Crystallization in PHB/DGEBA Blends

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ABSTRACT: Real-time experiments using small-angle X-ray scattering and differential scanning calorimetry on blends of the semicrystalline polyester poly(3-hydroxybutyrate) (PHB) and amorphous monomer epoxy DGEBA (diglycidyl ether of bisphenol A) were performed. Differences in the processes of melting and re-crystallization were observed in blends relative to pure PHB. The results obtained in this study indicated that re-crystallization is more important in blends with 50% DGEBA than in pure PHB. Moreover, segregation toward the interfibrillar region would facilitate re-crystallization. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2014**, *52*, 882–886

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INTRODUCTION A deep understanding of the physical process that governs the blending of polymers is an important goal of research in the field of novel materials. Specifically, with respect to thermoset/thermoplastic blends, when the thermoplastic component is able to crystallize, the morphology and, consequently, the final properties are the result of the interplay between phase separation and crystallization behavior.

Poly(3-hydroxybutyrate) (PHB) is a polymer frequently studied as a component for blending.[1,2] Microbially synthesized PHB has been increasingly studied since the mid-1970s because it is environmentally friendly, and although its discovery dates back to nearly a century ago,[3] the interest in this polymer is based on its properties of biodegradability and biocompatibility. In addition, PHB exhibits unique crystallization and melting behavior characterized by re-crystallization and annealing.[4] In this respect, Fujita et al. observed discontinuous growth in the lamellar thickness of a single crystal in PHB using small-angle X-ray scattering (SAXS) and WAXS and observed a temperature range over which two lamellar structures coexist.[5] Conversely, the three phase picture in which an amorphous interphase located between crystal and amorphous phases have been recently applied in the study of PHB showing the role of this interphase on the crystallization.[6–8]

Epoxy is a thermoset polymer widely used as a matrix in polymer composites or in the formation of interpenetrating networks. DGEBA (diglycidyl ether of bisphenol A) monomer is one of the materials most often used to develop epoxy networks. The blending of semicrystalline polymers with epoxy has been scarcely addressed in the literature.[9,10] During the curing at high temperature in a semicrystalline-thermoset blend can exists phase separation between the components due to the changes in miscibility because the molecular weight increment or due to the segregation of the thermoset out of crystallization front. Preliminary results obtained by the authors have shown that during the curing of epoxy containing PHB both process, crystallization and phase separation, can occur simultaneously, determining a variety of morphologies. Therefore, the study of PHB/DGEBA blends is a first step in the study of other blends. Besides, study of the crystalline phase suggests that the phase plays a role in the degradation of PHB.[3]

The authors have recently reported a study on miscibility and lamellar crystallinity in blends PHB/DGEBA.[11] Following this line of research, the goal of this work was to obtain information about the crystallization and melting process in melt-crystallized PHB/DGEBA blends through real-time SAXS experiments and differential scanning calorimetry (DSC), studying, in particular, morphological changes in the lamellar structure and the melting and re-crystallization process.

EXPERIMENTAL

PHB powder with the trade name Biocycle® was supplied by Industrial (Brazil). DGEBA monomer was supplied by Hunstman (Araldite MY 790). Pure PHB, DGEBA, and blend samples with PHB/DGEBA ratios (in weight) of 80/20 and

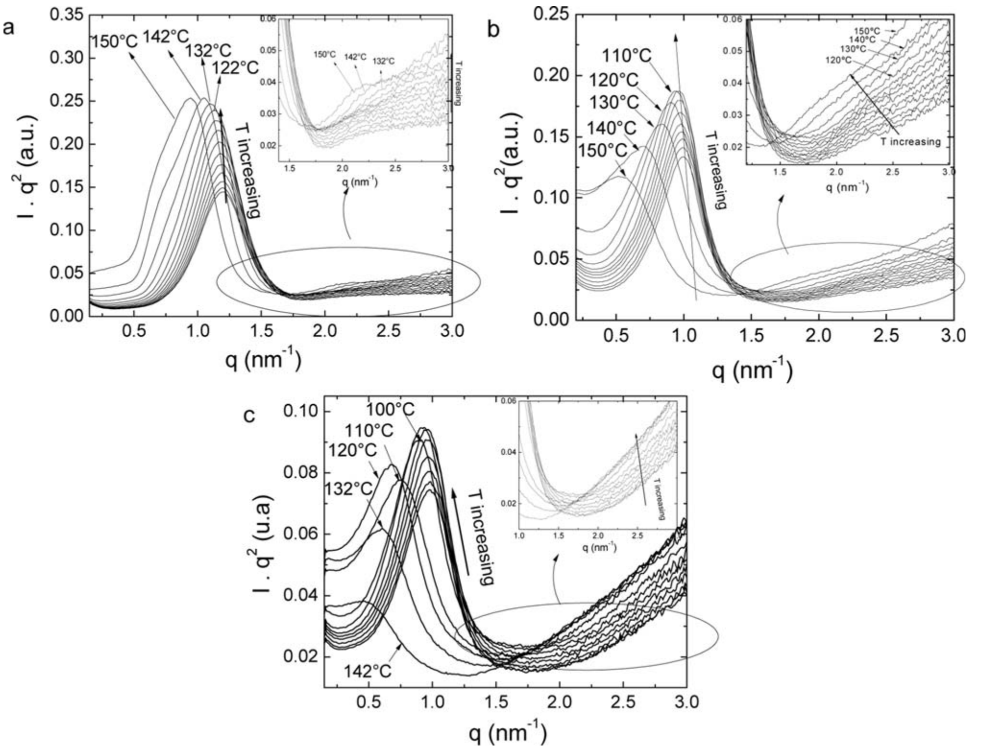

FIGURE 1 SAXS spectra at different temperatures: (a) pure PHB, (b) blend PHB/DGEBA 80/20, and (c) blend PHB/DGEBA 50/50. The inset shows a magnification of the range 1.4 nm^{-1} < q < 3.0 nm^{-1}.

50/50 were prepared. The samples were melted at 180 °C and then cooled at an average rate of $\approx$7 °C/min to room temperature, and they were then stored at room temperature. A homogeneous solution was observed at high temperature. A DSC study has demonstrated that this blend is miscible in the molten state.[11]

SAXS measurements were performed at the Brazilian Synchrotron Light Laboratory (LNLS) CNPEM/MCT, line SAXS 1 Campinas, Brazil. A wavelength of $\lambda = 1.55$ Å was selected for the monochromatic beam used in the experiments. The low-angle scatter was recorded for scattering vector values q ($q = (4\pi/\lambda)\sin\theta$), where 2θ is the scattering angle, between $q_{\min} = 0.16$ nm^{-1} to $q_{\max} = 3.00$ nm^{-1}. The measurements were performed using a 2-D detector with a spatial resolution of 172 μm located at a distance of 627 mm from the sample. The 2-D scattering profiles were averaged at several radii and converted to 1-D data using the program FIT2D V12.077. The experimental small-angle scattering curves were normalized by the integrated incident beam intensity. For the measurements, the samples were sealed in modified DSC pans with Kapton windows. SAXS measurements were performed at different temperatures between 30 and 150 °C in steps of 10 °C with a heating rate of 10 °C/min using a hot-stage cell (THM 600 Linkam). The measurement time was 5 s; the variation in temperature within that period was considered negligible. A set of measurements was performed to observe possible changes in the sample due to radiation exposure, but variations were not observed in the spectra obtained.

DSC measurements were performed using a Q20-TA Instruments differential scanning calorimeter. The calorimeter was calibrated using indium as a reference material. All measurements were performed at a heating rate of 10 °C/min under an argon atmosphere with a constant flux of 50 mL/min.

RESULTS

SAXS measurements were performed at different temperatures between room temperature and 150 °C. In Figure 1, the results obtained are presented in plots of $I.q^2$ versus q for pure PHB, PHB/DGEBA 80/20 and PHB/DGEBA 50/50 blends. The SAXS measurements performed at room temperature show a maximum q value of 1.14 nm^{-1} for pure PHB, 0.94 nm^{-1} for PHB/DGEBA 80/20 blend, and 0.8 nm^{-1} for PHB/DGEBA 50/50 blend. With increasing temperature, the peaks increase in height, but the position of the maximum, q_M, shift toward lower values of q. For pure PHB at temperatures above 132 °C, the SAXS spectra show evidence of an incipient, barely defined second peak located at q values lower than the first peak. At temperatures between 132 and 150 °C, both peaks shift toward lower values of q. A deformation in the SAXS curves is also observed in the blends at temperatures above 110 °C for the PHB/DGEBA 80/20 blend and at temperatures above 100 °C for the PHB/DGEBA 50/50 blend. Additionally, in the q range 1.5 nm^{-1} < q < 3.0 nm^{-1}, a small peak is observed for pure PHB [see inset in Fig. 1(a)]. This peak decreases in height when the temperature increases up to 132 °C, but it is clearly observed in the spectra collected at temperatures above 132 °C and in the

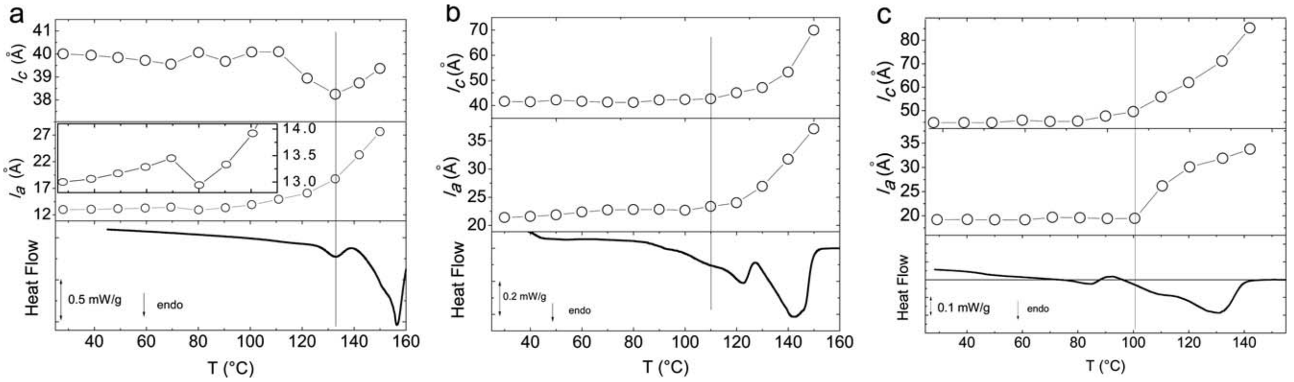

FIGURE 2 l_c and l_a parameters and heat flow as a function of temperature (experimental error bars are ±0.2 Å and are not plotted to avoid complicating the figure): (a) pure PHB, (b) PHB/DGEBA 80/20 blend, and (c) PHB/DGEBA 50/50 blend. The lines are shown to guide the eye. The vertical bars represent the temperatures at which two peaks are clearly identified in the SAXS spectra.

spectra obtained at room temperature after cooling. For PHB/DGEBA 80/20 blend, this peak is observed with a smaller height and it is not observed for PHB/DGEBA 50/50 blend. The peaks observed at high q values could be attributed to high-order scattering[12] or the insertion of lamellae between the original lamellae, as observed in polyoxymethylene.[13] The results obtained indicate that the intensity of the secondary peak is depending of blend composition. Therefore, this peak could be associated with the properties of the material. Therefore, the aforementioned peak could be associated with the lamellae that developed during the secondary crystallization with thickness lower than the thickness of lamellae developed during primary crystallization.

The principal peak can be related to lamellar periodicity, and considering an ideal lamellar structure, q_M can be used to estimate the average long period L as follows:

$$L = \frac{2\pi}{q_M}. \tag{1}$$

However, considering that several peaks were observed in the SAXS spectra obtained for PHB at temperatures above 132 °C, two or more lamellar structures could be expected.

In an ideal lamellar structure, the average long period L is considered to be equal to the sum of a crystalline component and an amorphous component with thicknesses l_c and l_a, respectively. The l_c and l_a values were determined from the normalized 1D correlation function $\alpha(r)$ (eq (2)), following the ideas reported in the literature.[14] $\alpha(r)$ was calculated using the code CORFUNC.[15] Extrapolation to low values of q was performed using Vonk's model, and extrapolation to high values of q was performed using Porod's law.[11]

$$\alpha(r) = \frac{\int_0^\infty q^2 I(q) \cos(qr) \mathrm{d}q}{\int_0^\infty q^2 I(q) \mathrm{d}q}. \tag{2}$$

Using $\alpha(r)$, it is possible to estimate the thicknesses of each phase present in a two-phase structure (l_1 or l_2), but to assign them to l_c or l_a, some considerations should be taken into account because the electronic density in a two-phase structure can be exchanged without affecting the correlation function.[14] The assignment of l_i to l_c or l_a can be achieved using the results of DSC measurements. In a previous study, the authors reported the assignment of each phase using the results of DSC and SAXS measurements performed at room temperature for PHB/DGEBA blends.[11] In this work, the assignment at different temperatures was performed following the results obtained at room temperature.

The assignment of l_i as either l_c or l_a is achieved by considering the bulk degree of crystallinity of the blend, ϕ_c, and comparing it with the linear degree of crystallinity X_c^{saxs}. X_c^{saxs} is always greater than or equal to ϕ_c because the morphology of the blend is not entirely lamellar.[16] ϕ_c can be calculated from DSC and $X_c^{\text{saxs}} = l_c/L$, and the results corresponding to the samples studied here have been presented previously.[11] As was mentioned, the assignment for the blend with a 50/50 composition was performed by considering monotonic behavior of l_c.

However, for the measurements performed at temperatures above 132 °C, in which two peaks were observed in the SAXS spectra and two lamellar structures could be expected, the values of L, l_c, and l_a were considered mean values.

Figure 2 shows thermograms of pure PHB and PHB/DGEBA 80/20 and PHB/DGEBA 50/50 blends, along with the results obtained for l_c and l_a from the analysis of $\alpha(r)$. As shown, the first endothermic peak overlaps with the second and third peaks. The first peak is located at 133 °C, 123 °C, and 85 °C for pure PHB, PHB/DGEBA 80/20 blend, and PHB/DGEBA 50/50 blend, respectively, and the overlapped peaks show maximum intensities at 155 °C, 142 °C, and 130 °C, respectively. For the PHB/DGEBA 50/50 blend, an exothermic peak can be observed between the first and the second peak.

The aforementioned first endothermic peak can be associated with the melting of crystallites formed during cooling from the melt state or during crystallization at room temperature. Conversely, the second peak and the third peak can be associated to the melting of re-crystallized material.[2,17] The melting, re-crystallization, and re-melting process can be analyzed by considering the scheme reported in the literature[4,18] in which an endothermic melting peak is superimposed on an exothermic re-crystallization peak and an endothermic re-melting peak. The overall result is that the thermogram presents two endothermic peaks and, depending on the heating rate, an exothermic peak. For the PHB/DGEBA 50/50 blend, an endothermic peak at ≈90 °C, an endothermic peak at ≈130 °C with a shoulder at low temperature, and an exothermic peak are observed; this last peak is more defined than in the other samples. Therefore, it could be concluded that in this sample the re-crystallization process is more important than in pure PHB and PHB/DGEBA 80/20 blend. The two overlapped peaks can be explained in terms of the devitrification of the rigid amorphous fraction (RAF) and the re-crystallization process. Righetti et al. reported that for crystallization temperature lower than 70 °C, during the heating that follows isothermal stage, the rigid amorphous fraction devitrifies and there is an enhanced mobility of amorphous chains, which encourages the re-crystallization process.[6] Then, crystals with a melting temperature higher than the original crystals are formed and superposition of melting peaks can be expected.

Figure 2 shows the results obtained for l_c and l_a as a function of temperature for each sample studied. Vertical lines indicate the temperature at which a deformation was clearly detected in the SAXS spectra.

Figure 2(a), corresponding to pure PHB, shows that l_c presents an average value of approximately 40 Å, with variation between 39.5 and 40.5 Å, until the temperature reaches the onset of the melting peak (≈110 °C). In the plot of l_a versus temperature, different behavior is apparent; two tendencies can be clearly observed [see the inset in Fig. 2(a)], and a step is evident at approximately 70 °C. Between 110 and 132 °C, l_c decreases and l_a increases. At temperatures above 132 °C, which matches the maximum of the first melting peak, both l_c and l_a increase. It is important to note that at temperatures above 132 °C two peaks are observed in the SAXS spectra. This temperature range agrees with the onset of the second melting peak and could be associated with the re-crystallization process.

For the PHB/DGEBA 80/20 blend [Fig. 2(b)], it can be observed that l_c remains constant at 41.8 Å as the temperature increases up to 110 °C. For the same increment in temperature, l_a shows a slightly increase. Over the range 110–130 °C, l_c increases slightly, and for temperatures above 130 °C, l_c increases markedly. l_a increases as a function of temperature between 110 and 150 °C. In the thermogram shown in Figure 2(b), it can be observed that near 145 °C there is a shoulder in the melting peak indicating peak overlap.

In the DSC results obtained for the PHB/DGEBA 50/50 blend, all peaks are shifted toward lower temperature values; for instance, the first endothermic peak shifts from 130 °C in pure PHB to 90 °C in the PHB/DGEBA 50/50 blend. Figure 2(c) shows that when the temperature is below 80 °C, that is, below the first melting peak, l_c remains approximately constant with an average value 45.2 Å, but between 80 and 100 °C, l_c slightly increases up to 49.5 Å. For temperatures below 100 °C, l_a remains constant within the experimental error. However, in the range 100–120 °C, both l_a and l_c increase with temperature. This temperature range corresponds to the second melting peak. At 120 °C, there is a shoulder in the melting peak, and at temperatures above 120 °C, l_a and l_c increase with a slope different from that observed in the preceding temperature range.

DISCUSSION

In the pure PHB sample, the onset of melting is characterized by a slight increase in l_a in the samples studied. However, the most significant changes are observed at temperatures that vary among the samples and that do not necessarily align with the onset of melting peak. The fact that l_c decreases for pure PHB at the onset of melting could be explained using the ideas reported by Heo et al., assuming l_c is not influenced by the melting of small, more imperfect crystals but only by large, more perfect crystals.[12] Similar studies in PHB and other polymers have observed an increase in l_c as a function of increasing temperature, although these studies used a lower heating rate;[12,19] however, Fujita et al. have observed a decrement in the lattice dimensions and crystallinity of single PHB crystals at temperatures nearer to the onset of the melting peak using a heating rate of 10 °C/min.[5]

More imperfect crystals could be formed during secondary crystallization in the amorphous layer regions; thus, it can be expected that l_a significantly increases because of the melting of imperfect crystals, but these crystals may not be the only ones that melt in temperature range of 110–130 °C. For temperatures above 130 °C, both parameters increase, which is attributed to the increase in the size of the lamellar structure formed during re-crystallization. The peak located in the q range 1.5–3.0 nm^{-1} decreases in height at temperatures below 132 °C, indicating the melting of lamellae formed during secondary crystallization. At temperatures above 132 °C, the height of the peak in the q range 1.5–3.0 nm^{-1} increases again, whereby during re-crystallization, secondary crystallization would also develop. The discontinuous increase in thickness would indicate that chain sliding is not produced but melting and re-crystallization were observed, according to the reported by Fujita et al. in single PHB crystal.[5]

However, the aforementioned behavior for pure PHB was not observed in the PHB/DGEBA 50/50 blend, for which l_c did not decrease but slightly increased. In this case, the re-crystallization process may have been more significant than in pure PHB and started at a temperature of ∼90 °C. When re-crystallization occurs, l_c increases because a new structure develops, generating a new peak in the SAXS spectra. This peak corresponds to crystals with higher l_c values and is associated with a higher melting temperature. As the temperature increases, the lamellae with lower l_c melt, and only the lamellae with higher l_c remain. Therefore, the mean l_c obtained from the correlation function increases when the temperature increases. However, in this sample l_a remained constant up to 100 °C, indicating that in this case, there is no melting of crystals in the amorphous layer. These crystals, which are attributed to secondary crystallization, would be located in regions outside of the amorphous phase. l_a only increases when the re-melting process starts. Thus, it could be expected that no secondary crystallization occurs in this blend or, if it does occur that the crystals are not formed in the amorphous layer. In fact, peaks were not observed in the q range 1.5–3.0 nm^{-1} in the PHB/DGEBA 50/50 blend; thus, it can be concluded that secondary crystallization was less significant in this sample.

It is worth mentioning that in the PHB/DGEBA 50/50 blend the relative area between the second and first DSC peaks is greater than that in the other blends and in the pure PHB, indicating that the re-crystallization process is more important in these blends. In a previous study,[11] the authors reported that for a PHB content in the range of 70–100%, l_a increases as the PHB content decreases, but for blends containing 60% and 50% of PHB, l_a decreases and remains approximately constant. This behavior was interpreted as the segregation of the non-crystallizable component, moving toward outside the lamellae at these compositions. This segregation could occur toward interfibrillar regions and favor re-crystallization. In this sense, Pearce et al. reported a trend toward re-crystallization and re-melting when more atactic proportion is added to the blend isotactic–atactic PHB.[4]

The small variation in l_a as a function of temperature located at approximately 70 °C could be associated to the rearrangement of the rigid amorphous fraction (RAF). In PHB, it has been reported that during the fast cooling until low temperatures the RAF vitrifies and only with posterior heating until temperatures higher 70 °C the RAF can mobilize and allow a rearrangement of the non-crystallized segments.[7] At this temperature, a small increment of l_a could be expected.

CONCLUSIONS

The melting of melt-crystallized PHB and PHB/DGEBA blends was studied using DSC and SAXS, yielding information regarding the melting process of a semicrystalline polymer and an epoxy resin. The processes of partial melting, re-crystallization, and re-melting were analyzed, and it was observed that the main peak in the SAXS spectra shifts and deforms, anticipating superposition. Secondary lamellar structures grow at high temperatures in PHB and in the blends; these secondary structures are believed to form during re-crystallization. This behavior would imply a discontinuous thickening and is analogous with the behavior reported in single crystals grown from solution. From SAXS spectra, the lamellar dimensions as a function of temperature were determined using the 1-D correlation function. In the thermogram of the PHB/DGEBA 50/50 blend, well-separated endothermic peaks and an exothermic peak were observed, indicating that re-crystallization was more pronounced in this sample than in pure PHB. In the PHB/DGEBA 50/50 blend, the segregation of DGEBA toward the interfibrillar region would facilitate re-crystallization but could hinder secondary crystallization within the amorphous region.

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