PROTON NMR STUDY OF POLYLACTIC ACID AND ITS MODIFICATIONS

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1. Introduction

Biodegradable polymers have attracted much attention in recent years because of their low environmental impact and properties comparable to conventional oil-based polymers. Poly(lactic acid) or polylactide (PLA) is a biodegradable, biocompatible, nontoxic linear aliphatic thermoplastic producible from low-cost renewable feedstocks. It is widely used in medicine, pharmacy and the packaging industry [1-6]. However, some physical properties of PLA (hardness, brittleness, creep under mechanical stress, low thermal stability) are not convenient for all commercial applications. A possible strategy for tuning its properties is blending PLA with other compounds (e. g. plasticizers) or polymers by means of compatibilizers [1-4].

Physical properties of polymers markedly depend on their morphology, which can be influenced by varying the crystallization conditions or by annealing at different temperatures during different time periods, or by quenching. PLA can crystallize in three types of crystalline modifications [1,5]. Totally amorphous PLA can be produced by quenching the melt or by injection moulding [5]. Recrystallization of amorphous PLA occurs through annealing at temperatures between the glass transition temperature T_g and the melting temperature T_m, and also by gradual heating in DSC experiments at temperatures higher than 97 °C [2,3,5].

Adding a suitable amount of triacetine (TAc) plasticizer improves PLA processability by enhancing its flexibility. Decrease in T_g and T_m was observed as a consequence of increase in the free volume and molecular mobility of PLA chains in the presence of the plasticizer. Blending PLA with appropriate volume of TAc brought about a decrease in the temperature of recrystallization [2].

Blending of polymers is usually used to improve their properties [1-4]. Adding compatibilizers into polymer blends is often needed to avoid formation of separate phases of polymers in a blend. Recent studies of PLA and poly(butylene-adipate-co-terephtalate) blends compatibilized with a multifunctional epoxy chain extender, Joncryl[®], resulted in increased thermal stability, intrinsic viscosity and elastic modulus of PLA owing to the reaction of PLA chain ends with molecules of Joncryl[®], leading to molecular weight increase [3, 4]. Polar interactions between Joncryl[®] and PLA restrain the mobility of PLA chains due to their extending and branching [4].

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful method for studying molecular dynamics [6,7]. Single-pulse ^{1}H NMR applied within a broad temperature range provides information on local motions in polymer chains [7]. The shape of the NMR spectra is influenced by the physical interactions in which the examined nuclei are involved. The solid-state ^{1}H NMR spectra are broad especially owing to strong direct dipolar interaction among protons. Molecular motion in the studied material averages out anisotropic interactions and to some extent the dipolar interactions as well, which gives rise to a narrowing of the solid state NMR spectra [6,8,9].

The current study aims to characterize the effect of polymer supermolecular structure, and the effect of mixing with compatibilizer Joncryl® and TAc plasticizer on the molecular dynamics of PLA in the glass transition temperature region.

2. Experimental

^{1}H NMR spectra were measured on four PLA samples: PLA-v, virgin pelletized PLA 4042D (Nature Works, LLC, USA); PLA-q which was prepared by quenching the virgin sample in cold water after melting in a twin-screw extruder at 190 °C; PLA-J and PLA-T which were prepared by melting PLA together with 2 wt. % of compatibilizer Joncryl® ADR-4368 (BASF AG, Germany) and with 10 wt. % of TAc plasticizer respectively, and then quenched under the same conditions as for PLA-q. All samples were supplied by the Polymer Institute of the Slovak Academy of Sciences.

The ^{1}H NMR spectra were acquired on a Varian NMR spectrometer (Palo Alto, CA, USA) at a resonance frequency of approximately 400 MHz. The samples were cut into small pieces before packing in 4 mm ZrO_2 NMR. Spectra were measured on static samples with a procedure suppressing the probehead background proposed by Chen [7]. In this method radio-frequency pulses with durations of 1.5 and 3 μs corresponding to $\pi/4$ and $\pi/2$ pulse respectively, were used for detecting the free induction decay (FID) with a recycle delay of 10 s. The spectral width was 100 kHz and the acquisition time was modified according to the duration of the FID signal, varying with the sample and temperature from 20 to 80 ms. All NMR spectra were obtained using Fourier transformation of the FID as an average of 16 scans. Spectra were processed and analysed using MestReNova software. The chemical shifts were referenced to tetramethylsilane using adamantan as an external standard.

The gradual heating of samples from room temperature up to 100 °C took approximately 8 hours. The sample temperature was stabilized for 20 minutes prior to each measurement. The temperature was controlled by a variable temperature system unit with the accuracy of ±0.1 °C.

3. Results

Solid-state ^{1}H NMR spectra measured on static samples generally consist of the superposition of broad Gaussian lines corresponding to protons in the rigid phase, and narrow lines assigned to more mobile protons in the polymer structure. The width of the peaks at their half height reflects the mobility of protons: the narrower the lines are, the more mobile are the spins in the studied material [1,6].

The ^{1}H NMR spectra measured at room temperature on static samples of PLA-v, PLA-q and PLA-J are nearly the same, and for illustration the spectrum of PLA-q is shown in Fig. 1a, bottom. The spectra consist of a broad peak which reflects the rigid system of CH_3 and CH protons, and a narrow line with considerably lower intensity confirming the presence of protons with higher mobility. The spectrum of PLA-T is slightly different (Fig. 1a, top), since the intensity of the narrow line is a little higher than for the other samples. The difference between the spectra of PLA-q and PLA-T is indicated by a rectangle in Fig. 1a.

The ^{1}H NMR spectra of all samples narrow with the temperature increase, as can be seen from the course of the temperature dependences of their linewidths depicted in Fig. 2. These changes in the spectra can be related to the changes in molecular motion in the amorphous regions of the studied polymers. The linewidth of the spectra of PLA-v, PLA-q and PLA-J was estimated at the half height of the broad component of the spectra. The linewidth of the ^{1}H NMR spectrum of PLA-v does not change up to the temperature of 60 °C, and it decreases at higher temperatures. So do the linewidths of the ^{1}H NMR spectra measured on samples PLA-q and PLA-J, but the onsets of their decrease are observed at slightly lower temperature of approximately 55 °C. The linewidth of the PLA-T ^{1}H NMR

spectrum was estimated at the half height of spectra in the whole temperature range (except the spectrum measured at 100 °C, when CH_3 and CH line splitting is observed). The linewidth decreases from room temperature up to 65 °C, and then it does not change at higher temperatures.
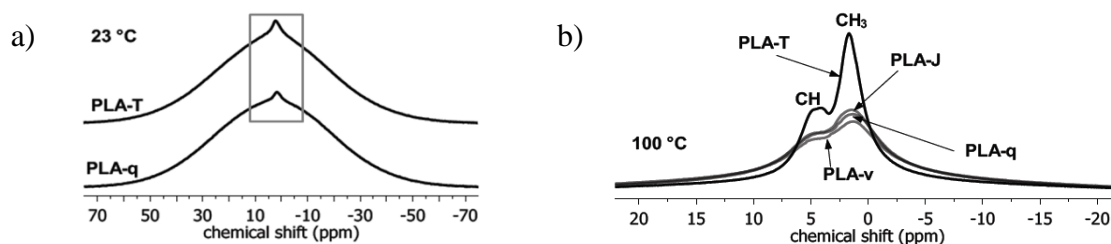

Fig. 1: *Solid-state ^1H NMR spectra measured on static samples as indicated a) at room temperature, b) at the temperature of 100 °C*

Line narrowing in ^1H NMR spectra with temperature increase was observed for all samples but more distinctly for PLA-T. The resonance of methyl (CH_3) and methine (CH) protons of PLA at chemical shifts of approximately 1.6 and 4.5 ppm respectively, can be recognized in the spectra measured at elevated temperatures. The peak related to the CH protons is visible in the spectra of PLA-v, PLA-q and PLA-J measured at 100 °C (see Fig. 1b) only as a shoulder of the central peak at the side of higher chemical shifts. However, for the PLA-T sample the central peak of the ^1H NMR spectrum is split into two peaks related to CH and CH_3 protons. The amplitude of the peak at 1.6 ppm corresponding to the methyl protons increases for the samples in order PLA-v, PLA-q, PLA-J and PLA-T, reflecting increasing mobility of this group in particular samples.
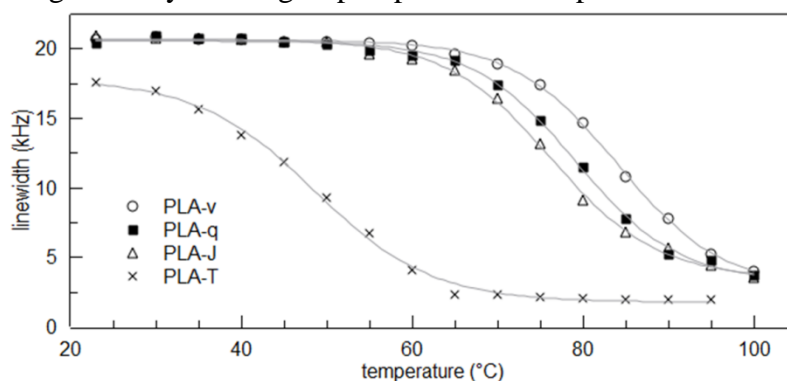

Fig. 2: *The temperature dependences of the linewidth of the solid-state ^1H NMR spectra measured on static samples of PLA-v, PLA-q, PLA-J and PLA-T*

The glass transition temperature T_g of PLA is about 60 °C. This transition is related to the release of segmental chain motion in amorphous regions of the polymer. [8,9]. At room temperature PLA chain segments are frozen in fixed positions and their mobility gradually increases when the temperature rises above T_g. For this reason temperature dependences of linewidths (Fig. 2) can be used for the determination of the glass transition, which is the temperature at which the onset of the linewidth decrease occurs. The relatively broad temperature range of the linewidth decrease indicates a distribution of molecular mobility in amorphous regions of investigated polymers [8]. The linewidth of the spectrum reflects average mobility in the sample, which depends on the distribution of local environments of resonating nuclei [9].

A recent ^{13}C NMR study of PLA confirmed that PLA-v is a semi-crystalline polymer with a crystallinity of 51 % [10] and PLA-q is amorphous. Larger linewidths of the ^1H NMR spectra measured at temperatures higher than T_g and a higher value of T_g estimated from Fig. 2 for PLA-v than for PLA-q can be explained by more restrained mobility of some part of

amorphous PLA-v chains due to the presence of crystalline regions, according to a three-phase model of semi-crystalline polymers [9]. For this reason some differences in the shape of ^{1}H NMR spectra measured at 100 °C are also observed (Fig. 1b).

Mixing a compatibilizer with PLA restrains the mobility of polymer chains [3,4], which should lead to broadening of the ^{1}H NMR spectrum and a shift of the glass transition to higher temperatures. However, a contrary effect is observed in Fig. 2 when PLA-J and PLA-q samples are compared. We assume that both samples are amorphous as they were quenched under the same conditions. A small difference can be observed in ^{1}H NMR spectra of PLA-J and PLA-q measured at 100 °C (Fig. 1b) – the amplitude of the peak at chemical shift of 1.6 ppm corresponding to methyl protons is higher for PLA-J, indicating higher mobility of this group in PLA-J than in PLA-q. The observed course of the temperature dependence of linewidths for PLA-J (Fig. 2) may be brought about by compatibilizer interaction with main chains of PLA, which affords more space for reorientation of methyl protons in PLA-J than in PLA-q.

Plasticizing PLA with TAc leads to increase in chain mobility of the polymer, as evident from the course of the temperature dependence of spectrum linewidth (Fig. 2). The glass transition temperature estimated from this dependence is about 35 °C for this sample, which is significantly lower than for the other studied samples. This result is in accordance with the T_g values obtained by DSC in [2], where adding 10 wt. % of TAc to pure PLA reduced the T_g value by 22 °C. The PLA recrystallization expected to take place at temperatures near 100 °C and in the presence of TAc at even lower temperatures can not be inferred from our obtained results. Deconvolution of the spectra is needed, and this will be the next step in our study of these samples.

4. Conclusion

PLA samples with different supermolecular structures and PLA samples modified with compatibilizer and plasticizer were studied using ^{1}H NMR in static mode in the temperature range including their glass transitions. Lower glass transition temperature and higher chain mobility were found in amorphous than in semi-crystalline PLA. Somewhat higher average mobility of protons in PLA with compatibilizer is probably caused by more mobile CH_3 groups in chains not interacting with compatibilizer. Plasticizer caused significant decrease in the glass transition temperature and increase in PLA chain mobility.

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