

Unexpected Shish-Kebab Structure in a Sheared Polyethylene Melt

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Scanning electron micrographs of a solvent-extracted sheared polyethylene (PE) blend revealed, for the first time, an unexpected shish-kebab structure with multiple shish. The blend contained 2 wt% of crystallizing ultrahigh molecular weight polyethylene (UHMWPE) and 98 wt% of noncrystallizing PE matrix. The formation of multiple shish was attributed to the *coil-stretch* transition occurring in sections of UHMWPE chains. Synchrotron x-ray data provided clear evidence of the hypothesis that multiple shish originate from stretched chain sections and kebabs originate from coiled chain sections, following a diffusion-controlled crystallization process.

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The subject of flow-induced crystallization in polymer melts is extremely important in polymer processing. This is because the final properties of polymers are direct consequences of the crystalline morphology, where the final morphology is often dictated by the early structure formation under flow [1–4]. The well-documented shish-kebab structure has been recognized as the fundamental form of the initial structure in crystalline polymers induced by flow, which was first observed in dilute polymer solutions [5,6]. This structure consists of a *single* extended-chain central fibrillar core (termed “shish”), which may consist of a single-crystal structure [5,6], a mesomorphic phase [7], or even a single aligned chain [8], and an assembly of folded-chain crystalline lamellae (termed “kebabs”) oriented perpendicularly to the shish [9]. However, in polymer melts, the exact molecular mechanisms and the nature of the shish-kebab formation still remain unclear, especially at the early stages of flow-induced crystallization.

The formation of the shish-kebab structure in a dilute polymer solution under extensional flow can be best explained using the concept of *coil-stretch* transition proposed by de Gennes [10]. Based on the kinetics theory, de Gennes predicted that a polymer chain, stretched from its equilibrium coiled state, follows an *S*-shaped diagram of chain extension versus deformation rate. In steady flow, the chain adopts one of the two stable molecular conformations: a highly stretched state or a compacted coiled state. The elegant experimental works of Keller and Kolnaar proved the existence of the *coil-stretch transition* in dilute solutions under elongational flow, where a sudden upturn in birefringence was observed at a critical strain rate. Recently, using simulation methods, Dukovski and Muthukumar have demonstrated that the calculated free energy landscape for a dilute polymer solution (with monodisperse chains) under extensional flow showed two populations of conformations [11], stretched and coiled, at a given flow, where the stretched chains crystallize into shish and the coiled chains are subsequently adsorbed onto the shish and form kebabs.

Keller and co-workers reasoned that the *coil-stretch* transition should also exist in an entangled polymer melt [1,12,13] because the observed flow-induced morphologies in pure melts were very similar to those observed in dilute solutions. Keller and co-workers argued that the final morphology served as a pointer to the preexisting state of chain extension in flow and vice versa. In other words, the shish-kebab morphology was the signature of the *coil-stretch* transition. Thus, in a polymer with a broad distribution of molecular weights, only the chains longer than the critical molecular weight (M^*) can remain in the stretched state after cessation of flow, while the chains shorter than M^* will relax back to the coiled state in a very short time. Recently, our laboratory has also verified the concept of M^* in polymer melt under shear flow using rheo-x-ray techniques [14,15].

In this Letter, we present experimental results of a sheared polyethylene (PE) blend that revealed, for the first time, an unexpected shish-kebab structure with multiple shish. In addition, the *in situ* x-ray study showed a diffusion-controlled growth of kebabs. The blend contained 2 wt% of ultrahigh molecular weight polyethylene (UHMWPE) and 98 wt% of low molecular weight PE copolymer matrix. The PE copolymer, consisting of the random sequence of ethylene and 2 mol% hexane, had a weight-averaged molecular weight (M_w) of 50 000 g/mol and a polydispersity (MWD) of 2.0 (designated as MB-50k); UHMWPE had a M_w of $5\text{--}6 \times 10^6$ g/mol and a MWD of about 9. The chosen experimental temperature was 128 °C, where the MB-50k matrix remained noncrystalline, allowing investigation of only the crystallization behavior of UHMWPE under flow. The polymer blend was prepared by solution blending (in xylene) to ensure the intimate mixing at the molecular level. *In situ* rheo-SAXS (small-angle x-ray scattering) and rheo-WAXD (wide-angle x-ray diffraction) measurements were carried out at the X27C beam line in the National Synchrotron Light Source, Brookhaven National Laboratory, using a Linkam CSS450 shear system. The details of this modified

shear apparatus and the typical experimental conditions have been described elsewhere [14].

Figure 1 shows selected 2D SAXS and WAXD patterns of the MB-50k/UHMWPE (98/2) blend collected at different times after cessation of shear (shear rate = 60 s^{-1} , shear time = 5 s, $T = 128 \text{ }^\circ\text{C}$, and the flow direction is vertical). The initial SAXS pattern (e.g., $t = 30 \text{ s}$) exhibited an equatorial streak and no meridional maxima. The meridional maxima appeared only at a later time (at about 75 s, data not shown), which was similar to the pattern at $t = 135 \text{ s}$. The equatorial streak is due to the formation of shish, containing extended-chain PE crystals, oriented parallel to the flow direction. The meridional maxima are due to the formation of kebabs, oriented perpendicularly to the flow direction. At the end of the experimental time frame (i.e., $t = 2610 \text{ s}$), a very clear pattern, consistent with the shish-kebab structure was seen in this blend. The WAXD pattern obtained at $t = 30 \text{ s}$ showed a pair of sharp (110) reflections on the equator, confirming the instantaneous formation of extended-chain shish crystals aligned parallel to the flow direction. With the increase in time, the subsequent kebab crystallization of coiled chains resulted in the superposition of (110) and (200) arclike equatorial reflections on the initial linelike (110) reflection with increasing intensity and decreasing orientation (e.g., $t = 135 \text{ s}$ in Fig. 1). Furthermore, the appearance of equatorial (200) reflections indicated that the UHMWPE kebabs were flat instead of twisted [1].

Figure 2 shows the time evolution of the total crystallinity and corresponding values for shish and kebabs (these values were estimated using the combined SAXS-WAXD method [16]) in the PE blend at $128 \text{ }^\circ\text{C}$ after cessation of shear. The total crystallinity estimated at the end of the experimental frame was around 2%, which was about the same as the UHMWPE concentration. At the temperature of the SAXS-WAXD experiment, the low molecular weight component did not crystallize, as evidenced by the separately obtained differential scanning calorimetry

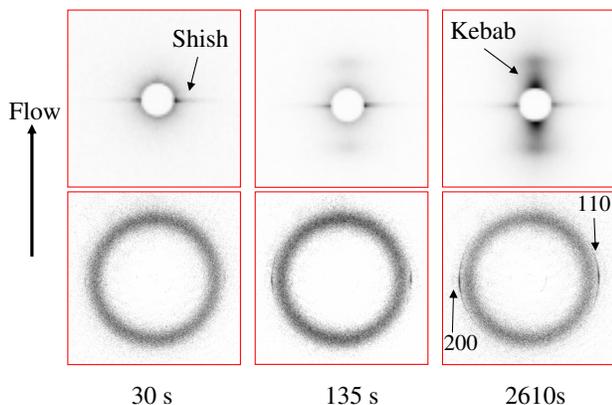


FIG. 1 (color online). Selected 2D SAXS (top) and WAXD (bottom) patterns of MB-50k/UHMWPE (98/2) after cessation of shear (shear rate = 60 s^{-1} , shear time = 5 s, $T = 128 \text{ }^\circ\text{C}$).

thermogram. Therefore, it was assumed that the value of total crystallinity was mainly aroused from the crystallization of UHMWPE chains (and nearly all of UHMWPE chains in the melt crystallize). In other words, the shish-kebab entities, observed by SAXS-WAXD, primarily contained the UHMWPE chains. Also, it was seen that the crystallinity of the shish component ($X_{c,\text{shish}}$) increased rapidly and reached a small plateau level ($X_{c,\text{shish}} \approx 0.08\%$ at $t = 30 \text{ s}$, $X_{c,\text{shish}} \approx 0.15\%$ at $t > 75 \text{ s}$), while the crystallinity of kebabs dominated the total crystallinity growth ($X_{c,\text{kebab}} \approx 1.85\%$ at $t = 2610 \text{ s}$).

Based on results of polymer blend systems containing similar noncrystallizing PE copolymer matrices (MB-50k and MB-100k with a M_w of 100 000 g/mol) and 10 wt % of a crystallizing linear PE homopolymer (MB-250k with a M_w of 250 000 g/mol and a MWD of 2.0) using the same experimental conditions as this study, we estimated that the M^* value of PE at the chosen experimental conditions should be around the order of 250 000 g/mol [17]. Thus, the UHMWPE chains in the blend are above the M^* threshold and can undergo the *coil-stretch* transition due to the imposed flow. But, do all UHMWPE chains exhibit a fully stretched state under shear and form shish? It was seen above that the contribution of shish to the total crystallinity of shish-kebab entities, which resulted mainly from the crystallization of UHMWPE chains, was only about 8%. Hence, the percentage of UHMWPE chains in a fully extended state could not have been large. In fact, the majority of the chains were in the coiled, entangled state, which formed kebabs. In the deformed melt, if the ratio of the stretched and coiled sections corresponds to the ratio of the shish and kebabs, it should be about 1:12.5. Therefore, we conclude that only certain sections of a UHMWPE chain have undergone the *coil-stretch* transition, not the entire chain. The stretched sections in UHMWPE are

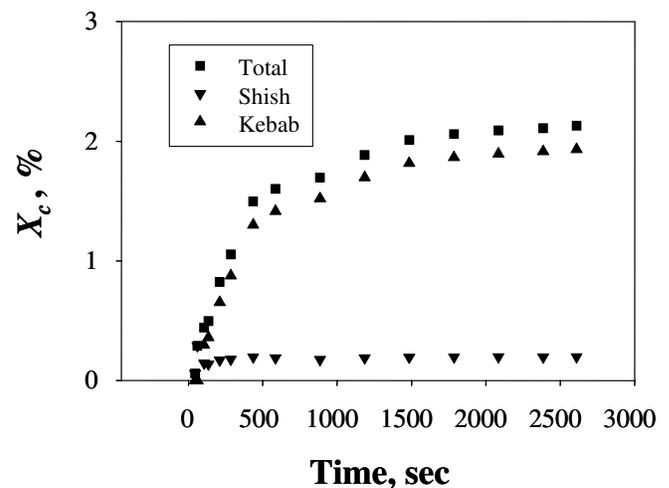


FIG. 2. Time evolution of the total crystallinity (X_c), values of crystallinity of shish and kebabs for MB-50k/UHMWPE (98/2) at $128 \text{ }^\circ\text{C}$.

responsible for the shish formation and the coiled sections are responsible for the kebab formation. The scanning electron microscopy (SEM) micrographs, presented below, provided direct visual evidence for the above.

The recovered sheared sample at the position of the x-ray illumination was subsequently treated with hot toluene at 100–105 °C to extract the shish-kebab moieties (the PE copolymer matrix dissolved in hot toluene, while UHMWPE crystallites were retained). The hot PE/toluene solution with insoluble UHMWPE residues was filtered by a 0.5 μm polytetrafluoroethylene filter at 100 °C. The UHMWPE residues were further washed by fresh toluene at room temperature twice and were dried in a vacuum oven for 24 h. The dried sample was directly examined by Zeiss DSM 982 Gemini field-emission SEM at an accelerating voltage of 2.0 kV. A typical high-resolution SEM image of the solvent-extract shish-kebab entity is shown in Fig. 3. Unexpected features in the UHMWPE shish-kebab structure can be clearly observed. First, multiple shish, which have a diameter of several nm, connecting adjacent kebabs, are present. This morphology is quite different from the conventional view of the shish-kebab structure, where only one shish is envisioned to be present [9]. It appears that some shish are connected between different kebab sections but others are not. Second, the shape of the kebabs clearly resembles that of folded-chain PE lamellar crystals with distinct facets. It appears that the growth of adjacent kebabs follows a preferred orientation rather than a completely random manner. Third, the average size of the kebab lamellae is about the same. Clearly the kebabs must have nucleated at about the same time.

SEM micrographs of lower resolution showed that the length of the shish-kebab structure varied substantially—the length of the longer one exceeded 10 μm , while the length of the shorter one was in the sub- μm range. The average radius of gyration of the UHMWPE chains in the melt is around 110 nm [18] and the average extended-chain length is about 25 μm . The wide distribution of the shish-kebab length is due to the distribution in extension of deformed chains; all chain sections (between the entangle-

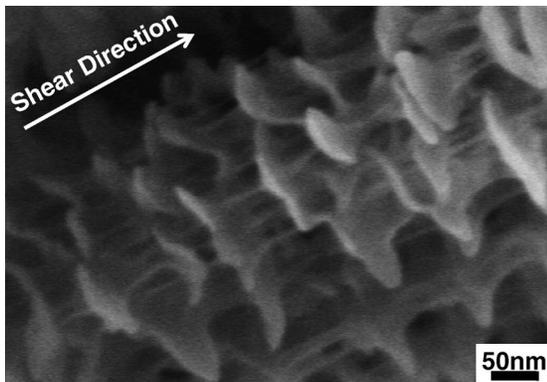


FIG. 3. A typical SEM image of toluene-extracted UHMWPE crystallites with a shish-kebab structure having multiple shish.

ment points) of some chains are stretched, while only certain sections of the others are stretched. Note that the variation of the flow field, particularly the total strain along the thickness direction in the parallel-plate rheometer (the strain was 300 near the rotating plate and 0 near the stationary plate) is also, partly, responsible for the above. Using a method proposed by Ruland [19], the average length of the shish-kebab structure was estimated from the equatorial streak in SAXS (e.g., the horizontal scattering streak at $t = 30$ s in Fig. 1). Results indicated that the average shish length immediately after shear ($t = 30$ s) was around 630 nm, rapidly decreasing to 515 nm after the kebab formation, and finally reaching 490 nm at the end of the experimental time frame. The significantly lower values of the shish length are evidence of full extension in sections of UHMWPE chain rather than its entire contour length. The decrease in calculated values of the average shish length may be attributed to (i) the relaxation of chain ends and loss in the average degree of orientation after cessation of shear, (ii) the development of kebabs imposing a local stress at several discrete points along the shish and relaxing its orientation with respect to flow direction, thus, “shortening” the overall projection length of the shish determined by x-ray data analysis, and (iii) the formation of a shorter shish-kebab from the less stretched chains at the later times.

Using the Ruland streak method [19], the average kebab diameter (D) was estimated from the meridional streak in SAXS (e.g., the vertical scattering streak at $t = 2610$ s in Fig. 1). The calculated kebab growth rate [$G(t) = dD(t)/dt$] as a function of time is shown in Fig. 4, which exhibited the diffusion-controlled kebab growth [i.e., $G(t) \propto t^{-1/2}$]. The secondary nucleation theory of polymer crystallization in a quiescent state predicts a constant spherulitic growth rate, where the mass diffusion is not the limiting barrier. However, Hobbs’s recent atomic force microscopy observations [20] of the kebab growth contradict the above and are consistent with this study. It is also

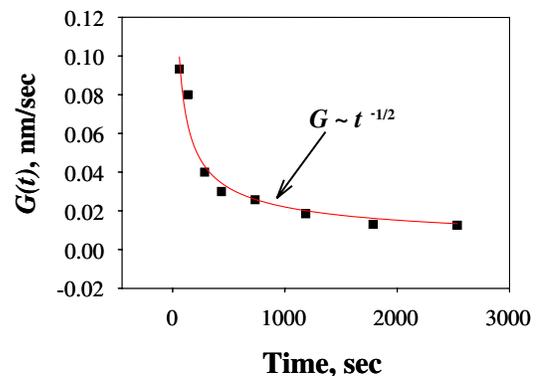


FIG. 4 (color online). The kebab growth rate [$G(t)$] as a function of time, determined by the Ruland streak analysis [19] of the meridional streak in SAXS. The solid line represents the $G(t) \propto t^{-1/2}$ relationship.

instructive to point out that the simulation work of the early stage shish-kebab formation in elongational flow by Dukovski and Muthukumar [11] clearly showed that the kebab growth was significantly influenced by the rate of addition or diffusion of chains. Thus, the diffusion-controlled kebab growth in the PE blend is, although not totally unexpected, another significant finding of the present work.

We envision that only certain sections of the chain exhibit *coil-stretch* transition determined by the initial conformation of chain segments within these sections. In other words, the disentanglements of UHMWPE chains in the blend, if any, were extremely low. If we consider an “entangled thread” upon stretching, a closer observation will show few straight sections with short thread lengths aligned parallel to each other and the remaining parts of the thread with entanglements or globular sections. This hypothesis is consistent with the observation of multiple shish in SEM micrographs. The instantaneous formation of shish as observed in SAXS supports the mechanism of its formation based on the concept of abrupt *coil-stretch* transition that occurs only in sections of the chain rather than in its entire contour length. Simulation results of Hu *et al.* [8] demonstrated that even a single aligned chain can act as a “template” or shish for polymer epitaxy or crystallization of kebabs. The generation of less thermodynamically stable folded-chain kebab lamellae from the partial surface of more thermodynamically stable extended-chain multiple shish also favors the mechanism of kebab formation through the adsorption process proposed by Dukovski and Muthukumar [11], rather than the conventional arguments based on the epitaxial growth of lamellae around the shish or the initiation of the free chain ends (cilia)/protrudes from the central shish surface [21].

In summary, we have presented *in situ* x-ray and *ex situ* SEM results in a binary PE blend containing noncrystallizing MB-50k (98 wt%) and crystallizing UHMWPE (2 wt%) under shear, which clearly indicated the shish-kebab formation in the initial stages of flow-induced crystallization. The solvent-extracted UHMWPE residues after shear revealed the existence of multiple shish, instead of a single shish, in the shish-kebab structure. Upon the application of flow, sections of UHMWPE chains undergo the abrupt *coil-stretch* transition. The stretched sections form shish, while the coiled sections are absorbed onto the shish and form kebabs (folded-chain lamellae), following a diffusion-controlled growth process. The results led to new insights into the structure and formation of polymer shish-kebabs under flow: specifically (i) stretched chain

sections arranged in a bundle form not one but multiple shish and (ii) kebab growth rate is diffusion-controlled.

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