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Critical specific work of flow for shear-induced formation of crystal nuclei in poly (L-lactic acid)

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ABSTRACT

Shear-induced formation of crystal nuclei in the poly (L-lactic acid) homopolymer was analyzed by shearing the supercooled melt in a plate-plate rheometer followed by evaluation of the kinetics of isothermal crystallization via viscosity measurements. The data revealed that shearing the melt for 10 seconds at 135°C and 140°C causes shear-induced formation of nuclei if the shear rate is higher than about 0.1 s^{-1}. If the shear rate at these conditions is higher than about 1 s^{-1} then row-nuclei, as detected by aligned spherulites, develop. Besides providing comprehensive data about the effects of rate and time of shear at 135°C and 140°C on the crystallization kinetics, the concept of specific work of flow was tested. Shear rate and time compensate each other to drive shear-induced nuclei formation, and the critical specific work required to form shear-induced crystal nuclei is around 20 to 50 kPa. Further conceptual work included the analysis of the microstructure along the radius of the sheared discs as it permits evaluation of the effect of a broad range of shear rates in a single experiment.

KEYWORDS
crystallization, morphology, nucleation, poly (L-lactic acid), shear-induced crystallization, specific work of flow

1 | INTRODUCTION

Poly (L-lactic acid) (PLLA) is a crystallizable thermoplastic polymer which is produced from short-term renewable resources like sugarcane or corn, with great potential to replace many conventional petroleum-based polymers in various fields of applications. Based on its biodegradability and biocompatibility/resorbability, PLLA can be used as a packaging material, in agriculture for decomposable sheets, or in medicine as a biomaterial. In addition, it found application as commodity thermoplastic in all areas including household, electronic industry, and automotive.[1–3] Many of these applications depend on the presence of crystals in the material as these contribute, among other characteristics, to the mechanical strength and heat resistance but also to delayed degradation.[4–6] Unfortunately, PLLA is a rather slowly crystallizing polymer, despite its crystal fraction may well exceed a value of 50%.[7–9] Typically, crystallization of the relaxed melt proceeds via spherulitic growth of lamellae[10,11] at sufficiently large supercooling below its equilibrium melting temperature of, roughly, 200°C.[12]

Processing of PLLA to semifinished or final products often involves conventional melt-processing technologies like extrusion or injection molding,[13–15] however, with the low-crystallization rate then being a challenging disadvantage if semicrystallinity is required. This is in particular true for injection molding, which typically involves rapid cooling of the melt at rates of the order of magnitude of K/s in a cold mold,[16,17] to achieve short cycle times. Such high cooling rate is in contrast to the maximum cooling rate of at best few 10 K/min below which crystallization of PLLA occurs.[18] To overcome the disadvantage of slow crystallization, it is common to add nucleating agents,[19] or to increase the mold temperature to above the glass transition temperature of around 60°C such that, on sufficiently long residence time of the melt in the mold, crystallization occurs.[20]

A further approach promoting crystallization of PLLA is to tailor the processing route such that the melt is sheared and elongated above a critical level since then flow-induced formation of crystal nuclei in a melt of lowered entropy occurs.[21–24] Shearing and flow of the melt cause orientation and stretching of macromolecules which then may form thread-like nuclei/crystallization precursors and accelerate the crystallization process, if surviving the path to the crystallization step which typically occurs at much lower temperature, often after cessation of shear work into the melt. The increase of the crystallization rate mainly depends on the amount of specific work of flow introduced into the melt, and the relaxation characteristics of the flow-induced formed structures, controlling the number of row-nuclei at the crystallization temperature.[25,26] Compared to the semicrystalline morphology, which develops in absence of shear and is then characterized by uniformly distributed spherulites, flow-induced crystallization can be recognized by both the higher crystallization rate and by the resulting anisotropic structures. These are, in particular, aligned spherulites grown from the thread-like crystallization precursors or so-called shish kebab structures being composed of long extended-chain-like crystals (shish) with lamellae grown perpendicular to the shish (kebab).[27–29] Flow-induced crystallization may affect the crystal growth rate[30]; however, it is mainly the largely increased number of rather stable nucleation sites,[31] which leads to an increase of the overall crystallization rate.

The importance of the injection-molding conditions on crystallization and mechanical properties of PLLA is well-reported in the literature, identifying both thermal profiles and shearing conditions crucial to enhance crystal formation.[32,33] In detail, shearing the melt of a PLLA fiber grade of unspecified D-isomer content at 1 s^{-1} for 480 seconds at various crystallization temperatures showed that below 120°C the spherulite density increased compared to crystallization of the quiescent melt while above 120°C cylindrite structures formed.[34] Analysis of nonisothermal crystallization after prior shearing of the melt at 150°C for 60 seconds, performed on the same PLLA grade, revealed that both the crystallization temperature and final crystallinity increased if the shear rate exceeds 5 s^{-1}.[35] In a further study, critical shear rates of 0.0076 and 0.45 s^{-1} were determined for a PLLA grade containing 1.3% D-isomers, required to orient and stretch the longest molecules of the molar mass distribution at a temperature of 135°C, respectively. Above the critical shear rate of 0.45 s^{-1}, the crystallization rate increased with both shear rate and time; however, for a given shear rate, a critical shear time exists above which the crystallization rate remained constant.[36] Shearing the melt of slowly crystallizing PLLAs containing 1.5% and 2.8% D-isomer co-units revealed a large effect of the shearing temperature on predominant formation of point-like nuclei. With decreasing shearing temperature, between 160°C and 146°C, and with increasing shear rate and time, the crystallization temperature during subsequent cooling increased, with a larger effect obtained for the sample containing 1.5% D-units.[37] Also, the effect of shear on the α/α'-crystal polymorphism[38,39] was analyzed and it was demonstrated that development of the more stable α-structure is enhanced on crystallization at around 100°C in presence of shear, that is, at a temperature at which typically α'-crystals form.[40] Further studies of shear-induced crystallization of PLLA focused on the effects of presence of blend components,[41] or long-chain branches,[42] with the employed PLLA grades containing 2% and 4% D-isomers, respectively.

Summarizing available literature data, as far as we are aware, there are not available reports describing shear-induced crystallization of the PLLA homopolymer being composed of L-isomer units only, despite it is well known that the crystallization behavior of PLLA is largely affected by the presence of D-units, even at low concentrations.[9,43] Therefore, with the present work, we intend to further increase the database about the correlation between the shearing conditions of the melt and the crystallization kinetics of PLLA, employing a homopolymer.

Moreover, the large variety of data describing shear-induced crystallization of PLAs is difficult to correlate, as experimental conditions often were different. As such, further advancing prior research, a major goal of the present study is the validation of the concept of the specific work of flow *w*, which needs being introduced into the melt to allow shear-induced formation of crystal nuclei. The specific work of flow is calculated according to Equation (1)[25,26]:

$$w = \int_0^{t_s} \eta \dot{\gamma}^2 dt \tag{1}$$

Here, $\dot{\gamma}$ and t_s are the shear rate and time, and η is the viscosity, which depends on $\dot{\gamma}$ and t_s. This concept predicts that shear rate and time are interconvertible, providing variables to tailor shear-induced crystallization in processing. As a major advantage of this concept, compared to observation of critical rates and times of shear, both depending on temperature, a single temperature-independent quantity is observed, allowing for example, comparing the effect of the molecular architecture on flow-induced crystallization. With specifically designed plate-plate rheometer experiments, allowing for the separate control of both shearing rate and time, we attempt with the present study to apply this quantity to describe shear-induced nucleation of PLLA.

2 | EXPERIMENTAL

A PLLA homopolymer grade with a mass-average molar mass and melt-flow index of 120 kDa and 8 g (10 min)$^{-1}$ (210°C, 2.16 kg), respectively, was obtained from Corbion (Netherlands).[44,45] The material was delivered in form of pellets, which were dried at 75°C for at least 8 hours before any experimentation.

2.1 | Rheological analyses

An Advanced Rheometer AR 2000 (TA Instruments, New Castle, DE, USA) equipped with an environmental test chamber, purged with dry air, was used for analysis of the effect of shearing the melt on isothermal crystallization. Measurements were performed in parallel plate geometry, with the diameters (*D*) of the upper and lower plates being

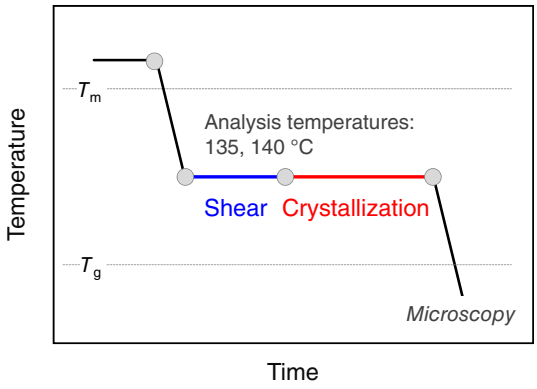

FIGURE 1 Shear and temperature protocol for analysis of the shear-induced crystallization of poly (L-lactic acid)

8 and 25 mm, respectively. The gap distance was programmed to 250 μm, to be within the recommended range of $D/(10...50)$ for the selected setup.[46] The dried pellets were placed on the lower plate, which was preheated to 220°C. After their melting, the gap distance was adjusted by lowering the upper plate, and subsequently the squeezed melt was removed. After the completion of the experiment, the upper and lower plates were unmounted along with the solidified sample and quenched in tap water, which allowed the solid disc to be removed for further analysis of the structure by microscopy.

Shear and crystallization experiments were performed according to the protocol shown in Figure 1. The relaxed melt was cooled using a rate of 4 K/min to analyses-temperatures of 135°C and 140°C before subjecting to rotational shear at rates between 0 and 10 s^{-1} for variable time between 0 and 900 seconds. After the shear step, the melt was kept at identical temperature, allowing crystallization, which was followed regarding its kinetics by measurement of the viscosity using an oscillatory frequency of 3 rad s^{-1} and deformation amplitude of 0.05%. Note that the viscosity was measured also during the shear step, to permit calculation of the specific work of flow, as described below.

2.2 | Polarized-light optical microscopy

The structure of the circular discs was analyzed by polarized-light optical microscopy (POM). Sections with a thickness of 10 μm were prepared by cutting parallel and perpendicular to the flow direction using a microtome, before observation in a Leica DMRX microscope in transmission mode between crossed polarizers.

3 | RESULTS AND DISCUSSION

Figures 2 and 3 show the evolution of the viscosity during crystallization (see red segment in Figure 1) at 135°C and 140°C, respectively. Prior to crystallization, the melt was sheared at identical temperature at different conditions. In plots (A) are shown data collected after shearing the melt for 10 seconds at different shear rates while in plots

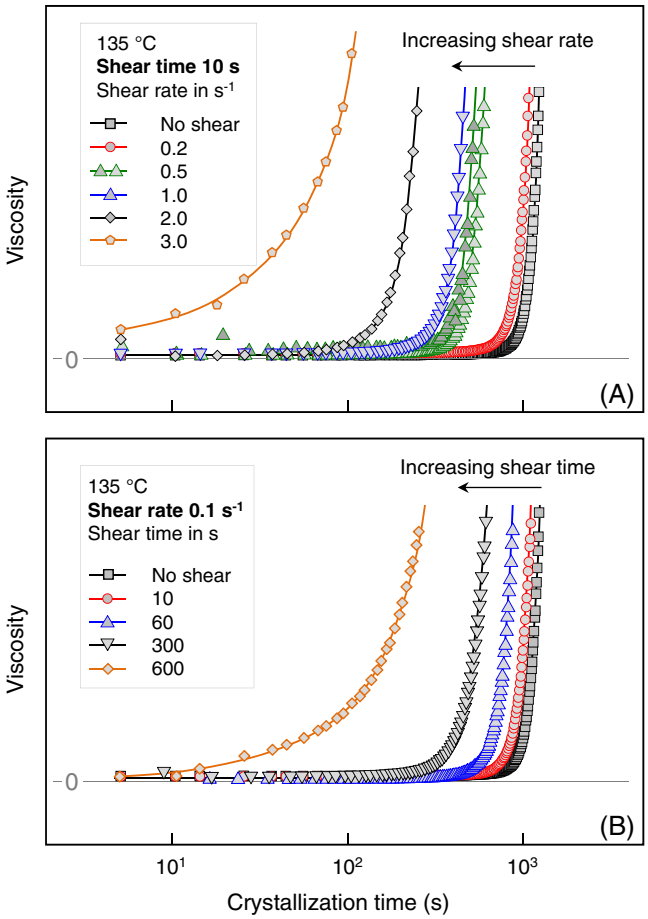

FIGURE 2 Viscosity as a function of the time of crystallization of poly (L-lactic acid) at 135°C, after shearing the melt at identical temperature. A, Shear time 10 seconds, variable shear rate; B, Shear rate 0.1 s^{-1}, variable shear time

(B), the shear rate was kept constant at 0.1 s^{-1} and the shearing time was varied.

The data of Figures 2 and 3 provide information about the effects of shear rate and shear time on the kinetics of crystallization. During crystallization, the viscosity of the system increases, which is therefore a reliable measure of the fraction of crystals forming as a function of the crystallization time. Note that we did not intend to gain knowledge about absolute values of the viscosity or crystallinity but rather observe the acceleration of the crystallization due to the shear-induced formation of crystal nuclei. Furthermore, for instrumental reasons, it was impossible to record viscosity data until completion of the crystallization process. Irrespective of this shortcoming, detection of the onset of the crystallization process is possible with high reproducibility as demonstrated for selected data sets (green triangles in Figure 2A, blue triangles in Figure 3B, and squares in Figure 3B; the latter represent data collected on the nonsheared melt).

Cooling the relaxed melt to 135°C or 140°C, and absence of shear, leads to crystallization starting after about 1000 or 2000 seconds (see black squares in Figures 2 and 3, respectively). This observation is in agreement with independent analyses of the crystallization kinetics of the PLLA homopolymer, and confirms the experimental approach of

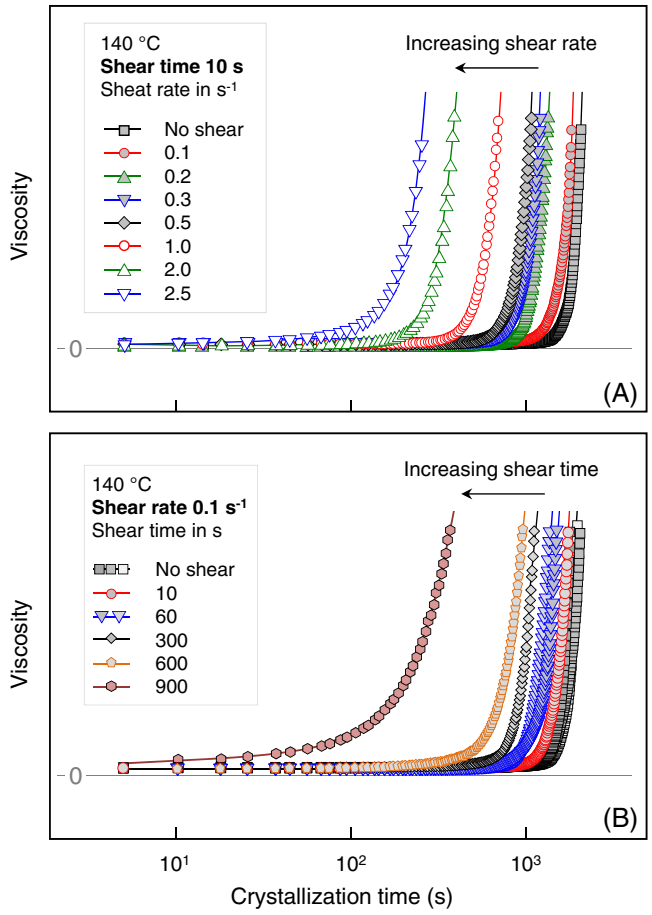

FIGURE 3 Viscosity as a function of the time of crystallization of poly (L-lactic acid) at 140°C, after shearing the melt at identical temperature. A, Shear time 10 seconds, variable shear rate; B, Shear rate 0.1 s^{-1}, variable shear time

employing viscosity data for analysis of shear-induced crystallization.[8,9,47] Both increasing the shear rate (Figures 2A and 3A) and shear time (Figures 2B and 3B) cause an acceleration of the crystallization process as is detected with the shift of the increase of the viscosity to shorter crystallization time (see horizontal arrows in the top right corner). For example, referring to the data collected at 135°C (Figure 2) crystallization of the quiescent melt begins after about 1000 seconds, while prior shearing of the melt at the same temperature for 10 seconds using a rate of 3 s^{-1} leads to immediate crystallization after completion of the shear step. A shear rate of 0.1 s^{-1}, in contrast, requires shearing for 600 seconds to cause immediate crystallization after cessation of shear.

Note, that in Figures 2 and 3, crystallization time is defined as starting at the end of the shear step. As shearing the melt and crystallization are occurring at identical temperature, however, an alternative representation of data would be the addition of the shearing time to the crystallization-step time. While for Figures 2A and 3A, the difference between those two time-scales (red segment vs blue plus red segments in Figure 1) may be negligible due to the rather short shearing step of 10 seconds, in Figures 2B and 3B, curves obtained after shearing for longer time will significantly shift toward the dated

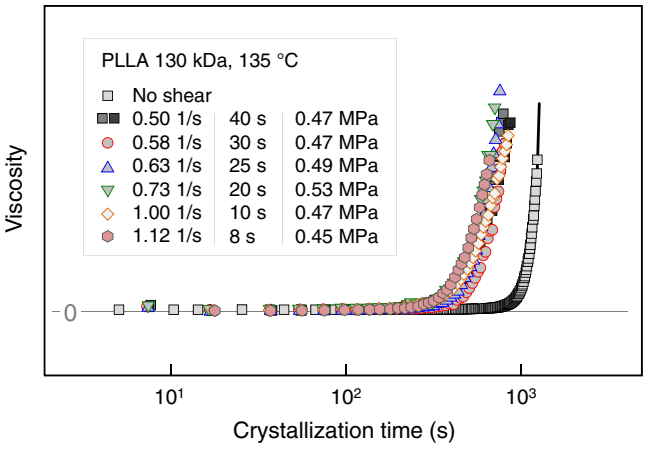

FIGURE 4 Viscosity as a function of the time of crystallization of poly (L-lactic acid) (PLLA) at 135°C, after shearing the melt, introducing a specific work of flow of about 0.5 MPa

collected from the nonsheared melt. This notwithstanding, also in that case, that is, shearing at 0.1 s^{-1}, there is observed distinct acceleration of crystallization.

As confirmed with Figures 2 and 3, both shear rate and shear time decisively influence the formation of crystal nuclei and with that the crystallization rate. It was hypothesized that these parameters may compensate each other to yield the same specific work of flow introduced into the melt by shear, according to Equation (1). To test whether the concept of the specific work of flow for crystal nucleation holds for PLLA, samples were exposed to different combinations of shear rate and time, followed by analysis of the crystallization rate.

Figure 4 shows the crystallization-induced increase of the viscosity as a function of the crystallization time at 135°C, after shearing the melt, introducing a specific work of flow of about 0.5 MPa; for comparison, with the light gray squares are included data from a nonsheared sample. For estimation of the specific work of flow, we measured the viscosity during shearing the melt at the specified rates (blue segment in Figure 1). Typically, during shearing the melt, the viscosity slightly decreases due to orientation of molecular segments and therefore in Equation (1) an average viscosity-value was employed for calculation of the specific work of flow.

Most important regarding the data of Figure 4 is the observation that similar specific work of flow leads to similar acceleration of crystallization, despite the different shear rate or times. In other words, low shear rate can be compensated by increasing the shear time to achieve a preset acceleration of crystallization.

To gain further information about the mechanism of the acceleration of crystallization after shearing the melt, the semicrystalline morphology of the sheared disks was analyzed by POM. Figure 5 shows the micrometer-scale structure of PLLA crystallized at 140°C after prior shearing the melt at the indicated rates for 10 seconds. The sketch at the top shows the disc of 250 μm thickness, with the direction of shear indicated with the red arrow. Thin sections for POM analyses were obtained by cutting the disc parallel to the flow direction at the outer perimeter (see dark gray rectangle). The top left image was obtained on a nonsheared sample, showing large spherulites

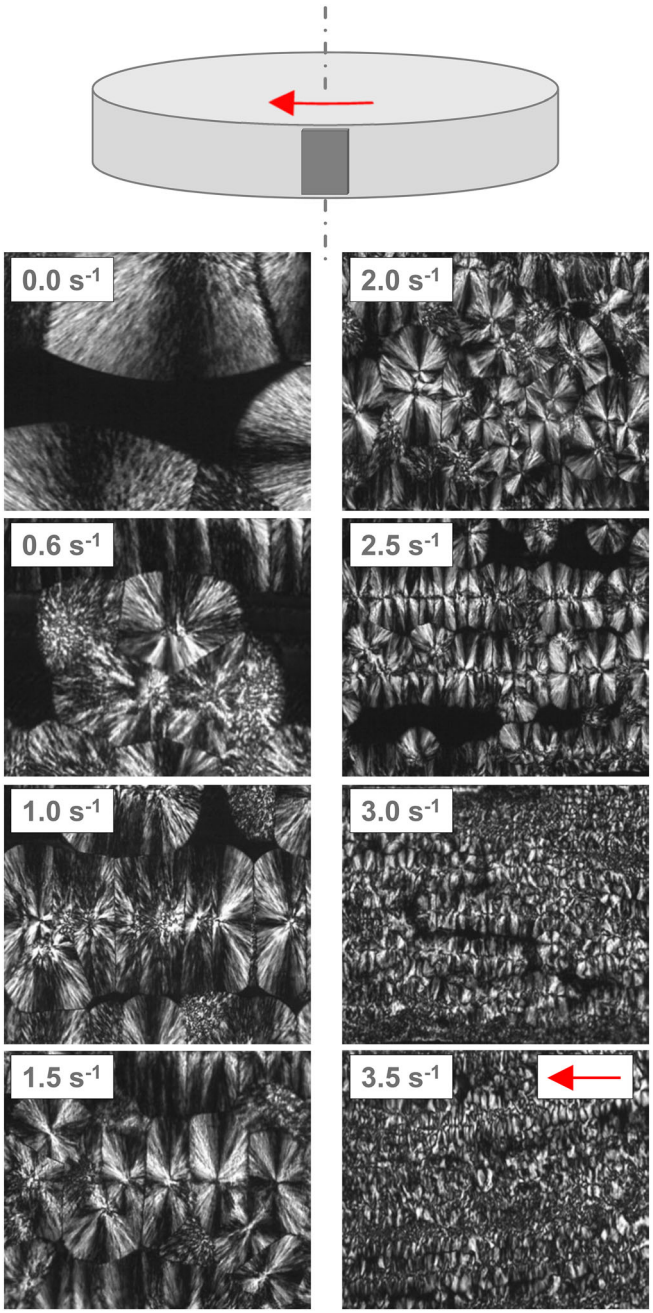

FIGURE 5 Morphology of poly (L-lactic acid) crystallized at 140°C after prior shearing the melt at the indicated rates for 10 seconds. The top sketch of the circular disc shows the sampling position and the red arrow indicates the flow direction. The height of the images corresponds to the thickness of the disc of about 250 μm

which grew from the top and bottom surfaces of the disc toward the center layer. In that case, crystallization was nucleated at the polymer/metal interface. The black area represents noncrystallized material as the sample was quenched to below the glass transition temperature before crystallization was finished. At low shear rate of for example, 0.6 s^{-1}, an increased number of spherulites is detected, which then, on further increase of the shear rate are row-like aligned (see image 1.0 s^{-1}). With increasing shear rate, both the number of threads/row-like structures and the frequency of nuclei within the individual rows increases, leading to a larger total number of spherulites of much reduced size (compare images obtained on samples sheared at rates of for example, 1 and 3 s^{-1}).

In addition, the structure of a sheared disc along the radius was analyzed. In the example of Figure 6, the sample was crystallized for 240 seconds at 135°C after prior shearing the melt at identical temperature for 10 seconds at 2.5 s^{-1}. The top left sketch illustrates with the dark gray slice the sampling position and with the red arrow the direction of flow. As such, the sample section shows the structure perpendicular to flow. While the image in the bottom part provides an overview of the change the morphology from the center (left edge) toward the outer perimeter of the disc (right edge), the top right reveals the structure near the outer perimeter. The length of the cut section shown in the bottom part of Figure 6 corresponds to the radius of the disc, being 4 mm. The shear rate in the center is zero and increases linearly toward the outer perimeter to the maximum value of 2.5 s^{-1}. In agreement with the data of Figure 2A, variation of the shear rate leads to different degree of crystallization. In more detail, absence of shear allowed onset of crystallization only after about 1000 seconds (see gray squares in Figure 2A). As such, in the center part of the sample shown in Figure 6, spherulites are almost completely absent because the crystallization time was only about 240 seconds. With increasing shear rate, the curves in Figure 2A shifted to shorter crystallization time, due to accelerated crystallization. With the specific sampling to image the microstructure of the disc along the radius in Figure 6, the effect of increasing shear rate is advantageously and directly illustrated by the increasing number and eventual alignment of spherulites along the horizontal position from left to right. For the sample volume subjected to a shear rate of close to 2.5 s^{-1} an almost space-filled spherulitic morphology is observed, which agrees with the prediction of Figure 2A (see black diamonds, obtained after shearing the melt at 2 s^{-1}). Noteworthy, though the thin section of Figure 6 shows the structure perpendicular to flow, there are also observed row-like aligned spherulites pointing to turbulent flow conditions (see top-right image in Figure 6) in the performed experiment, similar to those observed in polyamide 66.[31]

To obtain quantitative data about the correlation between the shearing conditions and the crystallization rate, the onset time of crystallization is plotted as a function of the specific work of flow in Figure 7. The melt was subjected to shear at 135°C (blue squares) and 140°C (red circles) for a period of 10 seconds, before crystallization at identical temperatures. Both data sets show the same trend, however, are vertically shifted to each other as crystallization at 140°C is slower than at 135°C. More important, below a specific work of, roughly, 20 to 50 kPa the crystallization kinetics is almost unaffected by shear and is similar to that of the nonsheared sample; note the dashed lines in the top right part of the graph, representing the crystallization onset time of the nonsheared sample. If the melt is subject to a specific work of flow higher than 20 to 50 kPa, then the crystallization onset time decreases due to shear-induced formation of nuclei. As such, the critical specific work of flow to initiate shear-induced formation of crystal nuclei in the melt of the PLLA homopolymer is 20 to 50 kPa.

Typical examples of the semicrystalline morphology formed after imposing the PLLA melt at a temperature of 140°C to different

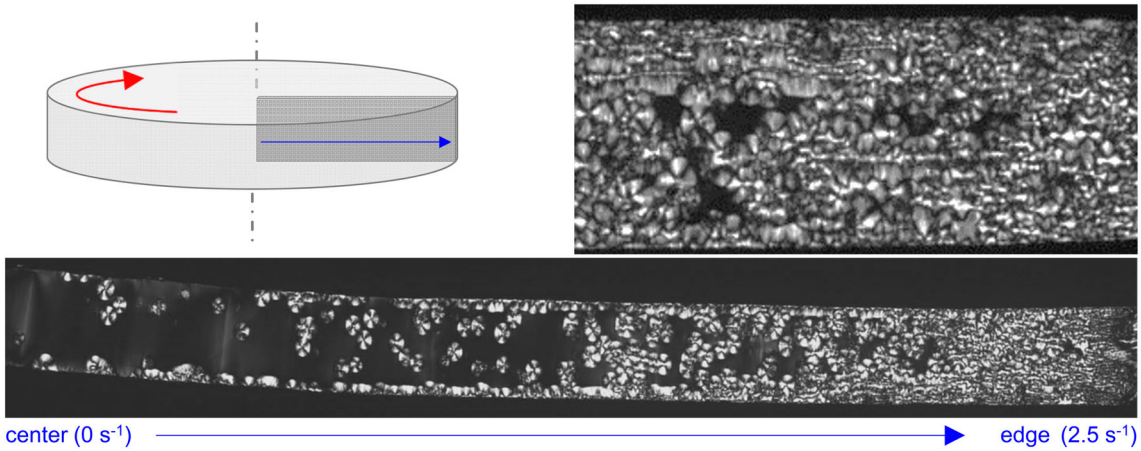

FIGURE 6 Semicrystalline morphology of a poly (L-lactic acid) disc along the radius, crystallized at 135°C for about 240 seconds after prior shearing the melt at identical temperature for 10 seconds at a rate of 2.5 s^{-1}. The top left part is a sketch of the circular disc showing the sampling position (dark gray slice) and the direction of flow (red arrow). The top right image shows the structure near the outer perimeter of the disc

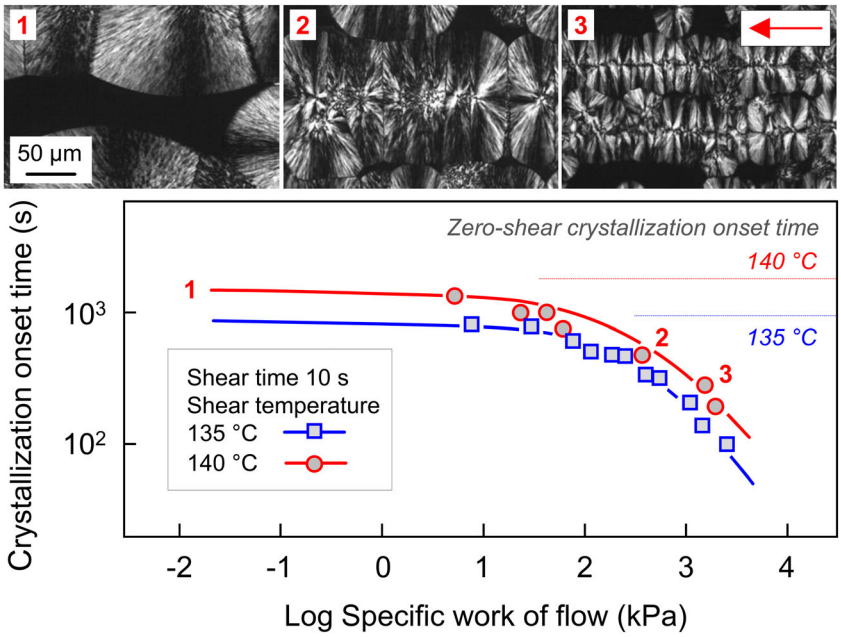

FIGURE 7 Onset-time of crystallization of poly (L-lactic acid) as a function of the specific work of flow. Shearing of the melt before crystallization was performed at 135°C (blue squares) and 140°C (red circles) for a period of 10 seconds. The zero-shear crystallization onset time is shown with the dashed lines in the top right part of the graph. The top images serve for qualitative discussion of the number of nuclei forming at different shear conditions at 140°C, as indicated with the Arabic numbers at the corresponding data set (red circles/curve) in the below plot

specific works before crystallization are shown with the three images at the top of Figure 7. The horizontal red arrow shows the direction of flow and the Arabic numbers allow an assignment to the flow conditions (see the corresponding numbers at the red data points/curve in the below graph). As such, the images labeled 1, 2, and 3 were obtained on samples crystallized after shearing the melt at 0, 1, and 2.5 s^{-1}, or after imposing the melt to specific works of 0, 360, and 1900 kPa, respectively. Over-critical shearing conditions are straightforward identified in images 2 and 3, which show aligned spherulites due to shear-induced nuclei formation.

4 | SUMMARY

The present study is a further attempt to gain knowledge about melt-crystallization of the biopolymer PLLA at processing relevant conditions. While the effect of the thermal profile, in particular rapid-cooling conditions, on crystal nucleation and growth was explored in detail recently, here shear-induced nuclei formation and crystallization is the focus. Although reports about shear-induced crystallization of PLLA exist in the literature, due to the employment of various grades differing in D-isomer co-unit content and molar mass/viscosity a cross-comparison of data collected at largely different shearing conditions (rate, time, and temperature of shearing) is impossible. Therefore, in the present work, we used a PLLA homopolymer composed of L-isomer co-units only, and analyzed shear-induced crystal nucleation from a conceptual point-of-view, providing ideas and pathways for upcoming in-depth studies. Most important is the need for applying the concept of the specific work of flow to obtain unique information about critical conditions for shear-induced generation of crystal nuclei. Only if that concept is applied, guidelines to tailor processing routes may become available as only then shearing conditions

including temperature (via the melt-viscosity), time, and rate of shear are expressed by a single quantity. With the data Figure 4, it was exemplarily demonstrated that the concept of specific work of flow holds for PLLA, while the data of Figure 7 provide quantitative information that the critical work for shear-induced formation of crystal nuclei in PLLA is approximately 20 to 50 kPa.

In addition to quantitative data about the acceleration of crystallization after shearing the melt at specific conditions (see Figures 2–3, and 7), the effect of shear rate on crystallization was determined in the entire shear-rate range from zero to the maximum value by inspection of the microstructure parallel to the radius of the sheared disc (see Figure 6). Such analysis permits identifying different modes/regimes of shear-induced formation of crystal nuclei as a function of the radius/shear rate, and may save time-consuming individual experiments in which the shear rate at the outer edge of the sample is varied.

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