

STUDY OF PLA/PHB BLEND MORPHOLOGY USING ^{13}C NMR SPECTROSCOPY – INFLUENCE OF PLASTICIZER AND COMPATIBILIZER

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1. Introduction

Biodegradable polymers are intensively investigated because of their low environmental impact and properties comparable to conventional oil-based polymers. Poly (lactic acid) (PLA) is a renewable resource-based compostable polymer having a favorable combination of material properties such as mechanical properties, biocompatibility, and moderate barrier properties, which allows its using as packaging materials and hygienic products [1]. However, some properties such as low thermal stability, low crystallization rate in comparison to conventional polymers, and brittleness limit its wider applications in industry. The possible ways for overcoming these problems are blending of PLA with other biodegradable polymers, plasticization and compatibilization of the polymer blend.

One of the suitable polymers for the PLA-based blend formation is biodegradable poly (3-hydroxybutyrate) (PHB). Morphology of the polymer blend strongly depends on miscibility of the polymer components. The miscibility of PLA and PHB has been studied in several works [2-4] and was found to be strongly dependent on molecular weight of both components. PLA is miscible with low and immiscible with high molecular weight PHB [2, 3]. Significant increases in crystallinity and crystallization rate were found in PLA blended with PHB as compared to those of pure PLA [5].

Plasticization and compatibilization are other ways how to change properties of PLA. Generally, addition of a small amount of plasticizer into polymer can lead to an enhancement of the molecular mobility and rate of the crystallization process. Effect of triacetine (TAC) as a plasticizer on morphology of PLA was recently investigated using NMR and DSC experiments and increase of the rate of the crystallization process, which is directly associated with free volume and molecular mobility was observed in plasticized sample [6]. Compatibilizer enables to reach better dispersion (better mixing) and consequently stronger interactions between the blend components. It was shown that compatibility between the poly (lactic acid) and poly (butylene-adipate-co-terephthalate) was significantly improved in the presence of the chain-extenders and in this way ductility of the blend was enhanced [7].

The solid-state NMR is an effective tool for the study of structure, morphology and molecular dynamics of polymers. In this paper, the morphology of PLA/PHB blend, PLA/PHB plasticized with TAC and PLA/PHB compatibilized with Joncryl was studied using solid state NMR technique. Single-pulse (SP) MAS ^{13}C NMR and cross-polarization (CP) MAS ^{13}C NMR spectra were measured for this purpose.

2. Experimental

Virgin pelletized PLA 4042 D (Nature Works), powdered PHB (Biomer, Germany), triacetine as plasticizer and Joncryl® ADR-4368 (BASF AG, Germany) (JON) as

compatibilizer were used for the samples preparation. Polymer blend PLA/PHB containing 85 wt. % of PLA, plasticized polymer blend PLA/PHB/TAC containing 10 wt. % of TAC and PLA/PHB/JON blend with 2 wt. % of compatibilizer were prepared by blending and melting of the respective components in a twin-screw extruder at 190 °C and subsequently quenching in cold water. The quenched samples denoted as PLA-q and PHB-q were prepared from virgin PLA and PHB by the same procedure as the polymer blends.

The high-resolution solid-state ^{13}C NMR measurements were performed on a Varian 400 MHz NMR spectrometer (Palo Alto, CA, USA) at the resonance frequency of 100 MHz with the use of 4 mm zirconium oxide rotors and magic-angle spinning (MAS) frequency of 10 kHz. The single-pulse and cross-polarization MAS ^{13}C NMR spectra were measured at room temperature.

Free induction decays at the SP and CP MAS ^{13}C NMR measurements were recorded with SPINAL pulse high-power proton decoupling. The SP MAS ^{13}C NMR spectra were measured under decoupling field of 90 kHz, recycle delay of 120 s, acquisition time of 20 ms and spectral width of 50 kHz. NMR spectrum was obtained using Fourier transformation of the FID, which in the case of SP measurements involved of 1400 - 1500 scans on average. The CP MAS ^{13}C NMR spectra were measured under decoupling field of 58 kHz, contact time of 80 ms and recycle delay of 6 s. The chemical shifts of all spectra were referenced to tetramethylsilane using adamantane as an external standard.

3. Results

SP MAS ^{13}C NMR spectra of semi-crystalline polymers generally consist of the superposition of broad Gaussian lines corresponding to carbons of disordered chains in the amorphous phase and narrow lines assigned to rigid carbons in the crystalline phase of the polymer structure. The SP MAS ^{13}C NMR spectra for PLA/PHB blend and its components PLA-q and PHB-q are depicted in Figure 1.

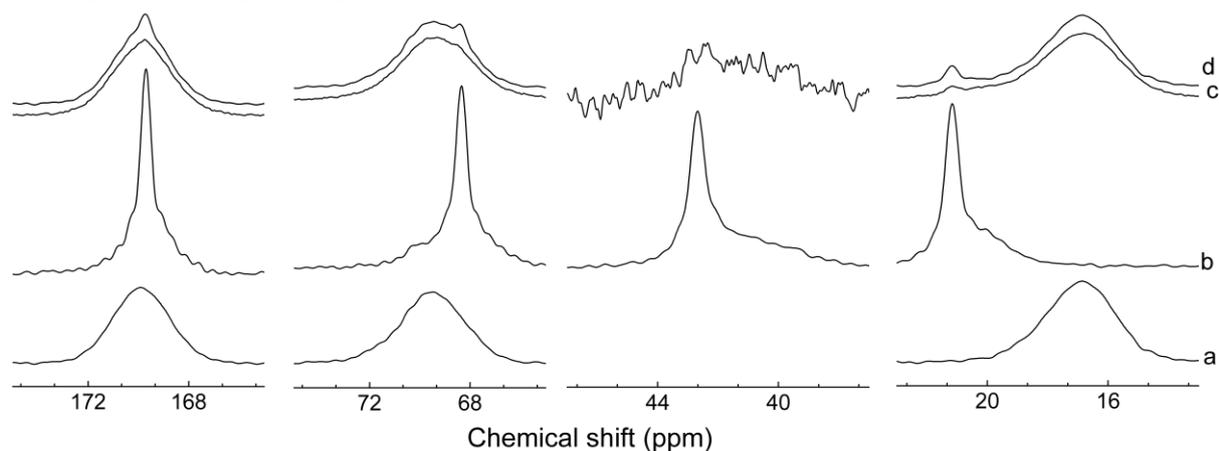


Fig.1: SP MAS ^{13}C NMR spectra of PLA-q (a) and PHB-q (b) and PLA/PHB blend (c). Spectrum (d) for PLA/PHB blend was determined by superposition of the spectra measured for PLA-q and PHB-q.

SP MAS ^{13}C NMR spectrum of PHB-q shows four resonance lines with chemical shifts corresponding to carbon nuclei in four different groups: carbonyl (CO) - 169.8 ppm, methine (CH) - 68.4 ppm, methylene (CH_2) - 42.8 ppm and methyl (CH_3) - 21.0 ppm. Despite melting and quenching, all resonance lines of SP MAS ^{13}C NMR spectrum for PHB-q consists of narrow and broad components arising from the crystalline and amorphous domains, respectively. Crystallinity X_c as high as 69% was estimated by deconvolution of the methyl resonance for this sample [8].

In the case of PLA-q, SP MAS ^{13}C NMR spectrum displays three broad singlet Gaussian lines characteristic for amorphous PLA [6, 9] assigned to CO (169.9 ppm), CH (69.5 ppm), and CH₃ (16.9 ppm) carbons.

Four resonance lines associated with CO (169.9 ppm), CH (69.5 ppm), CH₂ (about 43.0 ppm), and CH₃ carbons (16.9 ppm) are also observable in the SP MAS ^{13}C NMR spectrum of PLA/PHB blend. The resonance lines related to CO and CH groups are broad and symmetrical. On the other hand, the CH₃ carbon resonance is asymmetrical and its shape shows features of both blend components. The intensity of methylene resonance in this spectrum is very weak due to a very low fraction of PHB in the PLA/PHB blend.

The shape and widths of CO and CH resonances of PLA/PHB spectrum are very similar to those of PLA-q and reveal largely amorphous structure of PLA/PHB blend. Moreover, small peaks situated on the broad lines at 169.7, 68.5 and 21.2 ppm are visible in CO, CH and CH₃ resonances of the SP MAS ^{13}C NMR spectrum of PLA/PHB blend. Evidently, these peaks are associated with crystalline domains of PHB-q.

To estimate compatibility of polymer components of PLA/PHB blend, a superposition of the spectrum PLA-q and PHB-q with regard to the relative number of the carbon nuclei of both polymers in the blend was made and spectrum obtained by this procedure is shown in Figure 1d. The identical features of the measured (c) and superimposed (d) spectrum of the PLA/PHB polymer blend identify poor miscibility of PLA and PHB. Therefore, the PLA/PHB blend is a polymer system with PHB domains dispersed within amorphous PLA matrix.

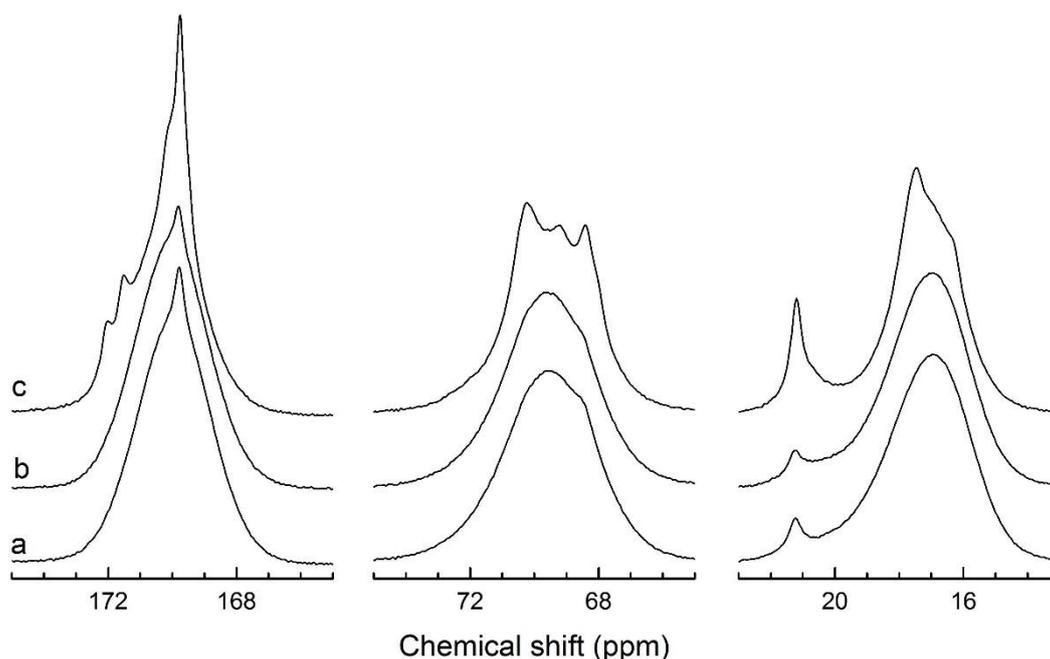


Fig.2: CP MAS ^{13}C NMR spectra of PLA/PHB blend (a), compatibilized PLA/PHB/JON blend (b) and plasticized PLA/PHB/TAC blend (c).

The effect of Joncryl as compatibilizer and TAC as plasticizer on morphology of the PLA/PHB blend was investigated by CP MAS ^{13}C NMR spectra, which are depicted in Figure 2. As we can see, CP MAS ^{13}C NMR spectrum of the compatibilized PLA/PHB/JON blend (b) is almost the same as CP MAS ^{13}C NMR spectrum for PLA/PHB blend (a).

Therefore, in light of solid state NMR, it indicates that addition of Joncryl into PLA/PHB blend does not significantly influences the morphology of PLA/PHB blend.

The spectrum of the PLA/PHB blend plasticized by TAC (Figure 2c) significantly differs from the spectrum of PLA/PHB. The well-resolved peaks at the positions of 172.1 ppm, 171.5 ppm, and 169.8 ppm in CO resonance, 70.3 ppm and 69.3 ppm in CH resonance and 17.5 ppm in CH₃ resonance are observed in the CP MAS ¹³C NMR spectrum measured for the plasticized PLA/PHB polymer blend. These peaks together with the shoulders at 170.2 ppm, 68.0 ppm and 16.3 ppm are in good accordance with the positions of the peaks observed in CP [10] or in SP MAS ¹³C NMR spectrum [11] of crystalline α form of PLA. The peak at the position of 21.2 ppm, which was also observed in non-plasticized sample, comes from the crystalline domains of PHB. Other peaks related to crystalline domains of PHB can be found at 68.4 ppm or as superposed lines of both polymers at 169.8 ppm. Thus, we can deduce, that plasticization supports the crystallization process of PLA in this blend.

4. Conclusion

Morphology of the polymer blend prepared from biodegradable polymers, PLA and PHB, and the changes in morphology caused by the addition of Joncryl and TAC, which were supposed to induce compatibilization and plasticization, respectively, were studied by means of the SP MAS ¹³C NMR and CP MAS ¹³C NMR spectra measured at room temperature.

The PLA/PHB blend with PHB domains dispersed within amorphous matrix of PLA was deduced from the SP MAS ¹³C NMR spectra. Compatibilization of the polymer blend with the small amount of Joncryl did not result in the change of the shape of the NMR spectrum, but the CP MAS ¹³C NMR measurements revealed that TAC plasticizer supports the formation of crystalline domains in PLA as well as in PHB regions of the polymer blend.

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