Solid-State NMR Study of Poly(3-Hydroxybutyrate) and Ecoflex® Blends

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Biodegradable blends of poly(3-hydroxybutyrate) and aromatic-aliphatic co-polyester Ecoflex® were studied by means of basic solid-state NMR techniques. ^{13}C NMR spectra pointed at existence of individual components in blends, however, existence of regions in which components affect each other was also deduced from changes of shape of some spectral lines. Analysis of proton spin–lattice relaxation process in laboratory frame running in blends with different fractions of components revealed poor miscibility of these polymers. The domain size of components was calculated based on the values of spin–lattice relaxation times in laboratory frame. Spin–lattice relaxation process in the rotating frame of Ecoflex® proton spin system was only slightly influenced by the blending. Incompatibility of these polymers was confirmed by all realized experiments.

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1. Introduction

The disposal of plastic waste has become a serious problem of waste management system over the world. New possibilities how to replace conventional plastics by biodegradable polymers with required properties are intensively explored. Renewable, biodegradable, biocompatible polyhydroxyalkaonates (PHAs) afford environment-friendly natural alternatives to the petroleum-based materials. Poly(3-hydroxybutyrate) (PHB), a class of PHAs, is due to its biocompatibility and biodegradability an attractive material inter alia for medicine and food packaging [1]. Mechanical properties of this semicrystalline polymer, except drawability, are comparable with those of synthetic isotactic polypropylene [2]. PHB is produced by a microbiological synthesis or by a chemical synthesis on the base of polymerization. Macromolecules of PHB are composed of the optically active units of D(-3-hydroxybutyric)-acid (Fig. 1a). PHB crystallizes in the orthorhombic system. The crystalline regions are separated by the amorphous phase and ^{13}C NMR studies indicate a large difference in molecular mobility between them [3, 4]. However, mechanical properties of PHB rapidly change with time. The methods to improve PHB mechanical properties include addition of additives and blend preparation.

Ecoflex® (ECO) is poly(butylene-adipate-*co*-terephthalate) (PBAT) used within agriculture, catering industry, etc. Physical properties of this biodegradable, compostable plastic reflect its specific molecular structure formed from modular units linked with the statistical copolyester units, including terephthalic acid, adipic acid and 1,4-butanediol (Fig. 1b). Modular system involves the incorporation of hydrophilic components of monomers with branching. Mechanical properties of Ecoflex® are comparable with those of low density polyethylene [5]. Due to its properties Ecoflex® could be a suitable material for blending with PHB.

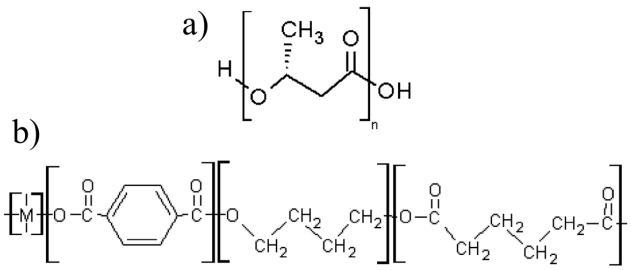

Fig. 1. (a) Monomer unit of PHB, (b) Ecoflex® structure.

Blending of two polymers gives rise to intermediate layers at the phase border. The character of these layers depends on compatibility of both polymers and has significant influence on the physical properties of blend [6]. The structure of polymers determines their properties and also molecular motion. The study of relaxation mechanisms can provide information on structure of polymers and their blends, respectively. Thus, solid-state NMR techniques provide an effective tool for the study of polymers and their blends.

PHB and its blends mostly with other PHAs were studied employing solid-state NMR techniques including ^{13}C direct polarization (DP) and cross polarization (CP) magic angle spinning (MAS) methods, measuring of relaxation times T_1(C), $T_{1\rho}$(C), indirect measuring of relaxation times T_1(H), $T_{1\rho}$(H) via polarisation transfer to

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carbon spin system and wide-line ^{1}H NMR and T_1(H) experiments [1, 3, 4, 7–12]. It was shown that PHB was composed of crystalline and amorphous regions with distinct molecular dynamics. The degree of crystallinity of PHB was determined by deconvolution of its methyl signal in ^{13}C DP MAS NMR spectrum. This signal was composed of a broader signal at lower ppm and a narrower one at higher ppm corresponding to CH_3 groups in amorphous region with the *trans/gauche* dominant conformation and to the methyl groups in the crystalline regions with the *trans* conformation of the backbone, respectively [1, 4, 7]. The shape of the methyl signal measured at elevated temperatures revealed existence of rigid and mobile amorphous phase of PHB [4]. Deconvolution of wide-line ^{1}H NMR spectra [1, 7] confirmed existence of regions with different mobility of PHB chains. Proton spin–lattice relaxation time in the rotating frame $T_{1\rho}$(H) measured via polarisation transfer from proton to carbon spins were found to be much shorter for amorphous regions of PHB (3–7 ms) than those of crystalline regions (77–98 ms) [1]. On the other hand, only single exponential $T_{1\rho}$(H) relaxation curves were observed for PHB and its blends in [8] by the same measuring method. It was also found that signals of PHB in ^{13}C NMR spectra changed their shape when PHB was mixed in miscible blends [9, 10] and almost the same values of the spin–lattice relaxation times in the rotating frame $T_{1\rho}$(H) were observed for both blend components [9]. Based on the spin-diffusion theory the proton relaxation times were used to estimate the domain size of the blend components [1, 9]. In the temperature dependence of the proton spin–lattice relaxation times measured at 200 MHz a minimum corresponding to free reorientation of the methyl groups was observed at –129 °C. Relaxation time decrease above T_g revealed another molecular motion but minimum connected with this process was not achieved in measured temperature range [3].

Solid-state NMR study of PBAT employed ^{13}C CP MAS techniques [13–17]. The existence of two components of the spin–lattice relaxation times T_1(C) for butylene-terephthalate units revealed incorporation of these units in both, amorphous and crystalline regions of polymer. However, there is no uniform opinion on the presence of butylene-adipate units in crystalline regions of PBAT [14–17]. Relatively short relaxation times T_1(C) ascribed to butylene-adipate units in crystalline regions of PBAT implied their high mobility or possibly incorporation of these units into an interface between crystalline and amorphous regions of PBAT [15]. Based on the existence of only single component of the proton spin–lattice relaxation time in the rotating frame $T_{1\rho}$(H) measured via CP method for butylene CH_2 peak, the size of crystalline regions of PBAT was estimated to be less than 3 nm [16]. Additional peaks in ^{13}C CP MAS NMR spectra of PBAT were observed by interaction of PBAT with composites [13].

Solid-state NMR techniques including ^{13}C DP method and measurements of proton spin–lattice relaxation times in laboratory and rotating frames were employed in our study of PHB, Ecoflex® (PBAT) and their blends. According to our knowledge, PHB-PBAT blends have not been studied by solid-state NMR until now.

2. Experimental

The samples of pure PHB, pure Ecoflex®, their blends (PHB/ECO) containing 10, 30 and 50 wt% of PHB, blend of 30 wt% of PHB and 70 wt% of Ecoflex® with small content (3 wt%) of additive (chain extender) Joncryl® ADR-4368 (PHB/ECO/A) were supplied by the Polymer Institute of the Slovak Academy of Sciences. Ecoflex® (ECO) and additive Joncryl® ADR-4368 are commercially produced by BASF AG (Germany), PHB foils were prepared from powdered PHB (BIOMER, Germany). The composition of Ecoflex® determined by ^{13}C NMR measurement is as follows: 22.2 mol.% of terephthalic acid, 27.8 mol.% of adipic acid and 50 mol.% of 1,4-butanediol [7]. Samples containing PHB were in the form of foils, the pure Ecoflex® was in pelletized form. Prior to NMR measurements all samples were cut into small pieces before packing in the rotor to achieve stable rotation in MAS experiments.

All NMR measurements were performed on Varian 400 NMR spectrometer under MAS conditions at the rate of 11 kHz using 4 mm rotor. The high resolution solid state ^{13}C NMR spectra were obtained with 90° pulse of 2.7 μs, a high power proton decoupling of 80 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.

^{1}H MAS NMR spectra of sufficient resolution were obtained with 90° pulse (2.7 μs), using a recycle delay of 8–10 s and averaging 10 scans. An inversion recovery pulse sequence combined with cross polarisation technique was used for measurements of spin–lattice relaxation time in the laboratory frame T_1(H). The amplitudes of peaks in the ^{13}C CP MAS NMR spectra were plotted against the delay time between 180° pulse and recording of the spectra and then fitted by single exponential function. The delay time was in the range of 0.02–10 s. The amplitudes of the most and the less intensive peaks varied in the range from about –75 to 85 and from –5 to 5.5 in arbitrary units, respectively. The radio frequency field strength for the Hartmann–Hahn condition of 51 kHz, contact time of 1 ms, relaxation delay between two consecutive scans of 10 s and high power proton-decoupling field of 80 kHz were used in the CP experiments. The spin–lattice relaxation times in the rotating frame $T_{1\rho}$(H) were measured by spin-lock method. The duration of spin-lock pulse of power of 47 kHz was in the range of 0.185–50 ms. Plots of peak amplitudes, varying in the range of 2.5–150 arb.u. and 1.5–40 arb.u. for the most and the less intensive peak, respectively, given by individual proton groups versus duration of spin-lock pulse were fitted by two-exponential decay.

The same experimental conditions and parameters in individual measurement methods were preserved for all

measured samples and spectra were processed by uniform procedure. The curve fitting was performed in SciDavis programme within the error of 5%.

3. Results and discussion

The ^{13}C NMR spectra of PHB and Ecoflex® are depicted in Fig. 2. In the case of PHB (Fig. 2, top) the ^{13}C NMR spectrum 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 technique. The peak positions of PHB are in accordance with published results [1, 4, 7–9, 11]. The intensities of individual peaks are not the same as during the repetition time (240 s) used in the spectrum acquisition only the methyl carbons completely relaxed [1].

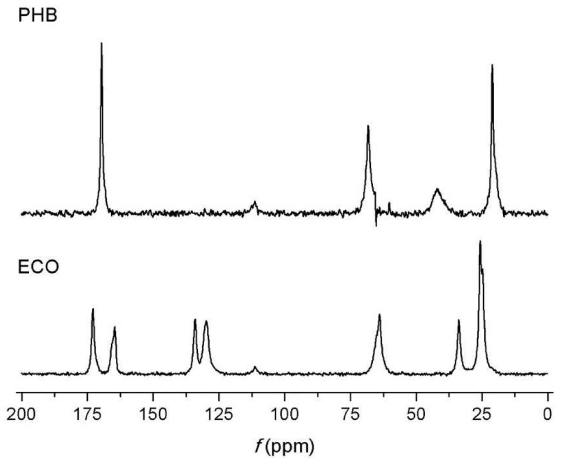

Fig. 2. ^{13}C NMR spectra of PHB (top) and Ecoflex® (bottom).

The peaks in the ^{13}C NMR spectrum of Ecoflex® (Fig. 2, bottom) are assigned as follows: split peak with chemical shift of 26 ppm — CH_2 carbons of adipic and butanediol units, 34 ppm — CH_2 carbons of adipic units bonded to COOR groups, 64 ppm — O-CH_2 carbons of butanediol units, 130 and 134 ppm — carbons in aromatic rings of terephthalic units, 165 ppm — COOR carbons of adipic units and 173 ppm — COOR carbons of terephthalic units. The peaks with chemical shifts of 111 ppm in both spectra displayed in Fig. 2 are given by the material used in the rotor cap. These results are consistent with those published in literature [13–18]. As the repetition time used by spectrum acquisition is long enough for relaxation of carbonyl and methylene groups [14], the fractions of adipic, butanediol and terephthalic units in Ecoflex® can be determined by means of intensities of the individual peaks as well as by means of the deconvolution of the spectrum. Calculated fractions are for about 1:2:1, respectively, which is in good agreement with the results reported in [19].

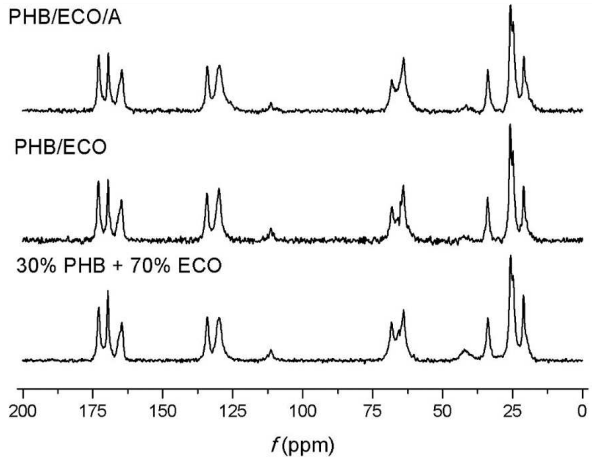

Fig. 3. ^{13}C NMR spectra of PHB/ECO-30/70 blends as indicated.

Figure 3 displays ^{13}C NMR spectra of PHB/ECO blends containing 30 wt% of PHB with (top) and without additive (middle), where the bottom spectrum is a calculated superposition of spectra depicted in Fig. 2. Only small differences between the measured spectrum of PHB/ECO blend without additive and calculated spectrum can be seen in Fig. 3. They concern methylene and carbonyl peaks of PHB with chemical shifts of 43 and 170 ppm, respectively, and methylene peaks of adipic and butanediol units of Ecoflex® 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 a small amount of intermediate layers at their borders [6]. Addition of additive gives rise to small changes in the shape of peaks related to Ecoflex® carbons in CH_2 groups of adipic and butanediol units (26 ppm), O-CH_2 groups of butanediol units (64 ppm) and in aromatic rings of terephthalic units (130 and 134 ppm) (Fig. 3). Signals of additive are not visible in the spectrum because of its small amount (3 wt%).

Existence of some intermediate layers in which the blend components affect each other can be inferred also from changes in shape of methylene peaks of adipic and butanediol units of Ecoflex® component (26 ppm) and methyl peak of PHB component with chemical shift of 21 ppm depicted in Fig. 4. Both mentioned peaks are obviously composed of two overlapping peaks. In the case of Ecoflex® these peaks correspond to the methylene carbons in butanediol and adipic units which may be built in crystalline or amorphous region of Ecoflex® [13–17]. In the case of PHB the methyl signal at 21 ppm is composed of a narrower signal at higher ppm of CH_3 groups in the crystalline regions with the *trans* conforma-

tion of the backbone and a broader one at lower ppm corresponding to methyl groups in amorphous region with the *trans/gauche* dominant conformation of the backbone [1, 4, 7]. Both the shape and the intensity fraction of these methyl peaks change with decreasing fraction of PHB in blends.

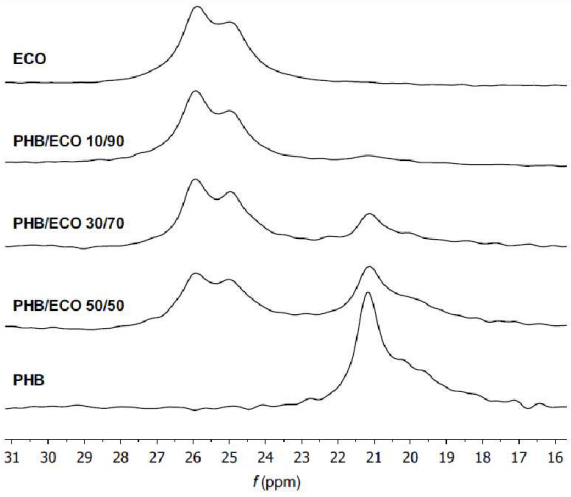

Fig. 4. ^{13}C NMR spectra of PHB, Ecoflex® and their blends PHB/ECO with wt fractions as indicated.

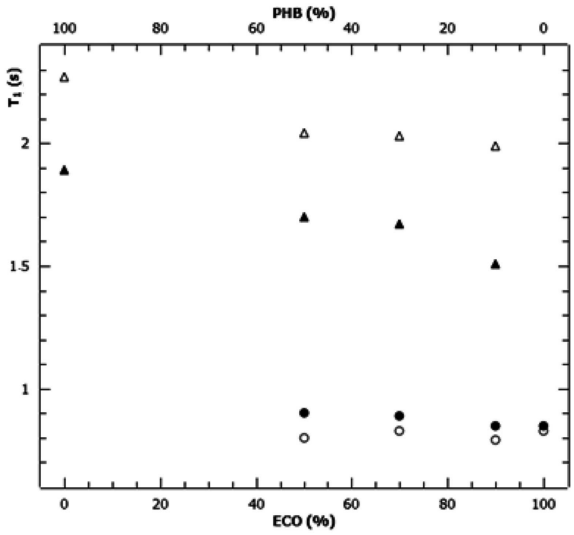

Fig. 5. Dependence of the spin-lattice relaxation times in the laboratory frame T_1(H) of methylene protons of Ecoflex® (circles) and methyl protons of PHB (triangles) of the component fraction in PHB/ECO blends. Full symbols denote the values measured at the room temperature, open symbols correspond to the values at the temperature of 90 °C.

The laboratory frame spin–lattice relaxation time T_1 characterizes the rate of establishing equilibrium between the spin system and its surroundings. It is mainly sensitive to motions with correlation frequencies at or near to resonance frequencies, i.e., hundreds of MHz. In motionally heterogeneous polymeric systems, the observed relaxation behaviour is determined both by the intrinsic relaxation behaviour of the different regions and by the magnetisation transfer either due to spin-diffusion or due to bulk diffusion of polymer chains. For T_1(H) relaxation with relatively long intrinsic relaxation times this often leads to the observation of a single exponential decay of magnetisation [20, 21]. Spin–lattice relaxation times in the laboratory frame T_1(H) obtained by inversion recovery pulse sequence combined with cross polarisation technique were determined for pure PHB, pure Ecoflex® and their blends with different ratios at the room temperature and at the temperature of 90 °C. The dependences of the spin–lattice relaxation times T_1(H) on the fractions of the blend components at both measured temperatures are depicted in Fig. 5. Due to the effective spin-diffusion the values of T_1(H) for protons in individual groups of the blend components are nearly the same varying in the range of 5%, hence, only T_1(H) for methyl groups of PHB and methylene groups of Ecoflex® are presented in Fig. 5.

Spin–lattice relaxation times T_1(H) of the components measured at the room temperature (Fig. 5 — full symbols) differ significantly from each other, but they do not change markedly by blending with various component ratios. That refers to the poor miscibility and incompatibility of the components. However, relaxation times T_1(H) of PHB-protons shorten slightly with increasing amount of Ecoflex® in the blend (up to 20% of the value for pure PHB), while those of Ecoflex®-protons are close to the value of pure Ecoflex® (within the estimation error). It follows that the dynamics of the PHB component is in some way affected by the presence of the Ecoflex® component as probed by T_1(H) measurements.

Spin–lattice relaxation times T_1(H) measured at the temperature of 90 °C (Fig. 5 — open symbols) show that spin–lattice relaxation was influenced by temperature increase more markedly in the case of PHB-protons. The values of T_1(H) belonging to individual components in blends do not converge and thus poor miscibility of the blend components is repeatedly confirmed. The glass transition temperature of PHB ($T_g \approx 5-15$ °C) [2] is near the room temperature, but it is not the case of Ecoflex® ($T_g \approx -30$ °C) [5]. We presume that the PHB chains are still in glassy state at the room temperature. In the temperature dependence of the relaxation time T_1(H) of PHB measured at static sample at the resonance frequency of 200 MHz the minimum connected with the free reorientation of the methyl groups was observed at –129 °C and the minimum connected with the glass transition was not achieved at highest measured temperature which was about 110 °C [3]. According to the condition for minimum of T_1(H) temperature dependence [21], the minima observed at our resonance frequency of 400 MHz are expected to be shifted to higher temperatures. We assume that higher values of the relaxation time T_1(H) measured for PHB at 90 °C are due to the fact that this temperature is on the high temperature side of the minimum of spin–lattice time temperature dependence attributed

to the motion of methyl groups of PHB and the spin-diffusion process is still effective at this temperature.

The same experiments were carried out for samples containing small amount (3 wt%) of additive. However, the effect of addition of additive was negligible. It follows that addition of additive influences neither the miscibility nor the dynamics of the spin–lattice relaxation of the blend components.

Based on the theory of ^{1}H spin diffusion, the T_1(H) values (Fig. 5) make it 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 8×10^{-16} m^2/s was substituted for PHB (rigid system), and the value of 0.5×10^{-16} m^2/s for Ecoflex® (mobile system) [22]. The estimated minimal domain size of PHB component varies in the range of 85–92 nm and it increases with the fraction of PHB in the blend. The estimated minimal domain size of Ecoflex® component remains almost unchanged with changing the fraction of Ecoflex® in the blend varying in the range of 15–17 nm. The values of T_1(H) indicate that the spin-diffusion process does not average the spin–lattice relaxation time through the whole proton system of both components. Hence, the blend components are phase separated even in the scale of 15–92 nm.

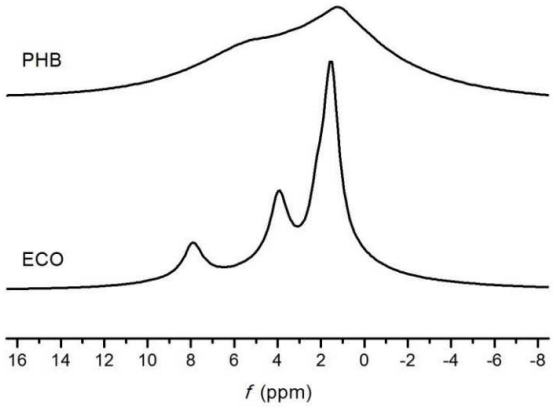

Fig. 6. ^{1}H NMR spectra of PHB (top) and Ecoflex® (bottom) (spectra were not normalized).

Liquid ^{1}H NMR spectrum of PHB in $CDCl_3$ consists of three multiplets with chemical shifts of 1.29 ppm for methyl protons, 2.57 ppm for methylene protons and 5.27 for methine proton [23]. Liquid spectrum of PBAT in $CHCl_3$ is composed of peaks of terephthalate unit at 8.1 ppm and adipate unit at 2.33 ppm and multiplets corresponding to OCH_2 protons of butylene unit centered at 4.15 ppm and to other methylene protons of adipate and butylene units in the range of 1.4–2 ppm [24]. In the measured solid state ^{1}H MAS NMR spectrum of PHB (Fig. 6, top) only one broad asymmetric peak at 1.3 ppm with a shoulder at about 5.4 ppm is observed as a consequence of dipolar interactions between protons. Solid state ^{1}H MAS NMR spectrum of Ecoflex® (Fig. 6, bottom) is better resolved which reflects that the mobility in its spin system is higher than that of PHB [25]. The spectrum of Ecoflex® consists of three peaks with different chemical shifts corresponding to protons in terephthalate unit — 8.0 ppm, OCH_2 protons — 4.0 ppm and CH_2 protons — 1.7 ppm. The spectra of Ecoflex® and PHB/ECO blends with and without additive (not displayed) are similar in shape due to the overlapping of the broad spectrum of PHB with the resolved spectrum of Ecoflex®. The peaks of PHB are not discernible in the spectra of blends. This is the reason why the spin–lattice relaxation times $T_{1\rho}$(H) in the rotating frame were not calculated for PHB-component in blends and only an effect of blending on Ecoflex® component can be described.

TABLE I

Spin-lattice relaxation times in the rotating frame $T_{1\rho,\mathrm{obs}}$ as the inverse of the population weighted rate average related to protons in individual chemical groups for PHB, Ecoflex® and blends PHB/ECO-30/70 with and without additive measured at the room temperature.

Sample	$T_{1\rho,\mathrm{obs}}$ [ms]			
	8 ppm	4 ppm	1.7 ppm	1.3 ppm
ECO	2.6	2.1	2.6	
PHB/ECO	3.0	2.7	3.0	
PHB /ECO /A	2.5	2.2	2.4	
PHB				5.6

The spin–lattice relaxation times $T_{1\rho}$(H) in the rotating frame were measured for pure samples PHB and Ecoflex® and for the blends containing 30 wt% of PHB with and without additive. The spin–lattice relaxation time $T_{1\rho}$(H) in the rotating frame is sensitive to molecular motions with correlation frequencies of the 10–500 kHz [21]. The interpretation of $T_{1\rho}$(H) data is rather complicated for motionally heterogeneous systems like semicrystalline polymers as the relaxation behaviour is determined not only by the intrinsic relaxation behaviour of individual regions but also by the effects of magnetisation transport. Thus, none of the observed components are simply related to the intrinsic relaxation characteristics of the regions with different mobility. However, the population weighted rate average (PWRA) of the relaxation components is always equal to the PWRA of the intrinsic relaxation behaviours and equal to the relaxation rate obtained from the magnetisation decay [20]. Thus, we calculated the inverse of PWRA as the time constant $T_{1\rho,\mathrm{obs}}$ characterizing proton spin–lattice relaxation in the rotating frame of our samples. The magnetisation decay was fitted by two exponentials with shorter $T_{1\rho\mathrm{A}}$ and longer $T_{1\rho\mathrm{B}}$ relaxation times with relative populations w_A and w_B, respectively. The values of $T_{1\rho,\mathrm{obs}}$ of the inverse of PWRA listed in Table I were evaluated by means of the best fit parameters $T_{1\rho\mathrm{A}}$, $T_{1\rho\mathrm{B}}$, w_A, and w_B according to the equation: $(T_{1\rho,\mathrm{obs}})^{-1} = w_\mathrm{A}(T_{1\rho\mathrm{A}})^{-1} + w_\mathrm{B}(T_{1\rho\mathrm{B}})^{-1}$.

The relaxation times $T_{1\rho,\mathrm{obs}}$ of Ecoflex® protons are markedly shorter than that of PHB protons. In the blend mixed closely at the molecular level domains should relax with the same apparent relaxation times $T_{1\rho}$ [9]. The relaxation times $T_{1\rho,\mathrm{obs}}$ of all proton groups of Ecoflex® in blend are slightly longer than in pure Ecoflex® indicating a bit slower spin–lattice relaxation of these proton groups in the presence of PHB. Described changes could indicate the existence of some small intermediate regions in the blends. After adding of additive into the blend, the relaxation of Ecoflex® protons is nearly the same as in pure Ecoflex® (Table I).

4. Conclusion

Blends of PHB and Ecoflex® were studied by means of basic solid-state NMR techniques. ^{13}C NMR spectra of blends point at poor miscibility of components. Small changes in the shape of peaks related to the individual components in the blends when compared with pure samples indicate some interaction of the blend components.

Spin–lattice relaxation study of blends composed of these biodegradable plastics show that components form domains in the blends. Existence of some small intermediate regions, in which the dynamics of one component is affected by the other, was also revealed. The spin–lattice relaxation times T_1(H) were used for the calculation of minimal domain size of the blend components. The sizes of the PHB domains decrease slightly with decreasing PHB content in the blend.

According to the measurements of the spin–lattice relaxation times $T_{1\rho}$(H) in the rotating frame the blending affects the relaxation dynamics of Ecoflex® proton spin system only slightly.

The realized NMR experiments show formation of PHB and Ecoflex® domains in the blends with some boundary regions in which the blend components affect each other.

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