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Feature Article

Shish–kebab of polyolefin by “melt manipulation” strategy in injection-molding: A convenience pathway from fundament to application

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ABSTRACT

Due to both theoretical and practical importance, the formation mechanism of shear-induced shish–kebab and the precise microstructure and molecular composition in shish–kebab have been extensively investigated for many years. However, a systematic review on the manipulation of shish–kebab superstructure in the injection-molded specimens, taken account of combining theoretical understanding, preparation processing, structural/morphological control and macroscopic properties, has rarely seen in the open publication by far. In this article, we will discuss mainly the topic of formation of fine polyolefin shish–kebab superstructure facilitated by “melt manipulation” strategy in injection-molding process. The main body of this review is governed by a logical sequence of (fundamental research)–(injection molding of melt manipulation)–(manipulation of shish–kebab)–(macroscopic mechanical properties). The fundamental understandings of the early stage of shish–kebab crystallization, transition process from random entangled chains network to stable shish–kebab cylindrulite, and the role of long polymer chains on shish–kebab formation, are very helpful for in-depth comprehension of shear-induced shish–kebab in realistic processing. Various highly oriented morphologies with fine shish–kebab superstructure in injection-molded bars of polyolefin melts, including single component polyolefin melt, biphase melts of blend and heterogeneous melts of polyolefin/inorganic filler composites, could be achieved via “melt manipulation” strategy, as demonstrated by the work mainly from our group.

1. Introduction

As a common view of point, the processing techniques of preparing polymer materials play crucial role to determine the macroscopic properties in application. Various forms of polymer product including film, fiber and geometrically regular part can be obtained via adopting appropriate processing means. However, for the optimized macroscopic properties, control/design of morphology and structure, realized through adjusting processing parameters and conditions, seems to be prominently important. In other words, the properties of a polymer product depend not only on the polymer itself, but also more importantly, depend on the processing technology and method used, depending on our capability to manipulate its internal morphology and structure. Undoubtedly, in-depth understanding of structural change and morphological development during polymer processing will make this event in a convenient and proper manner. Therefore, to establish a coherent link of (fundamental knowledge)–(processing of preparation)–(morphological/structural design)–(macroscopic properties) is very meaningful and important for ultimate application of one kind of polymer material (single component species or blend or hybrid or composite). Any items in the link should be not ignored. The main topic of this review is to illustrate a typical example of this methodology that theoretical exploration of shear-induced polymer crystallization could be well used to guide an efficient formation of especially crystalline shish–kebab superstructure in injection-molded processing, thus results in excellent mechanical properties in the prepared molded bars.

It is well known that external extension/shearing field can strongly impact the crystallization behaviors of semicrystalline polymer melts. In a common manner, after experiencing extensional deformation or shearing flow, the crystallization kinetics can be promoted significantly [1,2], and importantly some highly anisotropic crystal superstructures, such as shish–kebab and transcrystallization, can be easily generated from the oriented polymer melts [3]. By contrast with the traditional isotropic spherulites formed upon quiescent crystallization condition, the shish–kebab crystals possess specific anisotropic microstructures, in which the fibrillar-like entity occupies the central position acted as “shish”, while the lamellae perpendicularly crystallize on “shish” upon an epitaxial growth mode, termed as “kebabs” [4]; and that the shish–kebab crystals generated from the oriented polymer

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melts would rather take a preferentially aligned texture that whose longitudinal axis (shish) are parallel to the extension/shearing flow direction [5]. Many practical processing means of polymer products, including injection molding, extrusion, casting film, drawing fiber, etc., will involve intensive extension or shearing flow, which provide high validity of formation of shish–kebab structure in the prepared products. There is a prevalent consideration that formation of shish–kebab can markedly improve tensile strength [6], promote modulus and stiffness [7], decrease permeability [8] and increase thermal stability [9], and the higher the shish–kebab fraction, the better the property reinforcement is achieved. Generating fine shish–kebab superstructure with high volume percentage, realized through processing of polymer melts, has enormous values in both academy and industry, should gain more attention. Janeschitz-Kriegl et al. [1,2,10–12] constructed rheological apparatus to evaluate polyolefin crystallization behaviors under the mimic shearing conditions of realistic processing. In their research, shear flow promoted significantly nuclei density and nucleating kinetic, but yet, it was hard to efficaciously generate large amount of anisotropic precursors of shish–kebab, implied that formation of fine shish–kebab structure under the realistic processing conditions was difficult. The formation mechanism of shear-induced shish–kebab and the precise microstructure and molecular composition in shish–kebab have been extensively investigated in the past literature [13,14], especially a systematic, profound review focused on shear-induced shish–kebab precursor in entangled polyolefin melts has been contributed by Hsiao et al. [15], another one concerned mainly the flow-induced smectic mesophase before polymer crystallization has been demonstrated by Li and de Jeu [16]. However, to the best of our knowledge, a systematic review on the manipulation of shish–kebab superstructure in the processing prepared specimens, taken account of combining theoretical understanding, preparation processing, structural/morphological control and macroscopic properties, has rarely seen in the open publications by far.

For various melt processing means, injection molding may be the most convenient and efficacious one to prepare the polymer parts with regularly geometric profiles. Its parameters are easily modulated and controlled, and that its reproducibility is excellent. Since injection molding is extensively adopted in industrial fabrication, the morphological/structural control and structure–properties relationship in injection-molded parts have gained more and more attention from the academic communities. In a conventional injection-molding process, although intensive shearing can induce a high degree of melt orientation at the beginning stage of injection, the melt solidification performed upon quiescent condition frequently accompany a strong relaxation of oriented chains. A typical skin-core bi-layered structure is usually obtained through conventional injection molding. The low amount of oriented crystalline structures emerges in the skin region with less cross-section area, while the large amount of isotropic crystals (spherulites) exists in the core region with large cross-section area. So, it is difficult to form the shish–kebab superstructure, and the fraction of oriented crystals is very low, via conventional injection molding. In order to overcome this shortcoming, a modification technique has been developed, which was named as “melt manipulation” or “in-process morphology control” [17]. The key merit of “melt manipulation” strategy is that the external shearing is imposed on the polymer melts during the cooling solidification, which would reserve the degree of oriented morphology/structure of melts as much as possible, thus affords a high possibility to the formation of shish–kebab in the prepared molding parts. On the other hand, polyolefin is a kind of typical semicrystalline polymer with regular chain configuration and strong crystalline ability, which often serves as the ideal candidate for the research of polymer crystallization because of its facility in estimating the crystallization behaviors. For the open publications, polyolefin is most frequently chosen as the research object for shear-induced polymer crystallization [18,19]. The reasons may be that shearing easily induces orientation of polyolefin chains; the crystallization kinetic and grown mode can be adjusted conveniently; the crystallographic structure is relatively simple, and more importantly, their wide application.

In this review, we will focus our attention mainly on the topic of formation of fine polyolefin shish–kebab superstructure facilitated by “melt manipulation” strategy in injection-molding process. The main body of this review is governed by a logical sequence of (fundamental research)–(injection molding of melt manipulation)–(manipulation of shish–kebab)–(macroscopic mechanical properties), and organized as follows:

(1) The theoretical basis of shear-induced polyolefin shish–kebab will be elucidated firstly. A simple review of progress on the mechanism of shear-induced formation of shish–kebab is presented in Section 2.1. Section 2.2 includes some recent new findings on the precise microstructure of shish–kebab.
(2) The characteristics and functions of “melt manipulation” in injection-molding process are introduced in the third section. Moreover, some representative examples for morphological control in injection-molding process are also illustrated in the same section.
(3) “Melt manipulation” induced fine shish–kebab superstructure in various polyolefin melts, including single component polyolefin melt (Section 4.1), biphase melts of blend (Section 4.2) and heterogeneous melts of polyolefin/inorganic filler composite (Section 4.3).
(4) The effect of shish–kebab on properties reinforcement and the relation of structure–properties in the injection-molded bars obtained via “melt manipulation”, will be exhibited in Section 5.
(5) In the end, the conclusions of this topic are emphasized, and some perspectives involved this research field will be proposed.

2. Progress in fundamental understanding of shear-induced shish–kebab

According to the methodology proposed in Section 1, before demonstrating the control of shish–kebab morphology by injection molding of melt manipulation, some new research progresses involved shear-induced shish–kebab in polyolefin melts, should be clarified. While in this section, we would like to: firstly, briefly elucidate the progresses of the formation mechanism of flow-induced shish–kebab superstructure in semicrystalline polymer melts; secondly, illustrate some representative findings about the internal microstructure and molecular composition of shish–kebab. The illustrated investigations in this section are theoretical basis for well understanding and interpreting the emergence of shish–kebab superstructure in various injection-molded bars, which will be profoundly discussed in the later sections.

2.1. Brief review on the formation mechanism of flow-induced shish–kebab in polyolefin melts

Based on the rheo-birefringence investigation conducted on the dilute polymer solution, Keller and coworker [4,20,21] proposed quite a early formation mechanism of flow-induced shish–kebab. The representative viewpoints in their proposal were: an abrupt coil–stretch transition on polymer chains conformation would occur with increasing extension deformation rate, which resulted in the fully extended polymer chains, subsequently acted as the shish entities in the later crystallization stage; under a certain strain rate, only the longest fraction of chains, whose molecular weight was higher than a critical value (M^*), could undergo the abrupt coil–stretch transition; the slower the strain rate, the higher the critical M^* for threshold of coil–stretch transition was required. Simulations of shish–kebab formation in extensional solution were consistent well with Keller's mechanism. Simulation by Dukovski and Muthukumar [22] indicated that the coil–stretch transition was discontinuous; two distinct conformations of chains coexisted: the long chains were extended by extensional flow and would crystallize into shish, while the short ones remained coil and crystallized in folded-chain lamellae acted as kebab. Hu et al. [23] simulated a single extended chain induced shish–kebab crystallization in solution. Their research approved that a single extended chain was enough for causing epitaxy, implied that the model of extended chain originated shish–kebab formation was thermodynamically favorable.

As to the case of polymer melts, the theoretical mode of shear-induced shish–kebab seems to be more complicated than dilute solution status, because importantly numerous entangled sites existing between macromolecular chains may hinder conformation changes of chains, such as coil–stretch transition. Recently, aided by some advanced in situ research techniques, such as rheo-wide angle X-ray diffraction (WAXD) [24,25], -small angle X-ray scattering (SAXS) [25,26], -small angle light scattering (SALS) [27], -polarized optical microscopy (POM) [28,29] and -birefringence [30] and time-resolved atomic force microscopy (AFM) [31], some novel modifications were made on Keller's mechanism to describe reasonably the shish–kebab formation in the sheared semi-crystalline polymer melts. Logically, the shear-induced mesophase before shish–kebab formation and the precursor of shish (the primary nuclei) are extraordinarily important for in-depth understanding of shish–kebab formation mechanism, which has achieved intensive attention. A series of in situ rheo-WAXD/-SAXS experiments have been performed by Hsiao et al. to explore the very early stage of generating shish–kebab in the entangled polyolefin melts after cessation of shearing [25,32–35]. A layered ordering structure was detected in the sheared iPP melt at 175 °C [25], which was probably consisted of assembly of the oriented chain segments especially for the long chains. Since such metastable aggregation of chain segments was noncrystalline, proved by WAXD testing, it was believed to be the precursor of primary nuclei. Otherwise, when the melt temperature was 165 °C (near the nominal melting point of iPP), simultaneous SAXS/WAXD exploring indicated the formation of a noncrystalline fibrillar-like ordering structure, which might be the precursor of the primary nuclei of shish [33]. While a mechanistic pathway for the early stages of crystallization in sheared polymer melts has been proposed a scaffold (network) of oriented structures would be formed, which contained (1) primary nuclei (shish) with linear connectivity along the flow direction, and (2) shish-induced layered crystalline lamellae (kebabs) with poor lateral connectivity [33]. Corresponding to the research works of Hisao et al. [26,33], the earlier mode of shish generated in sheared polyolefin melt was similar to Keller's mechanism in dilute solution status, in which shearing induced the coil–stretch transition of chains in bulk polymer melt and the shish nuclei came from some stretched and paralleled single chains. However, an argument emerged that intensive entanglement and high viscosity retarded drastically the conformation change of polymer chains even if strong shearing deformation was imposed on the polymer melts, thus generating the entirely extended chains realized through the abrupt coil–stretch transition, seemed to be difficult. The precious structure and composition of shish were explored more and more (see the following section), especially after Han et al. [28] suggested that the shish composed a bundle of the stretched entangled network chains, Hisao et al. developed and modified their mechanism as that only sections of a chain undergo the coil–stretch transition in an entangled melt, not the whole chain [13,19]; the precursor structure of shish arises from an extended cooperative chains network [15], in contrast to the case of solution that entirely extended chains are unconnected with other ones at the moment of coil–stretch transition. In a traditional consideration, the growing sequence of shear-induced shish–kebab is that the ordering mesophase composed by assembly bundle of stretched chain segments, crystallizes into fibrillar-like primary nuclei (early shish); early shish further grows into stable shish entity; epitaxial growth of coiled chains on stable shish is to generate kebabs. Otherwise, Li and de Jeu [36–38] have developed a different model of shish–kebab formation in the sheared iPP melts, based on their in situ SAXS/WAXD research. The innovation in their model is that a smectic ordering structure composed by assembly bundles of extended chains with helix conformation emerges before iPP crystallization; the smectic entity can play the role of shish to induce coiled chains epitaxially crystallize into kebabs implied that shish does not always be crystalline state. But the powerful evidence for supporting their model is still unavailable by far, because in a recent publication de Jeu et al. [39] claimed that the SAXS peaks associated with the smectic ordering were actually caused by the presence of the additives of calcium stearate. Obviously, there is still a great challenge for exploring profoundly the very early stage of shear-induced shish formation.

After experienced the mesophase stage of crystalline precursor and the early crystalline stage of formation of primary nuclei (shish), the growing sequence will enter the stage of formation of kebab and fully developed shish–kebab, namely latter stage or full development stage. Combining the in situ X-ray result and the simulation research [22,23], Somani et al. [15] declaimed that the kebab entity mainly arises from the crystallization of coiled chains, which seems to follow a diffusion-controlled growth mechanism. The in situ X-ray exploring indicated a twisted kebab growth mode after formation of the early shish scaffold structure in the entangled HDPE melts, which seemed to be connected with the shear rate that the lower shear rate generated the stronger kebab twisting [40]. In a recent study on crystallization of iPP melts originated from low shear intensity, Han et al. [29] proposed a novel mode for describing the whole process of cylindrulite shish–kebab formation, which begins at network of entangled chains is stretched by shearing deformation to form row nuclei (early shish), and then epitaxial growth of shish–kebab-like cylindrulite takes place on row nuclei. Hobbs et al. [41,42] have implemented visually monitoring formation of shish–kebab in polyethylene melts through in situ AFM observation. A series of temperature-dependent AFM image with high quality showed the kebab crystallization from the extended chains backbone, and the subsequent process of kebab overgrowth and interdigitation indicating that the growth behavior of kebab is dominated by its surrounding environment. In the mechanism proposed by Ogino et al. [43], it was believed that the competition between the relaxation and the nucleation of stretched chains was dominant for generation of shish–kebab structure, and two requirements were necessary: (1) shear rate should be higher than a critical value for threshold of long-time stable orientation; (2) dense entanglements should exist between polymer chains.

Distinguishing clearly the roles of long chains and short chains on the formation of shish–kebab are another important issue that should be resolved for in-depth comprehension of the formation mechanism of shish–kebab. A simulation carried out by Wang et al. [44], on shear-induced crystallization of polymer melt, indicated that the oriented long chains crystallized into shish, while the short chains epitaxially crystallized on the lateral side of shish. Some experimental results also support the common standpoint that the long chains play crucial role on the formation of shish [27,45–47].

Based on a finding that the number density and thickness of shish were increased drastically when the concentration of long chain was close to the critical value for long chains overlap, Seki et al. [30] deduced that oriented thread-like structure arises from a cooperative mode of long chain–long chain overlap. Similarly, Somani et al. [45] found that, in the sheared iPP melts, a larger mount of high molecular weight (HWM) species could shorten significantly the evolution time of shish, which was regarded as a powerful evidence to support that the long chains were contributed to the shish formation. Moreover, in the case of shear-induced polyethylene crystallization, Ogino et al. [27] emphasized the important role of entanglement of long chain species on the shish–kebab formation, which was described as a gel-spinning-like mechanism, because a critical concentration of HWM-PE species was necessary for generating shish-like structure. The value of critical concentration of HWM-PE was promoted with the increase of crystallization temperature, implied that the competition between the relaxation and the crystallization of HWM-PE has remarkable effects on the shish–kebab formation [46]. For the sheared iPP melts with wide molecular weight distribution, Nogales et al. [47] suggested that only the polymer chains whose molecular weigh above the so-called 'critical orientation molecular weight' could become oriented under a certain shear rate, these long chains were most likely to form the shish. Logically, it is reasonable that the subsequent crystallization taken place after the formation of early scaffold of shish–kebab is probably dominated by the lower molecular weight (LMW) species [15], and such LMW species exist possibly as coiled chains.

2.2. Some new findings on the internal microstructure of shish–kebab

For a conventional expectation, the internal microstructure of shish–kebab must be very complicated, there still has a long way to entirely reveal this problem. Fortunately, some prominent progresses have been achieved, which more or less help us to better understand the intrinsic feature of shish–kebab. Through observation of the structural change of shish–kebab of isotactic polystyrene (iPS) during melting, Liu et al. [48] indicated that the complete shish–kebab entity could consist of four components: the central extended-chain micro-shish crystals, the partially extended-chain macro-shish, the overgrown micro-kebabs and the macro-kebabs. A complicated hierarchical structure of polyethylene shish–kebab has been revealed by Kanaya et al. [49], through a combination of small-angle neutron scattering (SANS) and SAXS measurements, which showed that the whole shish–kebab cylindrulite with a radius in the order of micrometers whereas the extended-chains shish with a radius of tens angstroms. Spatially resolving shish–kebab superstructure of iPS by Gutiérrez et al. [50], using simultaneous small- and wide-angle X-ray microdiffraction techniques, provided the structural information from the central to the edge of shish–kebab entity at the different evolution stages of shear-induced crystallization precursor. Interestingly, the high-resolution micrographs of field-emission scanning electron microscopy revealed that a multiple shish structure existed in the shish–kebab of ultra-high molecular weight polyethylene, and individual fibrils of shish were joined by the permeated lamellae (kebabs) [51]. In the AFM observation of iPP shish–kebab by Han et al. [29], amorphous sections (defects) appeared on the shish, which might be arisen from the aggregation of entanglement sites in the stretched chains network. It can, therefore, be concluded that the shish entity could be in the amorphous, mesomorphic or crystalline state [15]. As to the molecular composition in the shish, there is an obvious contradictory existed between different researchers. According to the above description that the long chains play an important role to form the shish, it is easily concluded that the shish composed mainly the HWM species. This supposition has been confirmed by a combination of SANS and SAXS measurements on the shish–kebab of deuterated LWM-PE/hydrogenated HWM-PE blend [27,49]. Nevertheless, in another research involved the shish–kebab in the deuterated and hydrogenated iPP blends, explored by the same SANS techniques, Kimata et al. [52] found that the long chains concentration in the shish was not higher than that in the surrounding environment of the shish. Based on their result, a novel mode for the formation of shish was proposed as the extended long chains might play a catalytic role to attract all types of adjacent chains to participate in the formation of shish. Anyway, more powerful evidences are necessary to resolve this confliction.

3. Melt manipulation in injection-molding process

For a conventional injection-molded bar, along its thickness direction from skin, sub-skin, transition layer to core, there exists a linearly decreased stress gradient and a non-linearly decreased temperature gradient [53] during the injection process, and subsequently the oriented melt subjects to relaxation and solidification (crystallization) under quiescent conditions. The cooperative effect of stress gradient and temperature gradient, as well as the competition between relaxation (disorientation) and solidification (crystallization) results in the complicated morphology and structure in the injection-molded bar. In general, the injection-molded bars have three morphological/structural characters: morphological anisotropy [54], diversity of morphology [55] and hierarchy of structure [56]. Morphological anisotropy implies a preferential orientation along the shear flow will exist more or less, diversity of morphology means variety of phase morphology and crystal morphology, while hierarchy of structure includes various structural species with different dimension scales. In many cases, the oriented degree of injection-molded bar is not high enough for efficiently reinforcing the mechanical properties, though the bar can be regarded roughly as an anisotropic entity. Therefore, formation of highly oriented morphology (molecular chains, dispersed phase domains, crystals, filler particles, etc.) in the injection-molded bar is greatly desired for meeting the requirement in the application of polymer materials. Novel injection-molding techniques have been developed, based on this thinking. For example, ultra-high pressure injection [57,58] approach can produce a bar with high stiffness and high strength. However, this approach requires rigorous processing conditions, which limited its application remarkably.

Another strategy that suppressing the relaxation of oriented chains during melt solidification is so-called, "melt manipulation" or "in-process morphology control" during injection molding, which has been proposed and intensively developed in recent years. A detail description about this molding strategy can be seen in a review by Kikuchi et al. [17]. In general, to achieve "melt manipulation", a macroscopic oscillating shear field is imposed on the polymer melt during the packing stage, resulting in a high orientation of molecular chains and anisotropic morphology. Several advanced injection molding techniques, including shear-controlled orientation in injection molding (SCORIM) [59], vibration- assisted injection molding (VAIM) [60], push–pull processing [61], injection spin processing [62] and the moving boundary technique [63], were developed to induce oriented superstructures in different ways, such as mounted external oscillatory units on molds in the SCORIM process [64], equipped second injection units in the push–pull process [61] and a vibrating injection screw axially in the VAIM process [65]. The structural features of the injection-molded bars prepared by "melt manipulation" processing were very different from that of conventional injection molding. "Melt manipulation" can be as an efficient technique for control of the formation of oriented morphology in the molded bars. For the injection-molded bars of noncrystalline polystyrene (PS), it was indicated by birefringence patterns that the residual stress distribution in the whole bar processed by VAIM was more uniform than in the bar processed by conventional injection molding (CIM) [66], and that VAIM significantly promoted the orientation of PS chains [67]. For the injection-molded bar of glass-fibre reinforced polypropylene prepared through push–pull processing, orientation of fibres parallel to the flow direction was found in the push–pull layer, while fibres were oriented perpendicular to the flow direction in the core region [62]. In the study by Zhang et al. [68], SCORIM approach induced a fibril-like microstructure in the molded bars of UHMWPE and HDPE; on the other hand, Li et al. [69] found that the low-frequency VAIM could bring a laminated morphology consisted of a layered structure with enhanced crystallinity. Moreover, "melt manipulation" can modulate the crystal structure. In the iPP molded bar prepared by SCORIM, the content of γ-crystal was higher, and β-crystal was lower than that obtained via CIM [70].

In our group, a type of SCORIM technique, namely, dynamic packing injection molding (DPIM), has been developed, in which the melt is first injected into the mold and then forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency, during the solidification progressively occurs from the mold wall to the core part. The schematic representation of the structure of DPIM equipment is shown in Fig. 1(a), the geometric sizes of DPIM bar are shown in (b). Its main feature was that the cooling melt was forced to move repeatedly in chamber (6) during packing stage by two pistons (3) and (9) that moved reversibly as an out-of-phase mode. Shear rate was in the order of $10\ s^{-1}$ calculated from the geometry of mold. Compared to the conventional molded bar comprised with a bi-layer skin–core structure, the main feature of molded bar obtained via DPIM is the shear-induced morphology with core in the center, the oriented region surrounding the core and the skin layer in the cross-section areas of the bars. The schematic illustration of the cross-section of dynamic sample is shown in Fig. 2. This morphology is formed due to the temperature difference between the mold and the melt, and due to the shear applied during cooling. The skin is frozen immediately after injection due to the fast cooling, and the orientation of macromolecular chains in the oriented zone can be remained because the melt is forced to move repeatedly during cooling. In the end, the core is cooled down after stopping the imported oscillatory shear. A principal advantage of DPIM technique is that it can reserve the orientation of molecular chains and anisotropy of morphology/superstructure at the best level, on the other hand, impose strong shearing on the polymer melt to disturb or distort the morphology (phase structure), thus to achieve a better control of morphology in the processed bars.

A series of research concerned morphological control of the DPIM bars have been conducted on polyolefin, polyolefin blends and polyolefin/inorganic filler composites in our group. Some interesting subjects are the role of shear on phase–phase miscibility or separation; shear-induced orientation and distortion of phase morphology; phase inversion point impacted by shear flow; shear-facilitated epitaxy of polyolefin blend; shear-induced inorganic filler dispersion and orientation and oriented crystallization in polyolefin/inorganic filler composites; and importantly in this review, manipulation of well-defined shish–kebab superstructure by shearing. PP/LLDPE (50/50) phase morphology evolution from the skin to the core, revealed by AFM measurement, indicated that high shear rate induced partial miscibility in the skin (co-continuous structure), otherwise low shear rate by DPIM results phase separation (sea-island like structure) [71]. Shearing obtained via DPIM could induce drastically oriented and distorted EPDM rubber particles in PP, which altered the impact toughness of the molded bars remarkably [72]. In the molded bars of PP/ethylene vinyl acetate (EVA) blend, the phase inversion would be shifted to lower EVA content when DPIM was adopted [73], a same result was also founded on the immiscible PP/PS blend [74]. Epitaxy of HDPE on iPP was distinctly detected in the DPIM bars of iPP/HDPE blends, which was facilitated by shear flow [75]. Fine transcrystalline structure was found in the DPIM bars of iPP/glass-fiber composite, arisen from shear-induced high orientation of glass-fibers and enhanced interfacial adhesion between iPP matrix and fiber fillers [76,77]. Shear stress field could efficiently enhance nanoclay tactoids exfoliation [78] and ordering alignment [79], as well as form highly oriented crystalline morphology [80] in the DPIM bars of iPP/nanoclay nanocomposites. The latter could be explained reasonably by a so-called shear amplification mechanism

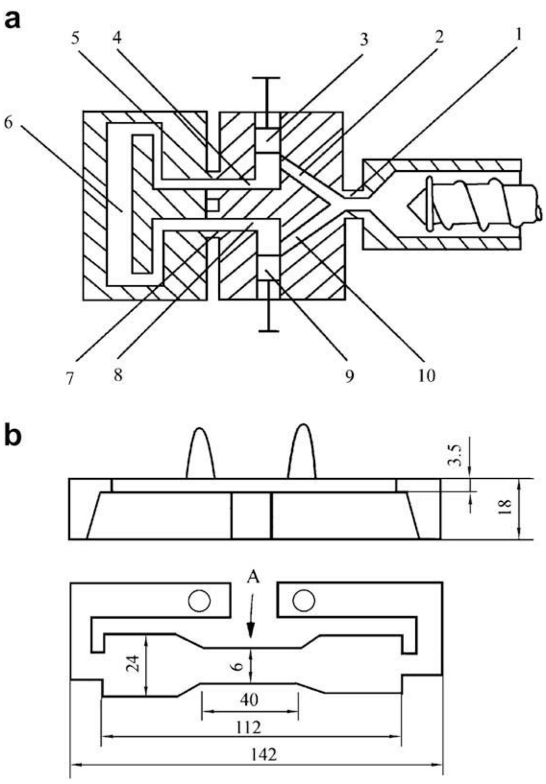

Fig. 1. (a) Schematic representation of dynamic packing injection molding (1) nozzle, (2) sprue A, (3) piston A, (4) runner A, (5) connector, (6) specimen, (7) connector, (8) runner B, (9) piston B, (10) sprue B. (b) Sketch of mechanical test specimen dimensions according to ASTM638M standard.

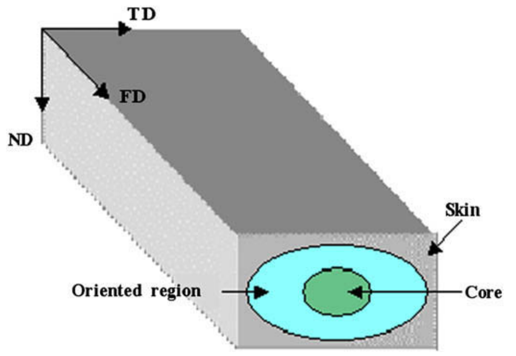

Fig. 2. Schematic illustration of triple complex structure in the processed bar of DPIM. FD, TD and ND represents the flow direction, the transverse direction and the normal direction, respectively.

suggested by Yalcin and Cakmak [81]. As to shear-induced shish–kebab superstructure in the injection-molded bars of "melt manipulation", it will be demonstrated in detail in the following section.

4. Control of polyolefin shish–kebab via dynamic packing injection molding

For conventional injection molding, a cooperative effect of shear flow and temperature gradient can preserve a fraction of oriented morphology in the molded bar. A typical polymer shish–kebab commonly formed in conventional injection molding is schematically illustrated in Fig. 3. It should be noted that the polypropylene shish–kebab is somewhat different from the general ones. There are two types of kebab coexisted on the PP shish–kebab superstructure. The *c*-axis-oriented kebabs are expected to form first, and then a^*-axis-oriented kebabs epitaxially grow on the substrate of *c*-axis-oriented entities [82–84]. The reason for the formation of a^*-axis-oriented kebabs may be that the supercooling melt affords a fast crystallization kinetics suitable for epitaxial growth. After all, the amount of shish–kebab in the CIM bars is less. A microbeam SAXS determination along the thickness of CIM iPP bar indicated that shish–kebab emerges at the sub-skin layer, which may disappear quickly with increase of thickness [85]. Nevertheless, Zhu and Edward [86,87] found that the shish structure is reversed even at deep position of molded bar with the presence of nucleating agent (NA). It was considered that NA may act as a template for facilitating oriented crystallization of polymer [88,89]. Contrasting to CIM, the oriented morphology will be maintained at the best level throughout the whole process of injection molding of "melt manipulation", which ensures a maximum formation of shish–kebab along the sample thickness.

4.1. Shish–kebab generated from the single component melt of polyolefin

Due to the features of sensitive response to shear flow and high flexibility in crystallization, for polyolefin chains both approaches of SCORIM and VAIM can efficiently produce shish–kebab superstructure in the molded bars of single component polyolefin [90–93]. Although shear flow has been exerted on the melt via SCORIM approach, AFM micrographs acquired at different regions of the molded bar of polybutene-1, exhibited that interlocking shish–kebab morphology formed at the shear region whereas the crystals were isotropic spherulites in the core region [91]. In a research by our group [94], the morphology and the effect of molecular weight on the formation of shish–kebab structure were investigated in detail by examining the crystal morphology of DPIM samples of high density polyethylene (HDPE) with different molecular weights, along the thickness of molded bar. A typical crystal morphology evolution along the thickness of the DPIM bar of HMW-HDPE is exhibited in Fig. 4. The fine shish–kebab superstructure is seen from 50 μm to 1200 μm away from surface. One can observe a specific structure of cluster-like crystallites at the depth of 50 μm (SEM image with higher magnification), from which it is found that these crystallites are formed rather by blocks of segments than by a bundle of extended chains.

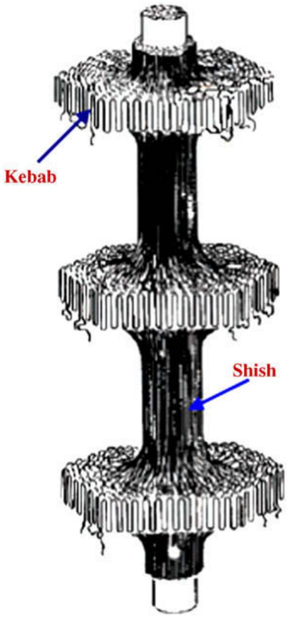

Fig. 3. Schematic diagram of typical shish–kebab structure formed in polymer processing. [Reprinted from Ref. [4]. Copyright (1997) VCH, New York.]

4.2. Shish–kebab generated from the biphase melt of polyolefin blend

In practical manufacture, preparation of polymer alloy (blend) is a convenient and efficient way to obtain new material with excellent synthesized properties. To achieve super polyolefin species, various molded bars of polyolefin blends have been prepared by DPIM technique. Similar to the single component polyolefin, fine shish–kebab superstructures were also found in various polyolefin blends, including PP/LLDPE [95,96], LLDPE/HDPE [97–99], iPP/HDPE [100], HDPE/EVA [101], PP/ethylene cellulose [102] and iPP/poly(ethylene terephthalate) (PET) [103,104]. For the DPIM bar of PP/LLDPE (50/50) blend, PP formed a shish–kebab structure throughout the whole thickness whereas a very unique crystal morphology and lamellar orientation of LLDPE were obtained, with the lamellar stack oriented either perpendicularly or 45–50° away from the shear flow direction [95]. The role of molecular weight of HDPE on the shish–kebab morphology has been inspected in detail [98]. Fig. 5 shows the typical SEM micrographs of LLDPE, LLDPE/HWM-HDPE and LLDPE/LWM-HDPE in the oriented zone of the DPIM bars. For pure LLDPE, it seems shish is absent, the alignment of lamella is loose, and the regularity is low. After LLDPE blending with HDPE, an obvious shish–kebab structure is observed, probably, with HDPE forming the shish and LLDPE lamellae forming the kebab. Interestingly, the thick but short lamellae are observed for sample blended with LWM-HDPE, while the thin but long lamellae are seen for sample blended with HWM-HDPE. It can be thought that the difference in kebab thickness is due to the difference of crystallization capability of LWM-HDPE and HWM-HDPE [99]. LWM-HDPE chains with a higher crystallization capability could form kebabs at high temperatures upon cooling, which would result in thicker lamellae; while HWM-HDPE chains have a lower crystallization capability and form kebabs at lower temperature, resulting in thin lamellae. Similar to the formation model of shish–kebab in sheared iPP/poly(ethylene-*co*-octene) blend melt, recently suggested by Han et al. [105], a schematic mechanism for elucidating the role of molecular weight of HDPE on shear-induced shish–kebab structure in LLDPE/HDPE blend is illustrated in Fig. 6, which taken into account entangled chains network stretched under shear to form bundles of shish, and then epitaxy of kebab took place at the position between adjacent entangled sites. For a PET/iPP blend containing microfibrillar network, the skin–core structure of its DPIM bar is effectively suppressed, and the orientation degrees of crystalline structure along the thickness were almost identical [104]. It was suggested that within

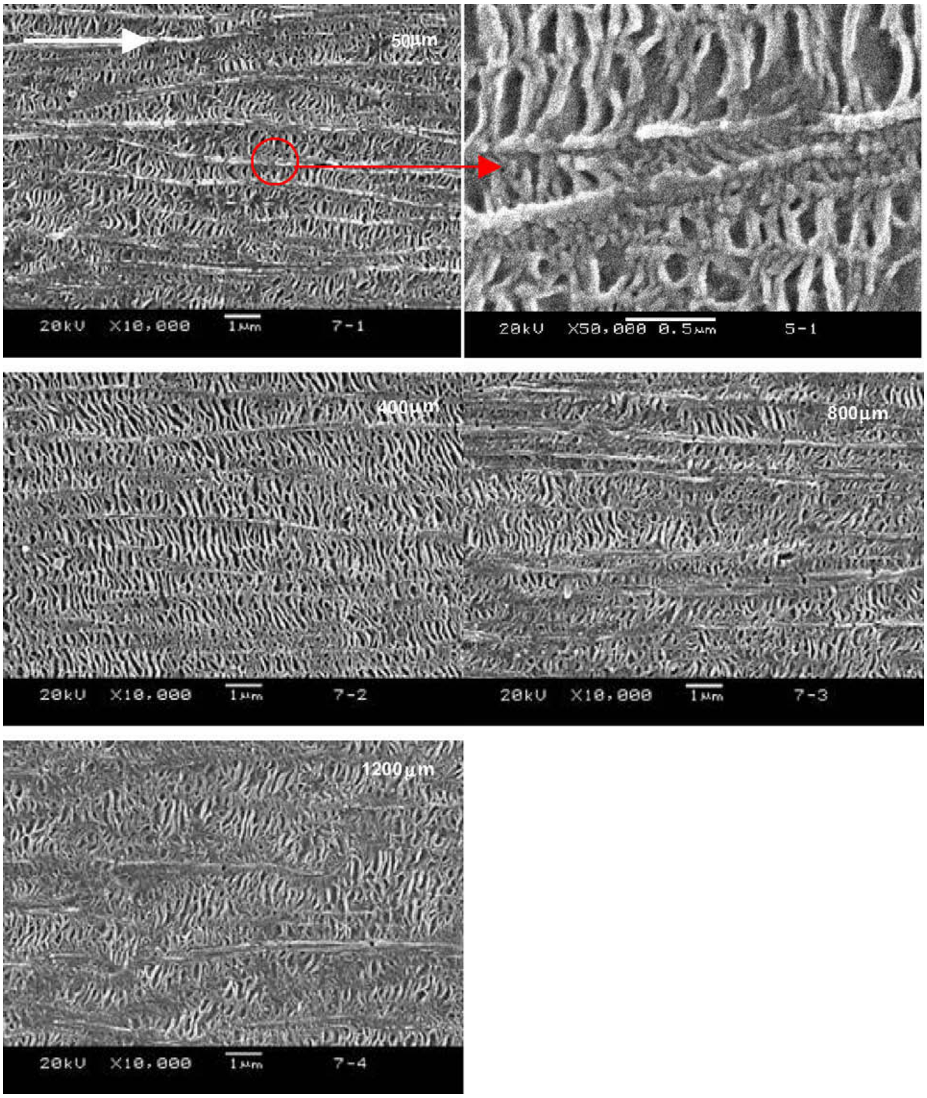

Fig. 4. SEM microphotographs of the etched DPIM bar of HWM-HDPE along the sample thickness. (The numbers on the images indicate the distance apart from the most out surface.) [Reprinted from Ref. [94]. Copyright (2006) Elsevier BV.]

microfibrillar network the shear-induced kebab growth obeyed two ways, as schematically shown in Fig. 7, namely kebab induced by shish and kebab induced by fibril. Moreover, shish–kebab superstructure dispersed in the whole region of DPIM sample, while only emerged in the skin and the intermediated layer for CIM sample.

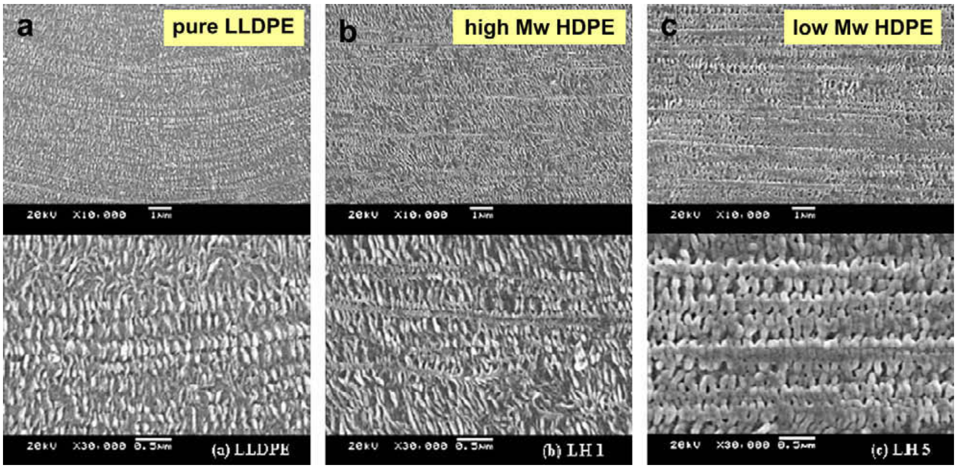

Fig. 5. Oriented crystalline morphology in the oriented zone of the DPIM bars of (a) pure LLDPE; (b) LLDPE/HWM-HDPE (90/10) blend and (c) LLDPE/LWM-HDPE (90/10) blend. [Reprinted from Ref. [98]. Copyright (2008) Elsevier BV.]

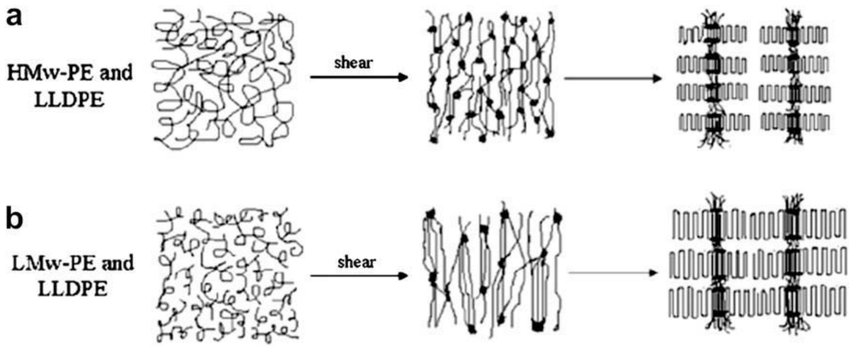

Fig. 6. Schematic mechanism for the role of HDPE molecular weight on shear-induced shish–kebab structure in LLDPE/HDPE blend: (a) high molecular weight and (b) low molecular weight. [Reprinted from Ref. [98]. Copyright (2008) Elsevier BV.]

4.3. Hybrid shish–kebab generated from the heterogeneous melt of polyolefin/inorganic filler composites

Contrasting to the traditional shish–kebab structure in which both shish and kebab are polymer, a novel shish–kebab, named as nanohybrid shish–kebab (NHSK), has gain intensive attention in recent years. For nanohybrid shish–kebab, fibril-like inorganic filler, such as carbon nanotube, will substitute row nuclei of polymer to play the role of shish, while coiled polymer chains epitaxially grow on the inorganic shish to formation kebab. The cause of formation of hybrid shish–kebab could be due to a synergistic effect of shearing and favorable interaction between fibrillar additives and basal polymer, similar to the iPP/aramid fibers system [106]. Moreover, as revealed by Li et al. [107], the grow mode of kebabs is mainly depended on the diameter of inorganic shish: kebabs are randomly oriented on the surface of thick fiber, while for small diameter CNTs, soft epitaxy dictates the parallel orientation between polymer chains and the CNT axis, leading to an orthogonal orientation between CNT and kebab surface. NHSK has exhibited tremendous potential in tailoring polymer properties. Nevertheless, in the published literature, most researchers utilized polymer solution crystallization method to prepare NHSK [107–111]. NHSK achieved through melt processing approach, is rarely seen by far. Although Ezquerra et al. [112] declaimed that determining NHSK structure in the injection-molded bar of poly(butylenes terephthalate)/single-wall carbon nanotubes (SWCNT), a visual evidence is unavailable. Our group has reported recently that hybrid shish–kebab (HSK) structure of polyethylene/SiO_2–MgO–CaO whisker (SMCW) was obtained via DPIM process [113]. The crystal morphologies of injection-molded bar of PE/SMCW composite are presented in Fig. 8. Interestingly, for the oriented layer, as shown in Fig. 8(b), one observes that the whisker is decorated with disk-shaped objects that are periodically located along the whisker axis. These disk-shaped objects are edge-on views of the PE crystal lamellae. Here one observes for the first time that in an injection-molded bar of PE/whisker composites, the whisker forms the central fibril (shish) and the PE crystal lamella (kebab) orients perpendicularly to the whisker axis, thus forming the HSK structure. Fig. 9 shows the structural models for HSK observed in the molded bar of PE/whisker composite and NHSK observed in PE/CNT solution.

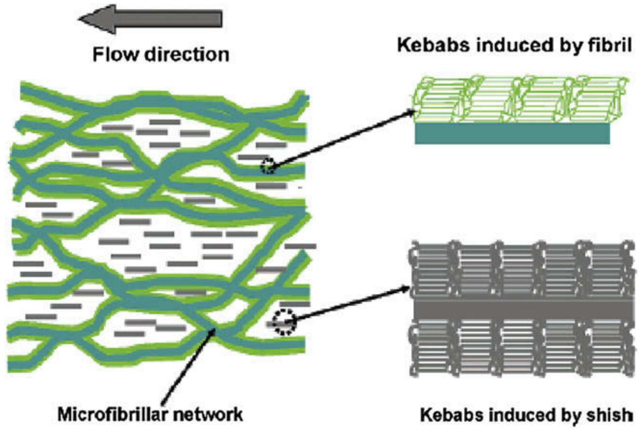

Fig. 7. Schematic sketch of kebabs induced both by shish and by microfibrillar network in injection-molded parts. [Reprinted from Ref. [104]. Copyright (2006) American Chemical Society.]

5. Mechanical properties reinforced by shish–kebab in injection-molded bar

Obviously, macroscopic mechanical properties are essentially determined by internal morphology and structure. In general, the injection-molded bars, obtained via various “melt manipulation” processes, have highly oriented morphology and anisotropic crystal structure. For such oriented molded bars, a remarkable improvement in mechanical properties is commonly expected, especially for stiffness, modulus and tensile strength. The relationship of structure–property in special oriented sample needs to be inspected profoundly, and has attracted intensive attention. An excellent synthesized mechanical property for both tensile strength and Young’s modulus was achieved in the SCORIM bar of iPP [64]. Such improved mechanical properties were attributed to the formation of shish–kebab morphology. Kalay and Bevis [70] found that shearing during SCORIM processing has significantly altered crystal-phase proportion that the content of γ-crystal was increased whereas the β-crystal content was decreased. The γ-crystal is considered to be benefit for enhanced Young’s modulus, whereas the β-crystal is responsible for decreasing Young’s modulus. In the research by our group [98,99], the precise morphology of shish–kebab has been closely corresponded to the tensile behaviors of the DPIM bars of LLDPE/HDPE blends. The representative stress–strain curves for the LLDPE/HDPE (90/10) blends containing various HDPEs with different molecular weights are shown in Fig. 10. The tensile behavior of oriented sample (DPIM bar) is obviously different from that of isotropic sample (CIM bar). A remarkable improvement in tensile strength as well as an obvious depression in ductility has been induced by DPIM. Interestingly, LLDPE blended with LWM–HDPE is found to possess much higher tensile strength than that blended with HWM-HDPE. This phenomenon can be explained reasonably that thicker but shorter kebabs were observed for the LLDPE/LMW-HDPE blend, while thinner but longer lamellae were seen for the LLDPE/HMW-HDPE

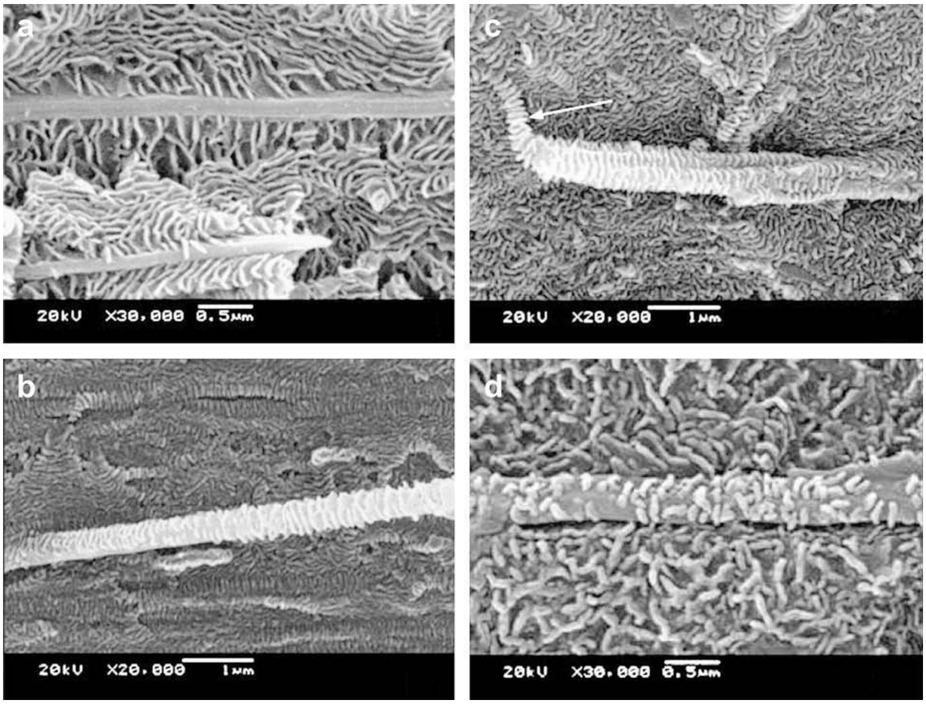

Fig. 8. SEM micrographs to represent the crystallization morphology of the PE/SMCW composites along the flow direction. (a) DPIM sample, skin layer; (b) DPIM sample, oriented layer; (c) DPIM sample, core layer; (d) CIM sample, core layer. [Reprinted from Ref. [113]. Copyright (2007) American Chemical Society.]

blend, which has been demonstrated in Section 4.2. However, a systematic research is necessary in future to construct a clear relation between shish–kebab superstructure and macroscopic properties for the practical molded product with high degree of orientation.

6. Concluding remarks

This review has elucidated in detail a subject of formation of fine shish–kebab superstructure facilitated by "melt manipulation" techniques in injection-molded processing, obeyed a logical sequence of (fundamental background)–(molded processing of approach)–(control of morphology)–(macroscopic properties). The description about theoretical understandings is inclined to early stage of shish–kebab crystallization, transition process from random entangled chains network to stable shish–kebab cylindrulites, the role of long polymer chains on shish–kebab formation, and contribution of long chains on shish and kebab composition. These items are meaningful for in-depth comprehension of shear-induced shish–kebab in realistic processing. "Melt manipulation" is an effective approach to induce highly oriented morphology in the injection-molding bars. Especially, the DPIM technique has been emphasized. The fine shish–kebab superstructure has been found in many molded bars of polyolefin obtained via DPIM process. We believe that a series of research on the formation of shish–kebab in the injection-molding process are important for well controlling of morphology/structure and properties of a polymer product.

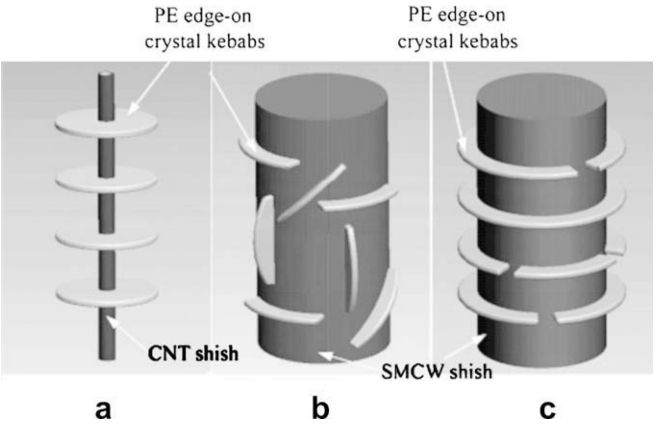

Fig. 9. Schematic representation of (a) NHSK structure observed in PE/CNT solution; (b) and (c) HSK structure observed in the CIM sample and DPIM sample of PE/SMCW composites. [Reprinted from Ref. [113]. Copyright (2007) American Chemical Society.]

Finally, we would like to propose the perspectives of generating shish–kebab upon realistic processing conditions, mainly corresponded to the future work in our group. (1) The roles of long and

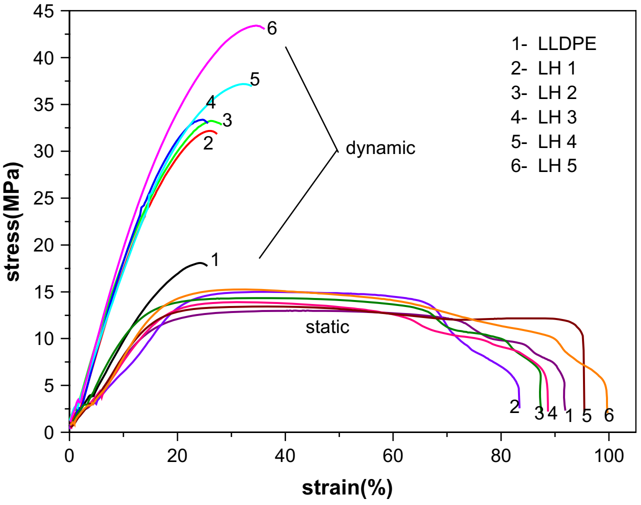

Fig. 10. Typical stress–strain curves for pure LLDPE and LLDPE/HDPE (90/10) blends. (The dynamic samples prepared through DPIM, while the static samples prepared through CIM. From LH1 to LH5, the molecular weight of HDPE decreases gradually.) [Reprinted from Ref. [98]. Copyright (2008) Elsevier BV.]

short polyolefin chains composed shish should be raveled in depth, especially for the biphase polyolefin blends and heterogeneous polymer/filler composites. (2) Conformation transition of chains in entangled polyolefin melt induced by shear flow seems to be very complex, but is also crucial for the formation of shish–kebab superstructure. The mechanism of conformation transition of entangle chains network upon practical injection-molding process will be described more clear. (3) Generally, abruptly changing temperature and stress in injection-molding process may disturb the crystallization of polyolefin, thus impedes the formation of fine crystalline morphology. It has great worth to establish a close link between realistic processing conditions and amount of shish–kebab. (4) At present, all shish–kebab superstructures were identified on the off-line injection-molded bars. Actually, our group has adopted in situ ultrasonic technique to investigate the dynamic processes of phase inversion and orientation during DPIM of polyolefin blends [114–116]. There is high possibility for monitoring shish–kebab formation process during DPIM through some on-line characterization techniques, such as ultrasonic, infrared, laser light scattering, X-ray scattering, etc. These in situ measurement approaches would provide more complete information for understanding profoundly the formation mechanism of shish–kebab upon shear flow conditions of realistic processing.

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