^{13}C NMR STUDY OF PHB/ECOFLEX BLENDS

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1. Introduction

Poly(3-hydroxybutyrate) (PHB) is an optically active polyester synthesized by a wide variety of bacteria. This semicrystalline thermoplastic polymer with similar mechanical properties as isotactic polypropylene has attracted great interest due to its biodegradability and biocompatibility. However, its industrial application is rather limited owing to its brittleness, stiffness and poor thermal stability at temperatures above the melting point. All of these drawbacks can be eliminated by its physical and/or chemical modification. Blending of PHB (Fig. 1) with other polymers is feasible way to acquire a material with targeted properties [1].

Ecoflex (ECO) is biodegradable aliphatic-aromatic polyester based on terephtalic acid, adipic acid, 1,4-butanediol and modular units (Fig. 2). Its mechanical properties are comparable to low density polyethylene [2]. This material was blended with PHB in order to improve PHB properties.

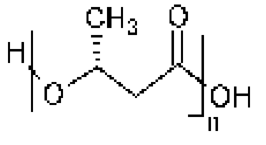

Fig. 1: *Structure of PHB.*

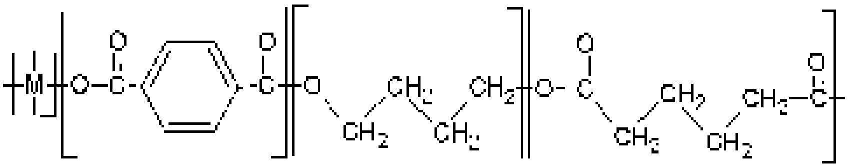

Fig. 2: *Structure of Ecoflex.*

Solid state NMR belongs to physical techniques which can provide information on the molecular structure, dynamics and interactions of polymers in blend [3] - characteristics which govern physical properties of polymer blends.

The blends of PHB and ECO with and without small amount of additive (A) were studied using ^{13}C NMR which detected the structural changes in the studied blends as observable changes in the shape of spectral peaks belonging to the individual chemical groups of the blend components.

2. Materials and experimental methods

The samples of pure PHB, pure ECO, blends of 30 wt. % of PHB and 70 wt.% of ECO with (PHB/ECO/A) and without (PHB/ECO) a small content of additive were supplied by the Polymer Institute of the Slovak Academy of Sciences. Samples containing PHB were in the form of foils, the pure ECO was in pelletized form. Prior to NMR measurements all samples were cut into small pieces before packing in the rotor.

The high resolution solid state ^{13}C NMR spectra were measured on Varian 400 NMR spectrometer under MAS conditions at the rate of 11 kHz using 4 mm rotor. ^{13}C NMR spectra were obtained with 90° pulse of 1.9 μs, a high power proton decoupling of 86.2 kHz, a recycle delay of 240 s, and averaging over 300-500 scans. All spectra were detected at the room temperature and then processed using the MestReNova software.

3. Results and discussion

The ^{13}C NMR spectrum of PHB (Fig.3 top) shows four peaks with different chemical shifts corresponding to carbon nuclei in individual chemical groups: 21 ppm - CH_3, 43 ppm - CH_2, 69 ppm – CH, and 170 ppm - C=O. The small peak with chemical shift of 60 ppm in the PHB spectrum is a spinning sideband arising from the use of MAS techniques. The peaks in the ^{13}C NMR spectrum of ECO (Fig.3 bottom) are assigned as follows: peaks with chemical shifts of 26 and 34 ppm - CH_2 carbons, 64 ppm - O-CH_2 carbons, 130 and 134 ppm - carbons in aromatic ring s, 165 and 173 ppm - COOR carbons. The peaks with chemical shifts of 111 ppm in both spectra displayed in Fig. 3 are given by the material used in the rotor cap.

Fig. 4 displays ^{13}C NMR spectra of PHB/ECO blends with and without additive, where the bottom spectrum is a superposition of spectra depicted in Fig. 3. Only small differences between the spectra in Fig. 4 can be seen. They concern methylene and carbonyl peaks of PHB with chemical shifts of 43 and 170 ppm, respectively, and methylene peaks of ECO with chemical shift of 26 ppm. That means that the environment of a small fraction of these chemical groups is changed in comparison with the pure samples. Therefore, we assume that the polymers are not interblended in both blends, but the blends consist of domains of individual polymers with only small amount of intermediate layers at their borders [4].

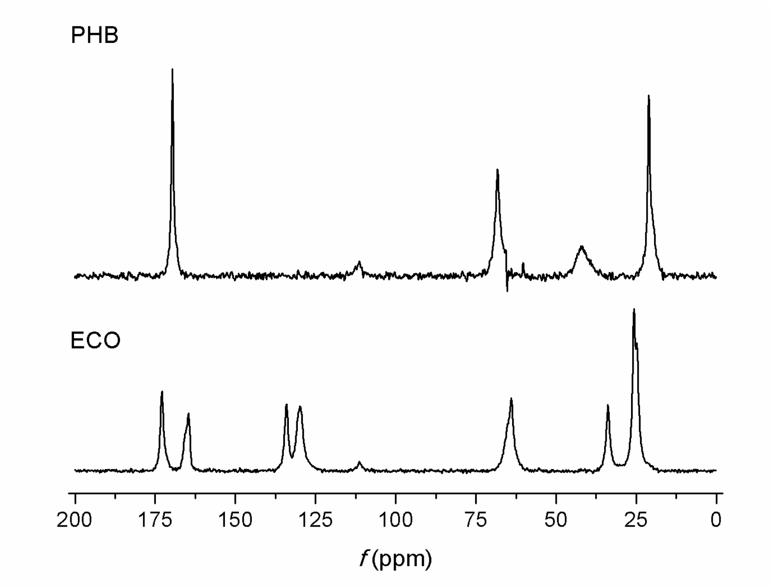

Fig.3: *^{13}C NMR spectra of PHB (top) and ECO (bottom).*

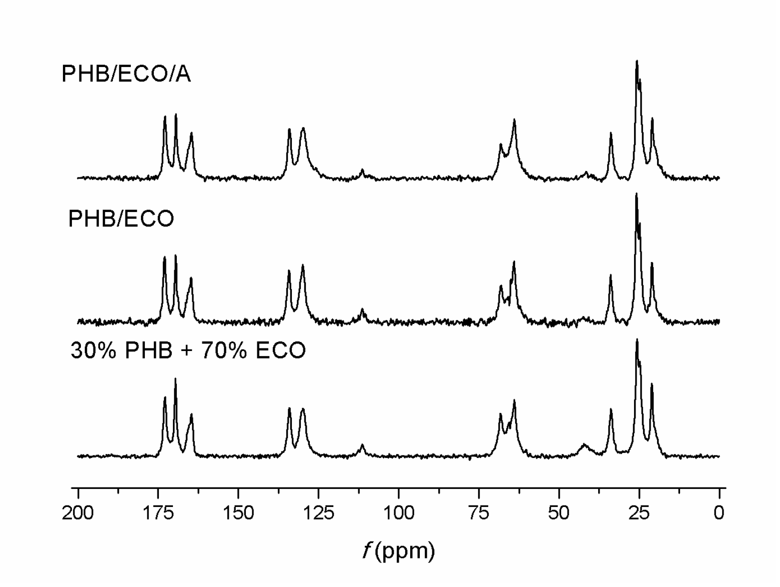

Fig.4: *^{13}C NMR spectra of PHB/ECO blends as indicated.*

Analysis of the methyl peak of PHB at 21 ppm in pure PHB and in both blends indicates the existence of intermediate layers. This peak is asymmetric and it can be decomposed into two peaks (Fig. 5), the higher and narrower one related to the higher chemical shift, and the lower and broader one related to the lower chemical shift correspond to methyl groups in the noncrystalline and crystalline regions, respectively [5]. The results of the decomposition are summarized in Tab. 1. The changes of the width of peaks indicate the changes in mobility of methyl carbons in particular regions. The fraction of CH_3 carbons in crystalline and noncrystalline regions calculated from the peaks areas is also affected by blending.

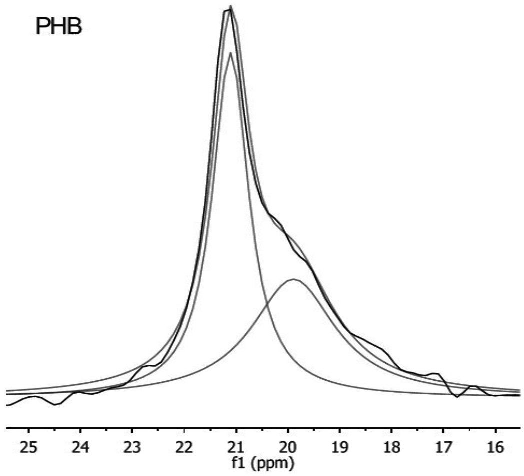

Fig.5: *Decomposition of the methyl peak of PHB sample.*

Tab. 1: *Results of decomposition of the methyl peak of PHB*

Sample	Crystalline		Amorphous	
	Width (Hz)	I (%)	Width (Hz)	I (%)
PHB	86	56	198	44
PHB/ ECO	109	73	142	27
PHB/ ECO /A	97	57	164	43

4. Conclusion

Biodegradable samples of PHB, ECO and their blends with and without additive were studied by means of ^{13}C NMR. Analysis of the spectra revealed, that the components of the blends are not interblended, but the blends are composed of domains of individual components with a small amount of intermediate layers.

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