

Effect of Matrix Polymer on Flow-Induced Nucleation in Polymer Blends

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Long-chain molecules in polymers are responsible for flow-induced nucleation (FIN). The role of a short-chain matrix in FIN was investigated using bidisperse blends of polyethylenelike high molecular weight long chains in short-chain polymer matrices. It was found that the critical specific work, w_c , measured for the onset of FIN in the blends has a power law dependence on the molecular weight of the matrix polymer with $w_c \propto M_w^{2.59 \pm 0.27}$ indicating that the matrix can affect the stretching of the long chains and limit their ability to act as nucleation sites for flow-induced crystallization.

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The crystallization of polymer melts starts with the formation of nuclei. At constant pressure the nucleation of polymer crystals is mainly controlled by temperature under quiescent conditions. The free energy difference per unit volume between the melt and an infinite crystal increases with the supercooling and, therefore, the lower the temperature of the melt from the polymer equilibrium melting point, the stronger the probability for a nucleus to be formed [1]. Under these conditions, the crystal nucleation of high molecular weight polymers is virtually independent of the chain length [2,3]. This situation changes dramatically when an external flow is applied. Classical nucleation theory suggests that a spontaneous solidlike embryo formed in a liquid phase will become a stable nucleus when it exceeds a critical size beyond which the volume free energy of the embryo overcomes its surface free energy [4]. The driving force for the nucleus to grow further is that its total free energy decreases with size. By accepting this classical scenario for polymer melts, without going into full details of kinetic constraints caused by a folding of long molecules, it can be concluded that external flow, supplying extra energy to the melt, may break the free energy balance and affect the nucleation [5]. For example, the macroscopic flow forces the polymer chains into elongated configurations, which lowers the entropic penalty for crystallization [6]. This may result in a flow-induced nucleation (FIN) of the polymer accompanied by a flow-induced crystallization (FIC) at a later stage. In the present study shear pulses have been used to generate flow. Since there is no fundamental difference between the impact of a shear flow and an extensional flow on the confirmation of polymer chains [7], the conclusions made in this work should be generic. Thus, “flow” terms (i.e., flow rate and FIN), and not more specific “shear” terms such as shear rate and shear-induced nucleation, are used in this Letter.

Recent advances in a combinatorial technique for studying FIC of polymers [8,9] combined with the results obtained in the previous studies have shown that FIC can be represented as a four-stage process [10,11], where each

stage is associated with particular flow conditions. The process is initiated by (i) stretching of molecules at flow rates $\dot{\gamma} > \dot{\gamma}_{\min}^{\text{LC}} = \tau_R^{-1}$ (where $\dot{\gamma}_{\min}^{\text{LC}}$ is defined by Rouse time, τ_R , of the longest chains, LC, in the polymer ensemble) [9,12,13], followed by (ii) the formation of persistent nuclei and (iii) their simultaneous alignment into rows in the melt occurring above a threshold of critical specific work (energy density) performed by the flow, w_c , [9,14] and completed by the (iv) aggregation of the nuclei into fibrills (shishes) taking place above the critical strain, γ_c [15–17]. The nucleation (stage ii) is accompanied by the alignment (stage iii) as the flow-induced nuclei, positioned along the flow direction, inevitably become aligned. In accordance with this FIC description, the first two stages correspond to FIN. Thus, thermodynamically stable nuclei can only be formed if the polymer has experienced more than a threshold value of mechanical work performed on its melt, at flow rates greater than the inverse Rouse time of the longest chains in the polymer ensemble.

While stretching of polymer molecules is well understood and can be easily predicted via τ_R measurements, w_c remains a relatively unexplored parameter that requires further theoretical developments to establish its relation to both physical parameters of the molecules and thermodynamic parameters of processing conditions. It was observed that the w_c required for the FIN increases with the temperature, especially in a range of temperatures close to, or above, the nominal melting point (the melting point of spherulites) [11]. This kind of behavior is predictable as the higher the processing temperature, the larger the critical size of the nucleus and, therefore, the more specific work is required to stabilize this nucleus. w_c also demonstrates a strong dependence on the polymer molecular weight. An increase of the molecular weight of the long-chain fraction in the polymer ensemble, all other conditions being similar, significantly reduces the threshold of specific work required for the FIN. The w_c is inversely proportional to the concentration of the long-chain molecules [9]. It can be expected that the surroundings of the

long-chain molecules, the polymer matrix, may also have an influence on the FIN that could be quantified via w_c . This Letter reports the first measurements and parameterization of the effect of the polymer matrix on the FIN in semicrystalline polymer blends.

Commodity polymers usually have a broad distribution of molecular weights [18]. However, their FIN behavior is controlled by a tiny fraction of the longest chains present in the continuous polymer blend. Using bidisperse polymer blends, comprised of a small amount of long chains in a short-chain matrix, is an effective way to study FIN in semicrystalline polymers. This approach separates the Rouse times of the molecules comprising the blend allowing the flow conditions to be chosen where the nucleation of crystallization is initiated selectively by the long chains.

Experiments were conducted on bidisperse blends of a 2 wt % high molecular weight hydrogenated polybutadiene (*h*-PBD) ($M_w = 1770$ kDa) in a matrix of either low molecular weight *h*-PBD or even lower molecular weight polyethylene wax (PE wax) [19]. The specially synthesised *h*-PBDs have 7 mol % ethyl side branches as a relic of their synthesis [20] whereas the PE waxes are linear. Both sets of material, however, have the same crystal structure and similar nominal melting points and quiescent crystallization kinetics. The viscosity of both the *h*-PBD and the wax matrix polymers [19] are in good agreement with the viscosity curves predicted for *h*-PBD using the full-tube theory for linear entangled polymers [21]. It is found, using Rubinstein-Colby theory for bidisperse blends [22], that the viscosity of the blends is also consistent with theoretical calculations [19]. However, this agreement requires an effective concentration and an effective molecular weight for the long-chain component (1.2 wt % and 700 kDa, respectively) to be used instead of the measured quantities (2 wt % and 1770 kDa) to obtain a good fit to the data. This systematic deviation is most likely caused by tube dilation of the long chains in the short-chain matrix. An estimation of the Struglinski-Graessley parameter $Gr = M_e M_2^2 M_1^{-3}$ (where M_1 and M_2 are the molecular weights of the matrix and the long-chain polymer, respectively) suggests that most of the blends ($M_1 < 52$ kDa) have Gr well above the critical value 0.064 when the tube dilation becomes relevant [23]. However, the conclusions drawn in this Letter are unaffected by this fact, as only experimental viscosities and the matrix polymer molecular weights have been used in the analysis. Using the tube model parameters for the *h*-PBD [19], the inverse Rouse relaxation time of the *h*-PBD matrix polymers ($\dot{\gamma}_{\min}^{\text{matrix}} = M_e^2 M_w^{-2} \tau_e^{-1}$) is always greater than the highest flow rates used in this study (300 s^{-1}) and they remain unstretched throughout.

A combinatorial technique based on torsional parallel-plates geometry, described previously [9,10], has been used to measure flow conditions for the onset of FIN in the *h*-PBD blends. The blends were loaded in the shear device (a modified Linkam CSS-450 shear cell, Tadworth,

U.K.), melted at 438 K, fast-cooled to a required temperature (388 K), close to the nominal melting point of the blends (386 K), subjected to a shear pulse, produced by a disk plate rotating at a constant angular speed Ω for a duration t_s , and subsequently crystallized by a further cooling to room temperature. Since the flow rate increases linearly with the radius in the torsional geometry [$\dot{\gamma}(r) = \Omega r/d$, where d is the shear gap, 0.5 mm was used], the crystallized disk represents a radial map of flow-induced morphologies as a function of flow rate [Fig. 1(a)]. In all experiments t_s was chosen to be at least 10 times longer than the start up of the polymer melt stress. If the range of flow conditions created during the shear pulse includes the conditions required for the onset of FIN in the polymer, the disk crystallized after shear contains two distinct zones with different morphologies. The central, low-flow rates, zone of the disk, corresponding to $w < w_c$ where no conditions for FIN are met, is composed of spherulites [Fig. 1(b)] and the outer zone, corresponding to $w > w_c$ where FIN occurred, is composed of oriented structures created by the flow-induced nuclei oriented along the flow direction [Figs. 1(c) and 1(d)]. The transition between unoriented spherulitic (nonbirefringent) and oriented (birefringent) zones of the sample can be identified by

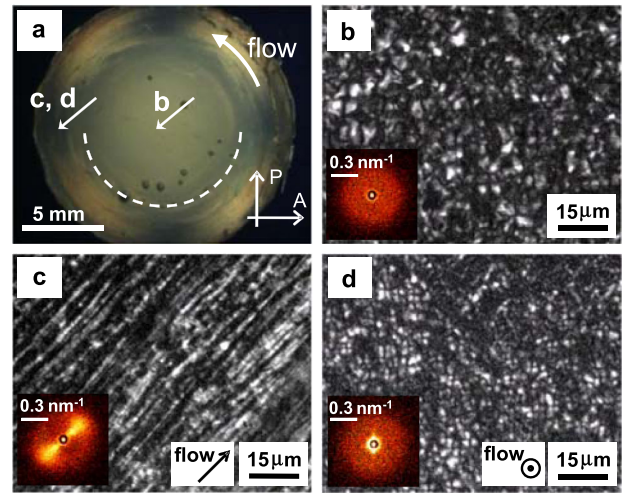


FIG. 1 (color online). A PLI of a *h*-PBD bidisperse blend disk (2 wt % 1770 kDa in 18 kDa matrix) crystallized after shearing at $T = 388$ K in a torsional parallel-plates geometry using an angular speed of rotation $\Omega = 3.3 \text{ rad s}^{-1}$ and a time of shearing $t_s = 40$ s (a) and a polarized light microscopy of microtome slices obtained from the unoriented part of the disk (b) and oriented part of the disk sliced either parallel (c) or perpendicular (d) to the flow direction. The location of slices is indicated in the PLI (a). The diameter and the thickness of the sheared polymer disk are 16 and 0.5 mm, respectively. The dashed curve line in the PLI indicates the transition from unoriented to oriented structure in the disk. The inset SAXS patterns were taken at the areas corresponding to the slices location with the x-ray beam normal to the image plane. A scattering vector scale bar is shown in the SAXS patterns.

polarized light imaging (PLI) of the sample demonstrating a clear boundary marked by a truncated Maltese cross pattern [Fig. 1(a)]. Alternatively, the onset of FIN can be identified by ex-situ small angle x-ray scattering (SAXS), detecting the orientation of lamellar structure created by alternating amorphous and crystalline layers of the semi-crystalline polymer. The lamellar structure of unoriented and oriented zones of a sheared sample produce distinctive SAXS represented by an isotropic ring [Fig. 1(b)] and an anisotropic pattern oriented along the flow direction [Fig. 1(c)], respectively. It was shown that measurements of the boundary flow rate, $\dot{\gamma}_b$, associated with the transition of morphology, from either the degree of lamellar orientation obtained by SAXS along the disk diameter or PLI patterns, produce the same result within experimental errors [9,10] and can be equally used to detect the flow conditions for the onset of FIN, that is the boundary specific work

$$w_b = \int_0^{t_s} \eta[\dot{\gamma}_b(t)] \dot{\gamma}_b^2(t) dt, \quad (1)$$

where $\eta[\dot{\gamma}_b(t)]$ is viscosity of the blend. w_b is constant at $\dot{\gamma}_b > \dot{\gamma}_{\min}^{\text{LC}}$ and corresponds to w_c .

Both SAXS and PLI techniques have been used to measure w_b for the onset of flow-induced nucleation in *h*-PBD blends at different flow conditions. These data have been used to determine w_c for each blend (Fig. 2) and show the striking behavior of w_c being independent of shear rate over a wide range of conditions once $\dot{\gamma}_b > \tau_R^{-1}$. The techniques have been reported in detail elsewhere [9,10]. Crystallized samples of the blends with polymer matrix

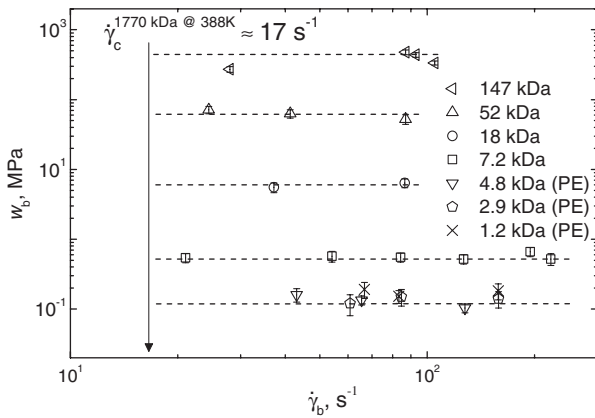


FIG. 2. A plot of flow conditions, boundary specific work, w_b , versus boundary flow rate, $\dot{\gamma}_b$, for the onset of flow-induced nucleation at $T = 388$ K in *h*-PBD bidisperse blends comprised of 2 wt % 1770 kDa and a low molecular weight matrix ($M_w = 147, 52, 18, 7.2, 4.8, 2.9$ or 1.2 kDa). Dashed lines indicate the critical specific work of the blends, w_c , which is the average of the corresponding w_b measured at $\dot{\gamma}_b > \dot{\gamma}_{\min}^{1770 \text{ kDa} @ 388 \text{ K}}$, where $\dot{\gamma}_{\min}^{1770 \text{ kDa} @ 388 \text{ K}}$ is the minimum flow rate for 1770 kDa *h*-PBD stretching, defined as the reciprocal of the Rouse time of the 1770 kDa *h*-PBD molecules at $T = 388$ K.

$M_w \leq 7.2$ kDa were brittle and difficult to recover from the shear cell. In this case an on-line technique, shear-induced polarized light imaging [8] was used to measure $\dot{\gamma}_b$.

The zero shear viscosity of the matrix polymers (Fig. 3) is consistent with the power law dependence reported for many polymers $\eta_0 \propto (M_w)^n$, where the exponent is $3.4 < n < 3.6$ for polymer chains with $M_w > M_e$ acting as an entangled network, and $1 < n < 2.5$ for $M_w < M_e$ where entanglements do not occur [24,25]. A similar result has been obtained for the *h*-PBD blends (Fig. 3). However, there is a pronounced deviation from the power law dependence for the blends composed of a low molecular weight matrix, which is associated with the viscous high molecular weight component (2 wt % 1770 kDa) dominating the η_0 of the blends. Indeed, the higher the molecular weight of the long chains and/or the higher their concentration, the stronger the contribution of the long chains to the blend viscosity and the higher the zero shear viscosity. Blends comprised of high molecular weight matrix (52 kDa and 147 kDa), where the contribution of the 1770 kDa *h*-PBD to the viscosity becomes insignificant, demonstrate η_0 similar to the matrix polymer following the standard power law molecular weight dependence.

In analogy with the zero shear viscosity of the matrix polymer, the critical specific work of the polymer blends also demonstrates a power law dependence on molecular weight of the matrix polymer (Fig. 3). This finding suggests that there is an effect of matrix polymer on the FIN initiated by the small fraction of long chains present in the blends. This effect can be expected, as the matrix viscosity opposes the flow, making it more difficult for the long chains to be transported in the stretched state, and this is why the critical work increases with M_w . It would be

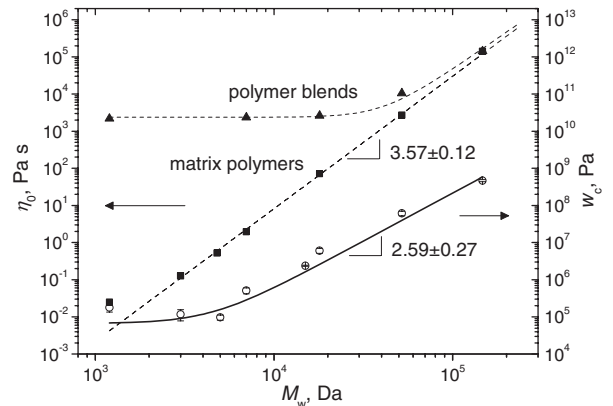


FIG. 3. The critical specific work, w_c , for the onset of orientation in *h*-PBD bidisperse blends and the zero shear viscosities, η_0 , of the blends and their matrix polymers at 388 K plotted versus the molecular weight of the matrices, M_w . The data point at $M_w = 15$ kDa was taken from another work [9]. The data are fitted by a power function, $y = a + bM_w^c$, where y represents either η_0 or w_c . The numbers next to the curves indicate the exponent c .

difficult to express the influence of the matrix polymer on the FIN, as existing theories require numerical approximations for evaluations of the shear thinning viscosity of bidisperse blends [22,26] and, therefore, a simple substitution of an analytical expression for $\eta(\dot{\gamma}_b)$ in Eq. (1) is currently not possible. Nevertheless, some estimations can still be made. It can be concluded that w_c is growing slower than η_0 with the increase of the matrix M_w —the w_c exponent (2.59 ± 0.27) is reduced by about unity in a comparison with the η_0 exponent (3.57 ± 0.12) (Fig. 3). Considering theoretical works on the dynamics of entangled polymer chains, this observation suggests that an increase of the matrix molecular weight facilitates the FIN in the blend. A tube model including the effect of constraint release, accelerating the relaxation of polymer molecules, predicts that the rate of constraint release of the molecules is slower in a matrix comprised of longer polymer chains [21,26]. This effect should facilitate stretching of the 1770 kDa molecules and help to form precursors for the nucleation under flow conditions. Accordingly, reducing chain length of the matrix polymer should have an opposite effect on the stretching of the long chains as the low M_w matrix chains, when very short, cannot maintain the chain stretching of the high M_w long chains and, therefore, limit their ability to act as nucleation sites for flow-induced crystallization. Thus, the w_c dependence on the matrix M_w is not simply dictated by the viscosity of the matrix surrounding long-chain molecules in the blend. An increase of the matrix M_w causes two contrary effects on the FIN: on one side viscosity of the matrix, opposing to the melt motion, increases w_c and on another side the rate of constraint release of the long-chain molecules (1770 kDa), responsible for the FIN, reduces w_c . The key point herein is that the matrix affects both the stretching of the long chains and the viscosity of the blend, the parameter describing the environment in which the stretched molecules flow, and it is both of these that determine the FIN.

The graph of the critical specific work suggests that w_c is independent of the M_w polyethylene matrix when it below 5 kDa. Thus, there is a threshold molecular weight below which the matrix polymers are unlikely to entangle with the long chains initiating the crystal nucleation. The minimum w_c value ($\sim 10^5$ Pa) represents the amount of flow required to form stable nuclei from the 1770 kDa *h*-PBD alone: that is without any contribution from the matrix. This value is related to the concentration and molecular weight of the long chains, to the architecture of the molecules and their underlying thermodynamic conditions. This conclusion is only valid when flow rate is above the minimum flow rate to stretch the long-chain component in the blend but still below the minimum flow rate to stretch the matrix polymer $\dot{\gamma}_{\min}^{\text{LC}} < \dot{\gamma} < \dot{\gamma}_{\min}^{\text{matrix}}$. At very high flow rates, when $\dot{\gamma} > \dot{\gamma}_{\min}^{\text{matrix}}$, all molecules of the blend will be in a stretched state and may participate as precursors for

nuclei formation. Under such extreme conditions the critical specific work dependence changes and is more likely to be independent of the polymer molecular weight.

For polymer blends composed of a high molecular weight matrix, where the matrix mainly controls the blend's rheological behavior, the viscosity can be expressed empirically via a power law function $\eta(\dot{\gamma}) = m\dot{\gamma}^{k-1}$, where m is a constant and k is about 0.5 for polydisperse polymers and tends to, but never reaches, zero for monodisperse polymers (see, for example the viscosity of the 1770 kDa polymer in Ref. [19]). Assuming that k is zero in the power law expression for $\eta(\dot{\gamma})$ the critical specific work can be rewritten as $w_c = m\dot{\gamma}_b t_s$ [using a simplified version of Eq. (1) assuming that flow rates are constant during the shear pulse and $\dot{\gamma}_b > \dot{\gamma}_{\min}^{\text{LC}}$]. Since $w_c \propto (M_w)^c$ ($c = 2.59$, Fig. 3), the relationship obtained shows that the strain required for the FIN in a polymer blend has a power law dependence on the molecular weight of the matrix polymer $\gamma_b = \dot{\gamma}_b t_s \propto (M_w)^c$. This relation shows, somewhat counterintuitively, that the higher the molecular weight of the matrix polymer the more the strain is required to create flow-induced nuclei in bidisperse polymer blends. This leaves the thorny problem of the strain required for the formation of a critical nucleus. Previous works have shown repeatedly that the strain to form a nucleus is dependent on the flow rate and that the only flow rate independent parameter is the specific work [8,9,14,27]. This study demonstrates that the matrix affects both the blend viscosity and the long-chain stretching and that their contribution determines FIN, illustrating the complexity of flow in polydisperse mixtures of homopolymers and the critical role of the related phenomena of shear thinning and constraint release. Bidisperse blends, like those studied here, are a useful starting point in understanding these complex, nonlinear, phenomena in polydisperse polymers. The results presented clearly show that as the molecular weight of the matrix increases so does the critical work and (in a nonlinear manner) the total strain to form nuclei.

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