow reorganization of polymer chains in amorphous domains and decrease in free volume in this phase or secondary crystallization and reduction of interphase between crystalline and amorphous domains resulting in stretched chains [1].

Increased temperature accelerates ageing process which in the view of not changed percentages of crystalline phase for PHB, PHB-Q and PHB-J samples should consist of reorganization of polymer chains in amorphous domains giving rise to more mobile polymer chains producing C3 lines with the narrowest linewidths (Tab. 1).

Triacetine induces higher mobility of polymer chains[4] and after PHB+T preparationplasticizer is assumed to be present mostly in amorphous domains of the sample. This is reflected in a lower value of C2 linewidth and larger intensity of C3 line when compared with other studied samples. C2 line probably also comprises interphase between crystalline and amorphous domains since when the temperature is incresed to 100 °C the intensity of C1 line of PHB+T sample increases. This could be explained by very fast secondary crystallization of PHB chains in the presence of plasticizer during stabilization the temperature (20 minutes) before NMR measurement.

Crystallinity of polymers can be determined from NMR spectra as the percentage of line intensities assigned to nuclei in crystalline domains. Crystallinities of PHB and PHB-Q samples are then equal to C1 line intensities, which are 59% and 57%, respectively. The PHB+T sample contains 10% of triacetine which is present mostly in amorphous phase and contributes to NMR signal of PHB+T sample with approximately 10% of hydrogen nuclei. For this reason crystallinity of this sample is 57% and 70% at RT and 100 °C, respectively. Crystallinity of PHB+J sample due to a very low amount of chain extender can be considered as equal to C1 line intensity.

The NMR parameters for PHB sample with chain extender (PHB+J) obtained from ^{1}H NMR spectrum analysisisare similar to those for PHB-Q sample except the C3 linewidth, which is larger for PHB+J sample at RT. This could reflect the restrictions in chain motion in amorphous domains due to the presence of chain extender.

Tab. 1.*The line intensities I and linewidths (lw) of lines assigned to hydrogen nuclei in crystalline phase (C1), rigid amorphous phase (C2) and mobile amorphous phase (C3) in the studied samples obtained from deconvolutions of ^{1}H NMR spectra measured at room temperature (RT) and 100 °C.*

Sample	RT						100°C					
	C1		C2		C3		C1		C2		C3	
	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$	$\frac{I}{\%}$	$\frac{lw}{\text{kHz}}$
PHB	59	32.8	37	25.1	4	6.3	60	32.3	35	7.2	5	2.4
PHB-Q	57	32.7	40	23.1	3	2.6	57	32.3	35	7.0	8	3.1
PHB+T	51	32.7	41	18.8	8	1.8	63	32.3	28	5.4	9	1.1
PHB+J	59	33.2	38	22.9	3	5.0	57	32.3	36	8.4	7	2.4

4. Conclusion

The broad-line ^{1}H NMR spectra of pure PHB and PHB samples modified by thermal treatment, chain extender and plasticizer provided information on the mobility of hydrogen nuclei in amorphous and crystalline regions of the polymer.Triacetine in PHB sample induces chain motion in amorphous domains and accelerates secondary crystallization at elevated temperature. The chain extender restricts chain motion in amorphous domainsat room temperature, however, this effect is negligible at 100 °C.

Acknowledgement

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