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Understanding the Aggregation of Bis(benzoxazolyl)stilbene in PLA/PBS Blends: a Combined Spectrofluorimetric, Calorimetric and Solid State NMR Approach

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Poly(lactic acid)/poly(butylene succinate) (PLA/PBS) blends, containing a small amount of 4,4'-bis(2-benzoxazolyl)stilbene (BBS) dye showed a chromogenic response after heating above 80 °C, due to the formation of BBS aggregates. This smart behaviour can be useful for many different applications, such as for the realization of time-temperature optical indicators, and the understanding of the processes lying behind chromophores aggregation is fundamental for improving their performances. In this work, the phase transitions occurring in the PLA/PBS polymeric matrix under heating were investigated in detail by combining spectrofluorimetric, DSC, and variable-temperature solid state NMR (SSNMR) measurements on both PLA- (in pellets and film) and PLA/PBS-BBS films. A detailed characterization of the phase behaviour of both PLA and PBS domains was achieved. More specifically, the SSNMR analysis of ¹H FID at different temperatures was found to be a very powerful and useful approach to investigate the phase transitions of PLA, complementary to DSC. Different phase and dynamic processes, PBS and PLA cold crystallization and PLA glass transition, seem to concur, at different levels, to promote BBS aggregation. A possible mechanism for the formation of BBS aggregates under heating was proposed.

Introduction

Thermally responsive polymer systems that show chromogenic behaviour in the solid state have been receiving impressive attention in the last years.¹⁻⁵ These “smart” devices are designed for many different applications, among which camouflage systems, anti-counterfeiting, optical sensors or informational displays.⁶ Soft intelligent materials, including among others synthetic polymers, are based on the assembly of different units performing specific functions; for example, compounds able to respond to thermal stimuli can be inserted within polymeric matrices (either in interfacial regions or in more complex supramolecular architectures) to obtain highly tuneable platforms.⁷⁻¹³ The high sensitivities generally arise from the incorporated chromophores, which respond to local environmental changes upon temperature variations, due to either polymer phase transitions or increased solubility of the dye within the polymer.

For example, kinetically trapped and molecularly mixed cyanooligo(p-phenylene vinylene)s^{9,13,14} or stilbene-based dyes⁸ inside the glassy amorphous phase of the host polymers can be thermally stimulated to aggregate above a certain threshold temperature. This yields thermodynamically stable micro/nano sized aggregates whose emission characteristics are mainly determined by the photophysical effects associated with the p-p stacking interactions among the planar aromatic backbones of the dyes.¹⁵⁻¹⁷

In a previous work,¹⁸ films of poly(lactic acid)/poly(1,4-

butylene succinate) (PLA/PBS) blends incorporating small amounts of 4,4'-bis(2-benzoxazolyl)stilbene (BBS) chromophore were reported to display a thermo-sensitive luminescent behaviour. This smart behaviour suggested applications in the field of intelligent packaging, since PLA blends are the most convenient alternative to conventional polyolefins for packaging applications, owing to PLA's availability from renewable resources, easy optimization of the thermo-mechanical properties and expected decreasing production cost.¹⁹ As far as thermochromic behaviour is concerned, after annealing at temperature higher than PLA T_g (60-70 °C), BBS emission clearly changed due to the occurrence of chromophore aggregation. This aggregachromic response triggered by thermal stimuli seemed to be related to the effects provided by the temperature on the mobility of BBS and change of polymer matrix thermal features.

The understanding of the structural and dynamic properties of these materials also at a nanometric and sub-nanometric scale and their correlation with their chromogenic behaviour appears very important to devise and develop systems with improved performances. To this aim, Solid-State NMR (SSNMR) is known to be one of the most powerful techniques, since, exploiting a variety of active nuclei and of spectral and relaxation properties, it is able to give detailed information on structural properties on a 0.1-100 nm scale, and on dynamic behaviour on a Hz-GHz interval.²⁰

The present study investigates in detail the phase behaviour of the polymeric matrix in PLA/PBS-BBS composites through the

combination of variable temperature solid-state NMR (high-resolution ^{13}C spectra and low-resolution on resonance ^1H FID analysis), DSC and fluorescence experiments. In particular, proton T_2 , being very sensitive to the degree of mobility in the 5 Hz-kHz frequency range, could be a very useful probe to follow the phase transitions occurring in polymeric domains over a wide temperature range. Neat PLA and PLA-BBS systems were also studied for comparison.

Experimental section

10 Materials

Poly(1,4-butylene succinate) (PBS, Bionolle 1001, $M_w = 1.8 \cdot 10^5$, $DI = 2.2$, Melt Flow Rate (MFR, $\text{g}/10\text{min}$ $2.16\text{Kg}/190^\circ\text{C}$) = 1.8 ± 0.2 , supplied by Showa Highpolymer CO, LTD., Japan) and Poly(lactic acid) (PLA, PLA2002D, Specific Gravity = 1.24, Melt 15 Flow Rate (MFR, $\text{g}/10\text{min}$ $2.16\text{Kg}/210^\circ\text{C}$) = 5-7, supplied by NatureWorks[®], USA) were used as polymer host matrices. 4,4'-Bis(2-benzoxazolyl)-stilbene (BBS, 97 %) was purchased from Aldrich and used without further purification.

Preparation of PLA85PBS15 films

20 PBS and PLA pellets were dried for 2 hours under reduced pressure (0.01 mbar) at 60°C before processing. Polymer blends were prepared in a Brabender plastograph mixer (mod. OHG47055, 30 cm^3) under nitrogen atmosphere by introducing about 40 g of the polymers in the set composition (100 % PLA or 25 85 wt% of PLA and 15 wt% of PBS) and 0.07 wt% of BBS in the mixer at 200°C with a rotor speed of 50 rpm. After 10 min, the mixing was stopped and the recovered materials were grinded at room temperature by using an IKA MF10 analytical mill. The powder obtained was successively moulded between two 30 aluminium foils under compression (max 5 atm) in a Collin-mod.200M press at 200°C for approximately 3 min. After removal from the press, the films were allowed to reach room temperature ($\sim 20^\circ\text{C min}^{-1}$), obtaining films having thickness of about 150-200 μm . Annealing experiments were performed by 35 placing the films on a temperature controlled hot stage in the range of 60 - 100°C .

DSC and fluorescence experiments

The thermal behaviour was evaluated by differential scanning calorimetry (DSC) under nitrogen atmosphere by using a Mettler 40 Toledo StarE System, equipped with a DSC822c module. Blend samples were heated from -80 to 220°C at $10^\circ\text{C}/\text{min}$ (1st heating), cooled to -80°C at the same scan rate (1st cooling), then heated again to 220°C at $10^\circ\text{C}/\text{min}$ (2nd heating). Melting enthalpies were evaluated from the integrated areas of melting 45 peaks by using indium for calibration. PLA and PBS crystalline content (χ) were evaluated from the measured melting enthalpy (ΔH_m) taking into account the melting enthalpy of the perfect PLA crystal (ΔH_m° , 93.1 J/g)²¹ and PBS crystal (ΔH_m° , 220.0 J/g)²², using equation 1:

$$50 \quad \chi = \frac{\Delta H_m}{\Delta H_m^\circ} \cdot \frac{100}{f} \quad (\text{eq. 1})$$

where f is the polymer fraction in the blend.

Fluorescence spectra were recorded at room temperature with the help of a Horiba Jobin-Yvon Fluorolog[®]-3 spectrofluorometer

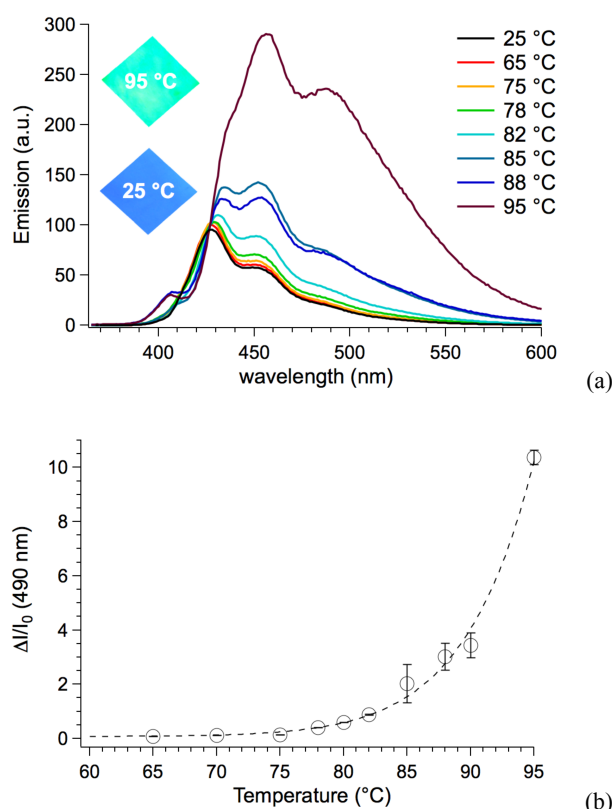


Figure 1. (a) Fluorescence emission spectra ($\lambda_{\text{exc.}} = 277\text{ nm}$) of 55 PLA85PBS15 films containing the 0.07 wt% of BBS as a function of the annealing temperature and (inset) pictures of the films at 25°C (blue emission) and after annealing at 95°C (green emission) taken under irradiation at 366 nm . For all cases the annealing time was 10 min; (b) Plot of the emission intensity variation at 490 nm as calculated from 60 PLA85PBS15 spectra as a function of the annealing temperature. The ratio values are an average of three measurements performed on different portions of the same film.

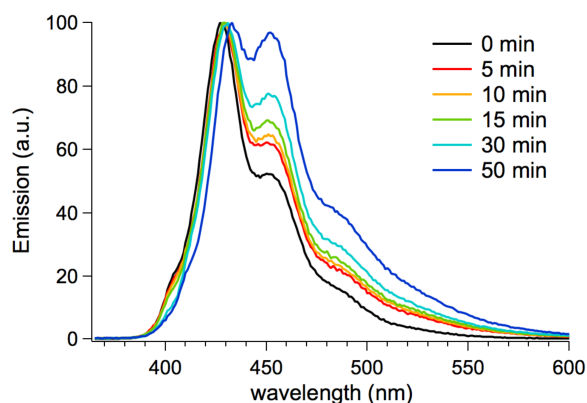


Figure 2. Fluorescence emission spectra ($\lambda_{\text{exc.}} = 277\text{ nm}$) of PLA films 65 containing the 0.07 wt% of BBS as a function of the annealing time at 100°C . The spectra are normalized to the intensity of the isolated BBS molecular peak (about 430 nm).

equipped with F-3000 Fiber Optic Mount plus fiber-optic bundles.

70 SSNMR experiments

The ^{13}C CP/MAS experiments were carried out on a dual-channel Varian InfinityPlus 400 spectrometer, equipped with a 3.2 mm

Cross Polarization/Magic Angle Spinning (CP/MAS) probehead, working at 400.03 MHz for proton and at 100.61 MHz for carbon-13, with ^1H and ^{13}C pulse durations of about 3 μs . All the spectra were acquired using a recycle delay of 5 s, a contact time of 5 ms, and a MAS frequency of 8 kHz. TMS was used as a primary chemical shift reference for all nuclei, while hexamethylbenzene was the secondary reference for ^{13}C .

On-resonance ^1H free induction decays (FID's) were recorded on a Varian XL-100 spectrometer coupled with Stellar lock and PC-NMR acquisition systems, at a Larmor frequency of 24 MHz, using a ^1H pulse duration of 4 μs . A solid echo pulse sequence was used, accumulating 200 transients with a recycle delay of 3 s and an echo delay of 12 μs . ^1H FID's were recorded by progressively increasing the temperature from 40 to 100 $^{\circ}\text{C}$ with different steps. For each experiment, the temperature was let to equilibrate for 10 minutes before the acquisition. Considering that the experimental time was about 10 minutes, the sample was kept at each selected temperature for about 20 minutes.

All the variable temperature measurements were carried out using air as heating gas.

Results

DSC and fluorescence results

80–160 mm thick PLA and PLA85PBS15 luminescent films, containing the 0.07 wt.% of BBS, were prepared by compression moulding of the respective polymer-dye mixtures, as already reported in our previous work.¹⁸

At room temperature pristine PLA85PBS15 (Figure 1a) and PLA (Figure 2) films showed emission features analogous to those reported for isolated BBS chromophores dissolved in solution,^{16,23} with emission peaks centred at about 430 and 460 nm. This behaviour indicates that BBS is molecularly dispersed in the amorphous phase of the polymers as non-interacting chromophores. We have also demonstrated that BBS is quite soluble in PLA, where it remains at monomer state up to a certain threshold concentration (0.15–0.20 wt%) after which aggregation takes place.¹⁸ Conversely, a significant amount of aggregate always forms in PBS even at very low BBS concentration (≥ 0.05 wt%).¹⁰

Temperature dependence of luminescence was then investigated in both systems for temperatures higher than PLA's T_g (62 $^{\circ}\text{C}$). As expected, a thermally dependent luminescent behaviour was observed for PLA85PBS15 films (Figure 1a).¹⁸ These films displayed the progressive development of the BBS aggregate band at about 480–500 nm whose intensity overwhelms the emission contribution of the isolated BBS chromophores (400–450 nm). This broad and unstructured emission, red-shifted with respect to monomer BBS emission, is attributable to aggregate arrangements of BBS chromophores.¹⁰ More specifically, the emission intensity variation at 490 nm, appeared more pronounced for annealing temperatures higher than 85 $^{\circ}\text{C}$ (Figure 1b). This behaviour is in keeping with literature reports on BBS dye/polymer dispersions.^{8,10} The ratio between the intensities of the aggregate band at 480–500 nm and the monomer band at 400–450 nm was not taken into account as indicator of BBS assembly due to evident auto-absorption phenomena in the

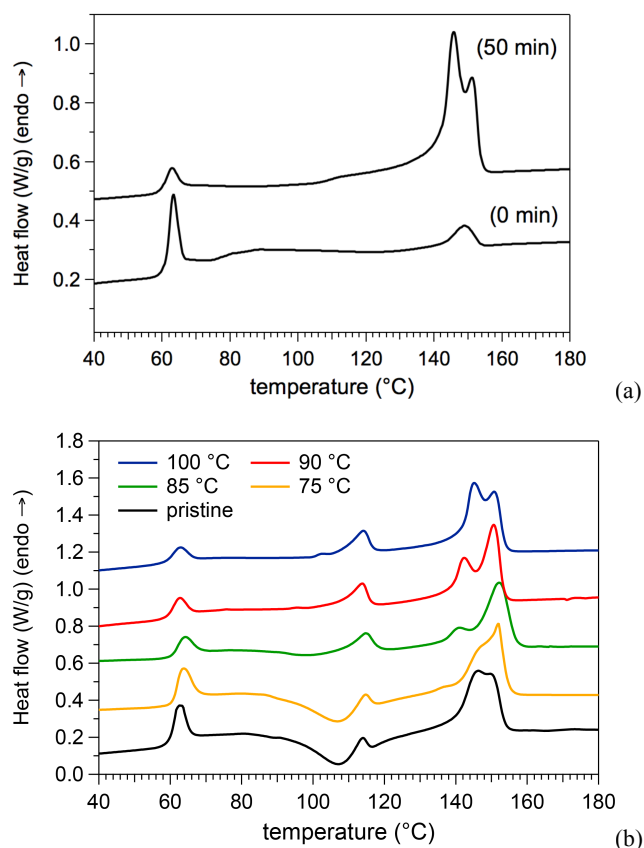


Figure 3. First heating DSC scans of (a) PLA films before and after annealing at 100 $^{\circ}\text{C}$ for 50 min and (b) PLA85PBS15 films before and after thermal annealing at different temperatures. All samples contain the 0.07 wt% of BBS.

high-energy emission regime.

Differently from PLA85PBS15 films, the thermal sollicitation of PLA films did not significantly alter the emission profile of BBS chromophores, even at 100 $^{\circ}\text{C}$ for 50 min (Figure 2). This finding highlights that the increase of polymer chain mobility, associated with the transition from the glassy to the viscous amorphous state, is not enough to promote the self-aggregation of BBS, possibly due to its relatively high solubility in the PLA matrix.¹⁸

To verify the relationship between polymers crystallization and formation of BBS aggregates in the blend, the 1st heating scans by DSC of PLA (Figure 3a) and PLA85PBS15 (Figure 3b) films were compared. The addition of BBS was already demonstrated to not alter the thermal behaviour of PLA and PLA/PBS films in the range of concentration investigated.¹⁸

PLA films displayed a glass transition temperature (T_g) at 60 $^{\circ}\text{C}$ and a melting point (T_m) at 150 $^{\circ}\text{C}$ with a crystalline content of 4 %, whereas the cold crystallization, usually pointed at 110 $^{\circ}\text{C}$,²⁴ gave only a small contribution to the thermogram. The annealing at 100 $^{\circ}\text{C}$ favoured PLA crystallization, thus providing a crystalline content of around 50 % after 50 min of heating (Table 1). As expected, the magnitude of the endothermic hysteresis peak at PLA T_g gradually decreases with increasing PLA crystallinity²⁵ due to annealing (Figure 3b).

Nevertheless, the remarkable reduction of PLA amorphous

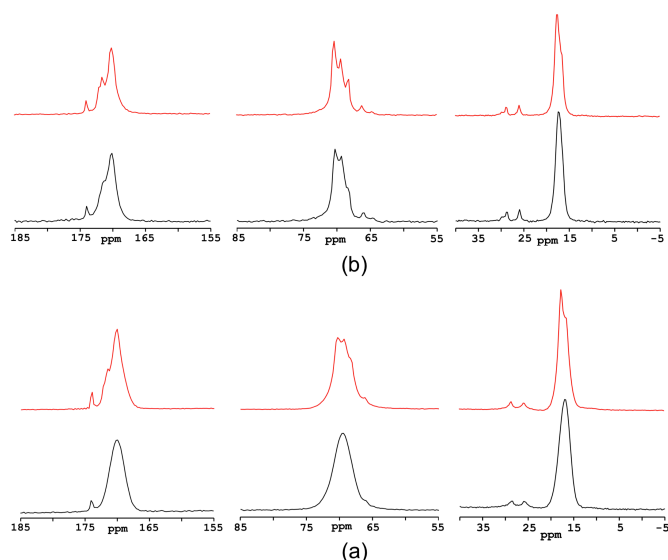


Figure 4. Expansions from the ^{13}C CP/MAS spectra of PLA85PBS15 before (bottom) and after (top) annealing, acquired at 20 °C (a) and 75 °C (b).

phase attained during the thermal treatment was not able to promote effective BBS aggregation (see Figure 2).

As reported recently,¹⁸ PLA is allowed to crystallize in pristine PLA85PBS15 blends as well, thanks to the cold crystallization of PLA and melts at around 115 °C. This yielded a PLA crystalline content in PLA85PBS15 of 28 % with respect to only 4 % in PLA film (Table 1). In both PLA and PLA85PBS15 samples, the presence of two melting peaks (at around 145 °C and 152 °C) reflects the process of melting of PLA crystallites having different sizes and/or perfection of ordering.^{26,27}

When PLA85PBS15 films were annealed from 75 °C to 100 °C, the contribution of PBS and PLA cold crystallizations lessened progressively along with the enhancement of their respective melting endotherms at 115 °C and 150 °C. This was expected when annealing temperature becomes higher than that of cold crystallization beginning.²⁸ Indeed, PLA crystallinity increased from 28 % to 50 %, while that of PBS from 2 % to about 12 %.

Table 1. Thermal behaviour of PLA and PLA85PBS15 films (1st heating scan) containing the 0.07 wt.% of BBS. The thermal properties were evaluated on films previously prepared at 200 °C for 4 min, $P_{\text{max}} = 5$ atm, then heated from 30 °C to 200 °C at 10 °C/min. Polymer crystallinity χ (%) was calculated according to equation 1.

Sample	T annealing (°C)	t annealing (min)	PLA χ (%)	PBS χ (%)
PLA	-	-	4	-
PLA	100	15	30	-
PLA	100	25	43	-
PLA	100	50	52	-
PLA85PBS15	-	-	28	2
PLA85PBS15	75	10	32	2
PLA85PBS15	80	10	33	3
PLA85PBS15	85	10	34	9
PLA85PBS15	90	10	42	13
PLA85PBS15	100	10	50	12

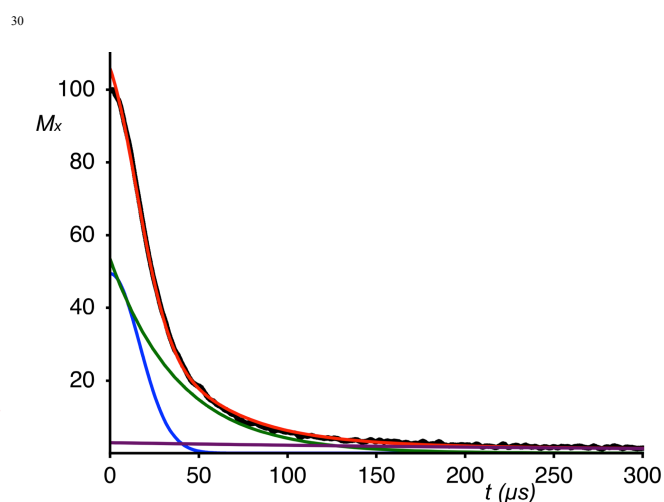


Figure 5. Fitting of the ^1H FID of PLA85PBS15 acquired under on resonance conditions at 70 °C. The figure reports the experimental FID, the fitting function of eq. 2 (—), and the single components, which are a Gaussian function with a short T_2 of 20 μs (—), an exponential function with an intermediate T_2 of 40 μs , and an exponential function with a very long T_2 of about 300 μs (—).

The comparison between luminescence experiments in Figure 1 and the evolution of PLA and PBS crystallinity suggests that 9-10 % of PBS crystallinity, which has arisen for annealing above 80 °C, is the key factor that contributes to effective BBS aggregation.

SSNMR results

In Figure 4 the ^{13}C CP/MAS spectra of the PLA85PBS15_BBS films subjected or not to annealing at 80-90°C, acquired at 20 and 75 °C, are shown. The main signals at about 16, 70, and 170 ppm are ascribable to PLA CH_3 , CH and CO carbons, respectively, while the small ones at about 27, 66, and 174 ppm to the PBS CH_3 , CH_2 , and CO carbons, respectively. At 20 °C in the not annealed film all the PLA carbons give rise to broad signals ascribable to amorphous PLA. In the film subjected to annealing a splitting of all the PLA carbon signals is observed, which indicates the presence of a PLA crystalline fraction,²⁹⁻³² possibly formed by PLA cold crystallization. In the spectra acquired at 75 °C the splitting of the PLA carbon signals is observable for both the films subjected or not to annealing, indicating that at 75°C the cold crystallization process has already started.

In order to further investigate the phase processes occurring in the polymeric matrix of the PLA85PBS15 under heating, we acquired and analysed the on resonance ^1H FID at increasing temperature, in the temperature range 40-100 °C. The ^1H FID analysis consists in the fitting of the ^1H FID with a linear combination of functions, chosen among exponential, Gaussian, Weibullian, Pake and Abragamian functions, each characterized by a different ^1H T_2 relaxation time (Figure 5).³³

This analysis allows polymeric domains with different phase and dynamic properties to be identified and quantified. Indeed the ^1H T_2 's, being determined by the ^1H - ^1H dipolar couplings, are dependent on the degree of mobility of the polymeric domains, while the coefficients of the functions in the linear combination are quantitatively related to the fractions of protons belonging to the domains.

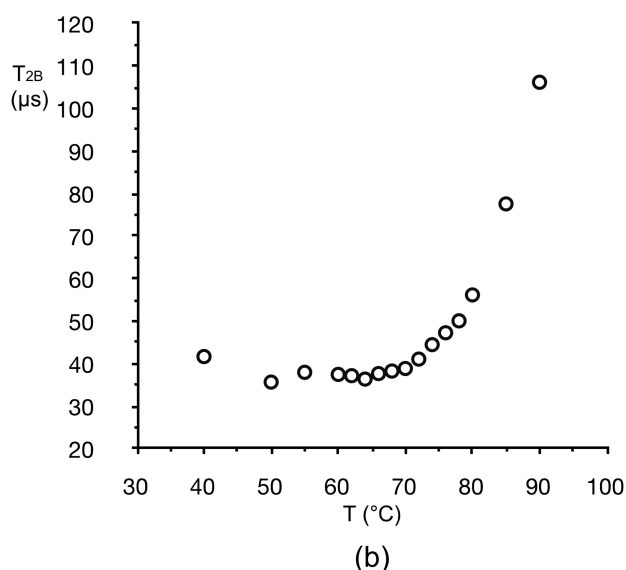
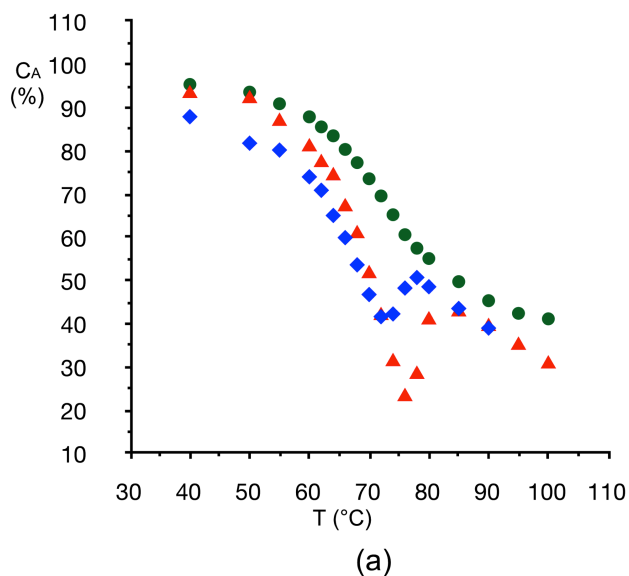


Figure 6. (a) C_A vs temperature curves obtained for neat PLA in pellets (●), neat PLA film (▲), and PLA85PBS15 (◆). (b) T_{2B} vs temperature curve obtained for PLA85PBS15.

At each temperature the experimental FID was fitted through the linear combination of functions:

$$Fit_Func = C_A A + C_B B + C_C C = C_A e^{-\left(\frac{t}{T_{2A}}\right)^2} + C_B e^{-\frac{t}{T_{2B}}} + C_C e^{-\frac{t}{T_{2C}}} \quad (\text{eq. 2})$$

A is a Gaussian function with a short ^1H T_2 of about 20 μs ; B is an exponential function with a ^1H T_2 which increases from 30 to about 200 μs with temperature; C is an exponential function with a very long ^1H T_2 of about 300 μs .

As far as the neat PLA in pellets and film are concerned, considering that PLA is a semi-crystalline polymer with a T_g of about 60°C,¹⁸ the component A was ascribed to rigid crystalline and glassy PLA domains, the component B to highly viscous amorphous PLA, whose mobility is expected to increase with temperature, and the component C to polymeric end chains as well as, for the high temperature FIDs (85-100 °C), to very mobile amorphous PLA. According to this interpretation, the

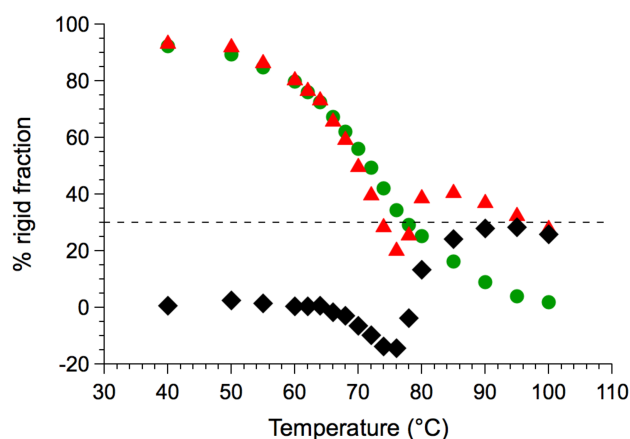


Figure 7. Determination of the final crystalline fraction of PLA in the neat PLA film. The percentages of the glassy amorphous PLA in the neat PLA in pellets (●) and film (▲), determined as described in the text, are shown. The difference between ▲ and ● (◆) is also reported.

coefficient C_A can be related to the percentage of crystalline and glassy PLA fractions.

In Figure 6a the trends of C_A with temperature found for the neat PLA in pellets and film are reported. In neat PLA in pellets C_A is almost constant up to about 50 °C, and then it regularly decreases tending to a plateau for high temperature values. This trend nicely represents the glass transition of PLA amorphous domains, which gradually pass from a rigid glassy state to a more mobile viscous one, and shows how this process is extended over a wide temperature range (50-100°C). The residual rigid fraction of about 40 % present at high temperatures can be ascribed to crystalline PLA, which does not undergo phase transitions in this temperature range.

Different results were obtained for the neat PLA film, for which a discontinuity in the decrease of C_A can be observed at about 75-80 °C: C_A decreases up to about 75 °C, increases from 75 °C to 80°C, and then starts to decrease again but with a lower slope.

This behaviour can be explained with the superimposition of the glass transition process with the cold crystallization of PLA. In particular, the latter would be responsible for the increase of C_A at about 75-80 °C, due to the increase of the PLA crystalline fraction. In order to separate the two contributions, we used the C_A curve of the neat PLA in pellets as a reference for the glass transition process. More specifically, we subtracted the crystalline fraction estimated from Figure 6 (40 %), which should remain constant under heating, from the experimental C_A , and we rescaled the result by 100/60, thus obtaining the trend of the amorphous fraction. This is reported in Figure 7, along with that obtained in a similar way for the neat PLA film, obtained by subtracting a crystalline fraction of 4 %, estimated on the basis of DSC result, and properly rescaled. The difference between the two rescaled curves was also calculated and it is reported in Figure 7. The difference is almost zero up to about 65 °C, it decreases, assuming negative values, between 65 and 75 °C, and finally it increases approaching an asymptote for high temperatures. This indicates that the rate of the glass transition process is almost the same in the neat PLA in pellets and film for temperatures below 70°C, and it becomes faster in the film when the temperature of PLA cold crystallization is approached. The

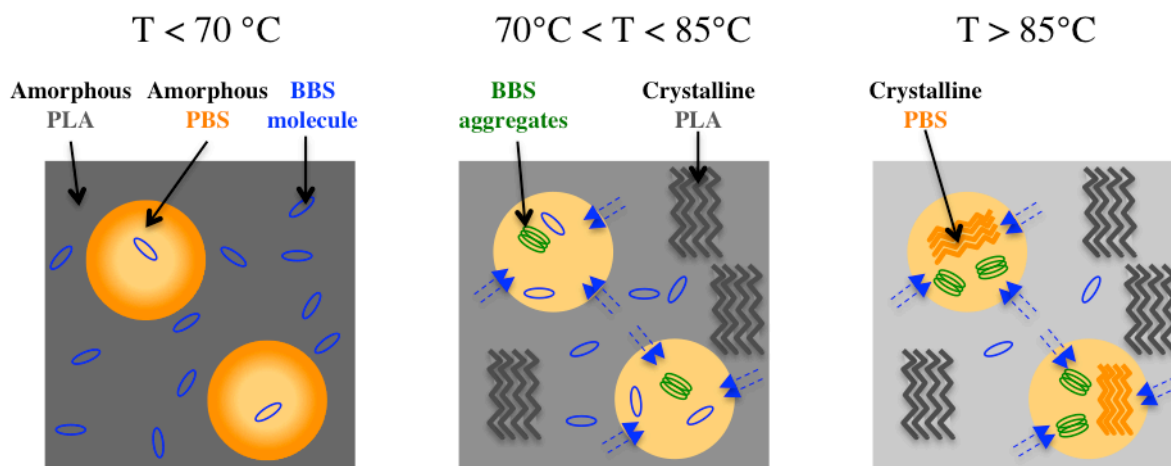


Figure 8. Representation of the mechanism of BBS aggregation in the PLA85PBS15 matrix under heating, as hypothesized on the basis of spectrofluorimetric, DSC and SSNMR results. The shade of colours, from the deeper to the lighter, represents the change of mobility of the polymers, from more rigid to more mobile fractions.

increase of the curve above 75 °C is representative of the increase of the crystalline fraction due to PLA cold crystallization occurring in the film, and the value of the asymptote at high temperatures corresponds to the final crystalline fraction of PLA. This is found to be about 30 %, in agreement with the DSC results for the sample annealed at 100 °C for 15 min (Table 1).

As far as the PLA85PBS15 film is concerned, the experimental C_A , reported in Figure 6a, shows a discontinuity at about 70 °C, similarly to what found for the neat PLA film, which can be mainly attributed to the occurrence of PLA cold crystallization. It is worth to notice that in PLA85PBS15 the PLA cold crystallization seems to take place at lower temperatures than in the neat PLA film, suggesting that PBS favours the kinetics of the process, possibly acting as nucleation agent. Moreover, in PLA85PBS15 the contribution of PBS to the ^1H FID cannot be completely neglected, being its fractional population of protons about 20%. From the DSC results, it is known that at room temperature, in a film not subjected to annealing, PBS domains are almost completely amorphous, and well above the glass transition temperature ($T_g \approx -30$ °C).¹⁸ Therefore it would be reasonable to expect that PBS mostly contributes to the B and C components. Nevertheless, in PLA85PBS15 the high initial value measured for C_A , significantly greater than the expected value of 80 %, indicates that at 40 °C a significant fraction (about 50%) of PBS is quite rigid. This might be due to an interaction between PLA and PBS domains, which could determine a stiffening of PBS domains at the interface.

Information on the mobility of the viscous PLA domains can also be obtained from the ^1H T_2 of the component B (T_{2B}). In Figure 6b the trend of T_{2B} with temperature obtained for PLA85PBS15 is reported. Similar results were found for the neat PLA in pellets and film (here not shown). T_{2B} is almost constant at the value of 40 μs up to about 70 °C, and then it steeply increases indicating a corresponding increase of the mobility of the amorphous PLA domains. This clearly shows that up to 70 °C the heat supplied to the PLA85PBS15 film is used almost completely to convert the glassy to highly viscous PLA domains, and only above 70 °C, when a significant fraction (almost 50%)

of glassy PLA has undergone glass transition (see Figure 6a), it can be available to increase the mobility of the viscous phase. The NMR behaviour is in good agreement with DSC results, also considering the endothermic hysteresis observed at PLA T_g (~ 60 °C).

Discussion

Aiming at the rationalization of the observed luminescence phenomena, spectrofluorimetric and calorimetric investigations confirmed that the peculiar behaviour of the PLA/PBS blend in terms of aggregation/disaggregation of BBS with varying temperature is related to the effects provided by the temperature on both polymer phase behaviour and mobility of polymeric chains. In particular, the presence of 15 wt% of PBS in the blend, in which the dye appeared less soluble than in PLA,¹⁸ resulted the key factor to promote BBS aggregation (Figure 1). Accordingly, BBS aggregation in PLA appeared less favoured upon thermal stress even at a temperature higher than PLA T_g (Figure 2).

Inspection of the 1st heating scan of pure PLA (Figure 3a and Table 1) showed that the annealing at 100 °C of PLA increases its crystalline content from 4 % to 30-50 %, depending on the annealing time. This behaviour well agrees with SSNMR ^1H FID analysis, from which a PLA crystalline content of about 30 % could be estimated (Figure 7), even though the thermal treatments experienced by PLA during DSC and SSNMR experiments cannot be straightforwardly compared.

Nevertheless, the remarkable reduction of PLA amorphous phase attained during the thermal treatment is not able alone to promote effective BBS aggregation (Figure 2), for which the presence of 15 wt% of PBS is needed.

In keeping with that reported by Yokoara et al.,²⁴ we observed that PLA crystalline content (determined by DSC) increased from 4 to 28 % in PLA85PBS15 blend with respect to pure PLA (Table 1).¹⁸ Once thermal annealing was applied to PLA85PBS15 films from 75 °C to 100 °C, PLA crystallinity increased from 28 % to 50 % (the same value reached for PLA alone), while that of PBS from 2 % to about 12 % (Table 1). In particular, ^{13}C CPMAS

NMR spectra confirmed that PLA crystallization takes place even when the sample is heated at 75 °C, and it is further promoted by annealing at 100 °C (Figure 4).

SSNMR ¹H FID analysis showed that PLA crystallization in the PLA85PBS15 film occurs at lower temperatures than in the neat PLA film, thus confirming that PBS may act as nucleating agent (Figure 6a). The influence of PBS on the kinetics of PLA crystallization suggests an effective interaction between the two polymers (thermodynamically immiscible but highly compatible)¹⁸, which are possibly intimately mixed at the interface within the blend film, as also indicated by the stiffening of PBS domains with respect to the neat polymer, as observed by ¹H FID analysis.

A steep increase of the mobility of the viscous PLA phase at temperatures higher than 70-75 °C (Figure 6b) was also observed. It is worth to notice that this increase appears very similar to that reported in Figure 1b and related to the aggregation extent of BBS chromophores evaluated by spectrofluorimetry. This result suggests that during the thermal annealing of PLA85PBS15 films containing the 0.07 wt% of BBS the following steps towards BBS aggregation may occur:

1) when relevant amounts of PLA amorphous phase give rise to cold crystallization, BBS isolated chromophores, originally dispersed in the PLA amorphous matrix, may come more in contact with the PBS amorphous domains, which are intimately connected with those of PLA: within PBS amorphous phase BBS molecules could tend to aggregate more easily than in PLA, given their worse solubility in the former;

2) the heat supplied during annealing above 70 °C, when a significant fraction (almost 50%) of glassy PLA has undergone glass transition (Figure 6a), is available to increase the mobility of the viscous phase: such mobility could further favour the aggregation of BBS molecules;

3) above 85 °C the increase of PBS crystallinity due to its cold crystallization seems to further promote the aggregation of BBS molecules.

In Figure 8, a cartoon is reported to outline the concepts here reported at the basis of BBS aggregation within the spherical domains of PBS segregated in the PLA matrix.

Conclusions

The combined application of Spectrofluorimetry, DSC and SSNMR revealed effective in giving detailed and complementary information concerning the phenomenon of BBS aggregation in PLA and PLA/PBS blends, which is relevant from the application standpoint in the field of intelligent films for packaging and was the subject of a previous investigation.¹⁸ In particular, an explanation of such phenomenon was attempted in terms of both PLA/PBS phase behaviour and mobility of their amorphous phases. In the case of PLA we were able, by ¹H FID analysis, to disentangle glass transition and cold crystallization, occurring in very similar temperature ranges. Although both PLA and PLA/PBS blend films produce similar amounts of crystalline PLA through cold crystallization, which was hypothesized to play a fundamental role in BBS aggregation, it was here clarified that a key role is played by the presence of PBS. This role is probably not limited to the stimulation of PLA cold crystallization, found to occur at lower temperatures with respect to pure PLA, but also

in "subtracting" BBS molecules to the PLA amorphous phase during cold crystallization, favouring their aggregation within PBS amorphous domains.

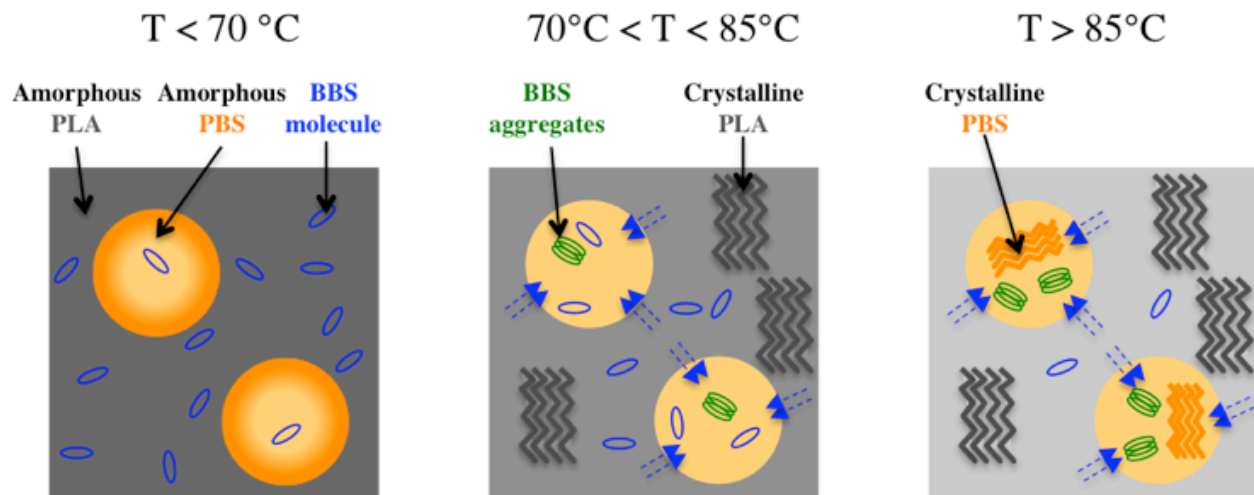
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Notes and references

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A combined spectrofluorimetric, DSC and SSNMR study allowed us to propose a mechanism for the aggregation of the BBS dye in a threshold-temperature luminescent indicator based on a PLA/PBS blend.