

NMR RELAXATION STUDY OF PHB/ECOFLEX BLENDS

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1. Introduction

Poly(3-hydroxybutyrate) (PHB) is a semicrystalline biodegradable polymer whose macromolecules are composed of the optically active units of D(-3-hydroxybutyric)-acid. It is produced by a microbiological synthesis, or by a chemical synthesis on the base of polymerization. The resulting polymer with degree of crystallinity in the range of 55-85%, has relatively good mechanical properties which rapidly deteriorate due to physical aging. The methods to influence PHB mechanical properties include polymer additivation and blend preparation [1].

Ecoflex is a biodegradable aromatic-aliphatic copolyester with physical properties which reflect its specific molecular structure formed from modular units linked with the statistical copolyester units, including terephthalic acid, adipic acid and 1,4-butanediol. Modular system involves the incorporation of hydrophilic components of monomers with branching [2].

2. Experimental

The following samples supplied by the Polymer Institute of the Slovak Academy of Sciences were studied: pure Ecoflex (ECO), pure PHB, PHB modified with 5 wt.% of low molecular additives A (PHB/A), blend PHB/ECO with the fraction of 30/70, and blend PHB/ECO modified with 5 wt.% of low molecular additive A (PHB/ECO/A). The samples were not treated except cutting into small pieces prior to NMR measurements.

The NMR experiments were performed on a Varian 400 NMR spectrometer with 9.4 T superconducting magnet. The measurements were performed at room temperature. Laboratory frame spin-lattice relaxation times T_1 were measured using the inversion recovery method and rotating frame spin-lattice relaxation times $T_{1\rho}$ measurements were done with the use of the spin-locking method. Duration of ^1H 90° pulse was 2.7 μs , spin-lock field strength

in $T_{1\rho}$ experiments was 77 kHz. The magic angle spinning experiments on samples containing PHB and on pure ECO were performed at spinning rates of 6 kHz and 11 kHz, respectively.

The spin-lattice relaxation times T_1 of protons located in particular functional groups of pure ECO, pure PHB, and blend PHB/ECO were acquired by inversion recovery of the proton spin system magnetisation with consecutive transfer of magnetisation via cross polarization (CP) technique to the carbon spin system. The radio frequency field strength of 51 kHz and the contact time of 1 ms were used in CP experiments and the high power proton-decoupling field of 85 kHz was applied during data acquisition. Measurements were carried out under MAS with the rate of 11 kHz.

3. Results and discussion

The T_1 values were determined by the fitting of exponential recovery function to the magnetisation decay and are listed in Table 1. The measured ^1H NMR spectrum of PHB consists of one broad peak with the chemical shift of 1.3 ppm while the spectrum of ECO is better resolved, consisting of three peaks with different chemical shifts corresponding to protons in aromatic ring - 8.0 ppm, OCH_2 protons - 4.0 ppm and CH_2 protons - 1.7 ppm. The spectra of ECO and PHB/ECO blends are very similar due to the overlapping of the broad spectrum of PHB with the resolved spectrum of ECO.

From the data in Table 1 it can be deduced that the additive does not influence the spin-lattice relaxation process in PHB. However, a different relaxation behavior is observed in the case of polymer blends. Due to spin diffusion among the proton spin systems of different domains only single exponential decays of magnetisation, and hence, only single value of the proton relaxation times connected with the individual peaks in spectra were acquired. The relaxation times related to ECO sample were increased by 7% - 12% after blending with PHB. The modification of the blend with additive increased the values of T_1 related to ECO peaks by 3% - 5% in comparison with a pure sample.

Tab. 1: *The spin-lattice relaxation times $T_1(H)$ related to the functional groups of PHB, ECO and PHB/ECO blends.*

Sample	T_1 (s)			
	8.0 ppm	4.0 ppm	1.7 ppm	1.3 ppm
PHB				1.50
PHB/A				1.51
ECO	0.826	0.821	0.810	
PHB/ECO	0.929	0.888	0.869	
PHB/ECO/A	0.957	0.930	0.909	

Tab. 2: *The spin-lattice relaxation times $T_1(H)$ related to the functional groups of PHB, ECO and PHB/ECO blend measured by polarisation transfer to carbon spin system.*

Sample	T_1 (s)							
	134 ppm	130 ppm	68ppm	65 ppm	43 ppm	34 ppm	26 ppm	21 ppm
PHB			1.89		1.89			1.89
PHB /ECO	0.85	0.84	1.72	0.89	1.79	0.87	0.84	1.72
ECO	0.86	0.84		0.83		0.84	0.85	

The $T_1(H)$ values of protons in the individual functional groups measured by polarisation transfer to carbon spin system are given in Table 2 for pure PHB, pure ECO, and for the PHB/ECO blend. As can be seen, the $T_1(H)$ values related to the functional groups of ECO are approximately the same for the pure sample ECO and for PHB/ECO blend which suggests PHB/ECO blend has domains of pure PHB and pure ECO. On the other hand, the $T_1(H)$ values related to the groups of PHB are lower by 4.5 % - 9.5 % for PHB/ECO blend in comparison with a pure PHB sample.

Tab. 3: *The rotating frame spin-lattice relaxation times $T_{1\rho A}$ and $T_{1\rho B}$ related to the faster and slower magnetization decay, respectively.*

Sample	$T_{1\rho A}$ (ms)				$T_{1\rho B}$ (ms)			
	8.0 ppm	4.0 ppm	1.7 ppm	1.3 ppm	8.0 ppm	4.0 ppm	1.7 ppm	1.3 ppm
PHB				3.3				36
PHB/A				3.6				37
ECO	1.7	1.6	2.08		6.4	5.8	6.2	
PHB/ECO	2.2	1.7	2.01		22	18	13	
PHB/ECO/A	2.0	1.6	1.76		20	17	15	

Tab. 4: *The relative number of protons w_A and w_B related to the relaxation times $T_{1\rho A}$ and $T_{1\rho B}$, respectively.*

Sample	w_A (%)				w_B (%)			
	8.0 ppm	4.0 ppm	1.7 ppm	1.3 ppm	8.0 ppm	4.0 ppm	1.7 ppm	1.3 ppm
PHB				55.6				44.4
PHB/A				55.2				44.7
ECO	59.0	67.3	62.6		41.0	32.7	37.4	
PHB/ECO	76.0	80.8	84.2		24.0	19.2	15.8	
PHB/ECO/A	73.4	75.0	83.9		26.6	25.0	16.1	

The $T_{1\rho}$ values were derived from the fitting of the magnetisation decay to two exponentials. The results are listed in Table 3 and Table 4. The $T_{1\rho B}$ value measured for the pure PHB sample is in agreement with the results published in [3] where $T_{1\rho}$ of protons in individual function groups were measured using the CP method but magnetisation decay, due

to the used technique, was fitted only to one exponential function. The shorter and longer $T_{1\rho}$ values can be related to crystalline and amorphous regions of polymers, respectively. The $T_{1\rho A}$ values differ very slightly from one another (Table 3), however, the data in Table 4 show that blending results in the significant increase of the relative numbers of protons w_a . In the case of slower magnetization decays the changes of $T_{1\rho B}$ values as well as relative number of protons w_B are observed. The changes of fractions of faster and slower relaxing nuclei can be explained by the existence of some small intermediate layers in the blends (Table 4).

Based on the theory of ^1H spin diffusion, the $T_1(\text{H})$ values (Table 2) make possible to estimate the size of domains of blend components since for the maximum diffusive path length L holds: $L = (6DT_i)^{1/2}$, where for the spin-diffusion coefficient D the value of $8 \cdot 10^{-16} \text{ m}^2\text{s}^{-1}$ was substituted for PHB (crystalline component), and the value of $0.5 \cdot 10^{-16} \text{ m}^2\text{s}^{-1}$ for ECO (amorphous component) [4]. For the blend PHB/ECO we have obtained the size of domains 90-93 nm and 15-17 nm, for PHB and ECO, respectively.

4. Conclusion

The proton spin-lattice relaxation times T_1 and $T_{1\rho}$ were determined for PHB, ECO as well as for their blends. The effect of the small amount of additive on the relaxation behaviour was also studied. The experimental results show that the modification of PHB with a small amount of additive does not influence its relaxation process, but it can influence relaxation behaviour of the PHB/ECO blend. The $T_{1\rho}$ values confirm that PHB/ECO blend has domain structure with pure PHB and ECO domains and with small intermediate layers. These results make possible to calculate also the domain size of blend components.

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