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Research and Analysis on Polypropylene Fiber Orientation Crystallization Technology and Its Impact on Material Strength Properties

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Abstract： Polypropylene (PP) fiber is widely used in textiles, medical applications, geotechnical construction, and composite materials due to its excellent characteristics such as light weight, low cost, and chemical resistance. The final performance of the fiber, especially mechanical properties like strength and modulus, largely depends on its internal microstructure, including crystallinity, crystal morphology, and the degree of molecular chain orientation. Orientation crystallization technology is a key means to regulate the microstructure of polypropylene fibers, thereby significantly enhancing their mechanical properties. This paper systematically reviews the technical principles and development of inducing orientation crystallization in polypropylene fibers through processes such as high-speed spinning and electrospinning. First, the paper elaborates on the crystallographic fundamentals of polypropylene, including crystal forms, crystallization kinetics, and their relationship with molecular chain structure. Secondly, it focuses on analyzing the induction mechanisms of flow fields and stretch fields during spinning on polypropylene molecular chain orientation, nucleation, and crystal growth, discussing the influence of molecular weight and its distribution, and spinning process parameters (such as spinning speed, cooling conditions) on orientation crystallization behavior. Subsequently, the paper summarizes various methods used to characterize the crystalline structure and mechanical properties of polypropylene fibers, such as density gradient column, inverse gas chromatography, X-ray diffraction, and mechanical testing. Based on existing literature research, this paper deeply discusses the formation conditions of the highly oriented shish-kebab structure and its decisive contribution to fiber strength. The results indicate that by optimizing the orientation crystallization process, the crystallinity and crystal orientation of polypropylene fibers can be effectively improved, leading to an order of magnitude increase in tensile strength and elastic modulus. Finally, this paper prospects future research directions for polypropylene fiber orientation crystallization technology, such as multi-component system induced crystallization and green processing technologies.

Keywords: Polypropylene fiber; Orientation crystallization; Strength properties; Crystallinity

1. Introduction

1.1 Research Background and Significance

Polypropylene (PP), as one of the most widely produced general-purpose plastics globally, finds greatly expanded value space in its fiber form. From everyday non-wovens and carpet backing to high-performance geotextiles, filter materials, and composite reinforcements, polypropylene fibers play an indispensable role. However, the mechanical properties, especially strength and modulus, of polypropylene fibers produced by conventional methods, lag behind traditional synthetic fibers like nylon and polyester, as well as increasingly prominent high-performance fibers, which limits their application in high-end fields. [1]

The fundamental factors determining the properties of polymer materials are their microstructure. For semi-crystalline polypropylene, crystallization behavior — including crystallinity, crystal morphology (such as spherulites, shish-kebab), and crystal orientation—is the core affecting its mechanical properties, thermal properties, and dimensional stability. From Figure 1, the characteristic Maltese cross extinction pattern of polypropylene spherulites under polarized light microscopy between crossed polarizers can be observed. Among these, the orientation of molecular chains and crystals is the key bridge connecting processing technology and final fiber performance. [2] During the fiber spinning process, by applying high-speed stretching or shear to the melt or solution, randomly coiled molecular chains can be aligned along the fiber axis and crystallize in this oriented state, forming a highly ordered crystal structure. This "orientation crystallization" process can effectively transfer the high strength and high modulus in the direction of the strong covalent bond backbone of the molecular chains to the macroscopic fiber, thereby achieving a leap in mechanical properties. [3]

Therefore, in-depth research on the orientation crystallization technology of polypropylene fibers, revealing the entire process from molecular chain motion, nucleation, growth to the formation of a stable oriented structure, and precisely establishing the structure-property relationship between process, structure, and performance, has extremely important scientific significance and engineering value. [4]This can not only provide theoretical guidance and technical pathways for developing high-strength, high-modulus polypropylene fibers but also actively promote the high value-added utilization of polypropylene materials and expand their application boundaries.

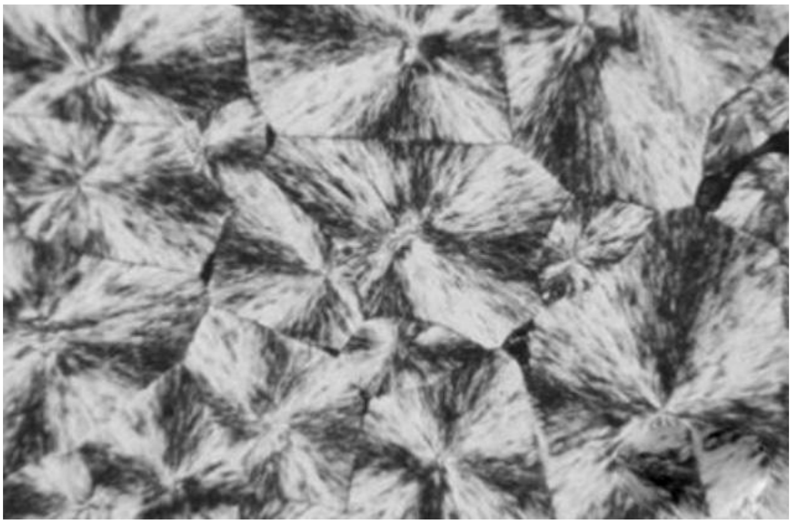

Figure 1 Polarized Light Micrograph of Polypropylene Spherulites

1.2 Domestic and International Research Status

Research on the crystallization and orientation of polypropylene fibers has a long history and continues to deepen with the development of characterization techniques and theoretical models.

In terms of crystallinity characterization, early research focused on developing and applying various measurement methods. Wu Jinhui systematically discussed the feasibility and accuracy of using the density gradient column method to determine the crystallinity of polypropylene fibers, providing basic data support for subsequent research. Fang Shubin, Cai Zhengying, and others pioneered the application of Inverse Gas Chromatography (IGC) for the direct determination of polypropylene fiber crystallinity, and detailed the influence of experimental conditions on the determination results, demonstrating the unique advantages of IGC technology in studying the surface physical properties of polymers. [5]

Regarding the influence of spinning process on crystallization, Lu Fumin's classic research deeply analyzed the profound impact of the molecular weight and molecular weight distribution of the raw material resin on the crystallization behavior of the melt on the spin line during high-speed spinning. [6]This study clearly pointed out that lower molecular weight and narrower molecular weight distribution are conducive to accelerating crystallization kinetics, which has important guiding significance for raw material selection and process optimization in industrial production.

In terms of crystal structure and transformation behavior, Zhang Xiuqin et al. studied the crystallization transformation behavior of syndiotactic polypropylene (sPP) fibers with different initial structures during melting, revealing the influence of thermal history on the stability of complex crystal forms (such as Form I and Form II). Liu Shuangyang et al. successfully prepared isotactic polypropylene (iPP) fibers using electrospinning technology and observed the phenomenon of fibers inducing crystallization in the homogeneous matrix (i.e., the "self-reinforcement" effect), providing new ideas for preparing high-performance PP materials through microstructure design. Figure 2 shows the crystallization transformation process of syndiotactic polypropylene (sPP) fibers with initial structure during melting. [7]

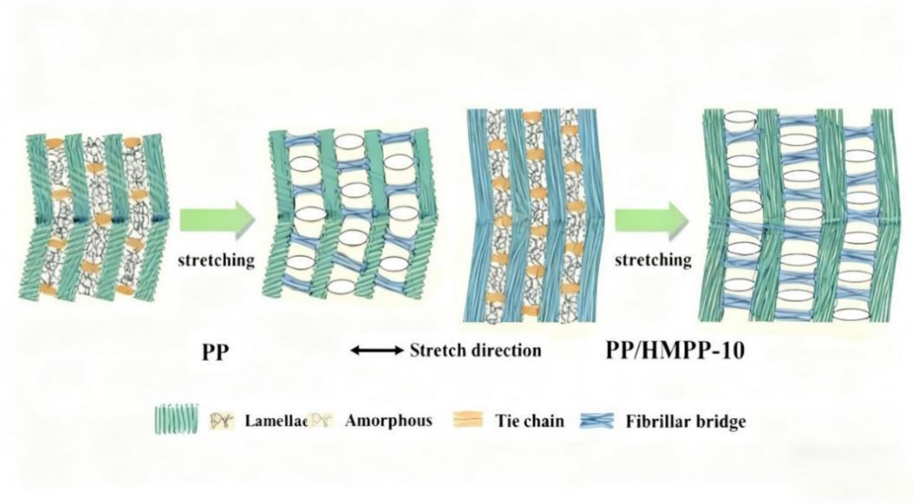

Figure 2 Crystalline transition process of syndiotactic polypropylene (sPP) fibers with initial structure during melting

Furthermore, reports from the industry show technological trends in developing ultra-high crystalline polypropylene fibers and films, reflecting the market's urgent demand for high-performance polypropylene products. In recent years, several graduate theses have also deepened the understanding of the crystallization behavior, kinetics, and microstructure evolution during deformation of polypropylene and its alloys from different perspectives, indicating that research in this field is developing in a more refined and in-depth direction. [8]

1.3 Main Research Content of This Paper

This paper aims to provide a systematic review and summary of orientation crystallization technology for polypropylene fibers and its impact on strength properties. Centering around this theme, this paper will develop the following content:

Systematically elaborate the basic theory of polypropylene crystallization, including its polymorphism, crystallization kinetics and thermodynamics, to lay the theoretical foundation for understanding orientation crystallization. [9]

Deeply analyze the principles, processes, and mechanisms of major orientation crystallization technologies (focusing on high-speed spinning and electrospinning) for inducing molecular chain orientation and the formation of specific crystal structures.

Summarize the key factors affecting orientation crystallization, including the polymer's own structural parameters (molecular weight, tacticity) and external process parameters (spinning speed, draw ratio, cooling rate, etc.).

Systematically review characterization methods for the crystalline structure and mechanical properties of polypropylene fibers, and focus on discussing the intrinsic relationship between oriented crystalline structures (especially the shish-kebab structure) and fiber strength and modulus.[10]

Based on summarizing existing research results, prospect the future development trends and research directions of polypropylene fiber orientation crystallization technology.

2. Theoretical Basis of Polypropylene Crystallization

To understand orientation crystallization technology, it is essential first to grasp the basic principles of polypropylene crystallization. The crystallization behavior of polypropylene is far more complex than that of many other polymers, mainly due to the specificity of its chain structure and rich polymorphism.

2.1 Molecular Chain Structure and Polymorphism of Polypropylene

The monomer of polypropylene is propylene, which has chiral carbon atoms in its molecular chain. Depending on the spatial arrangement of methyl groups, it can be divided into isotactic (iPP), syndiotactic (sPP), and atactic (aPP) types. Among them, isotactic polypropylene (iPP) with high stereoregularity is the easiest to crystallize and is the main raw material for fiber production. Isotactic polypropylene is known to exist in multiple crystal forms such as α, β, γ, and δ (smectic).

The α form is the most common and stable monoclinic crystal structure, with molecular chains adopting a 3/1 helical conformation.[11]

The β form is hexagonal and usually forms under specific nucleating agents or temperature gradient fields; its mechanical properties (such as toughness) differ from the α form.

The γ form mainly appears under low molecular weight or high-pressure conditions and belongs to the triclinic crystal system.

The δ form (smectic) is a metastable crystal form, usually formed under cold drawing or quenching conditions, and transforms into the α form upon heating.

Different spinning and post-treatment processes promote the formation and transformation of different crystal forms. Research by Zhang Xiuqin et al. on syndiotactic polypropylene also shows that sPP similarly has different forms such as Form I and Form II, and its transformation behavior during melting strongly depends on the initial crystallization history.[12]

Table 1 Summary of Characteristics of α, β, γ, and δ (Smectic) Crystal Forms of Isotactic Polypropylene

Characteristic	α form (Alpha Form)	β form (Beta Form)	γ form (Gamma Form)	δ form (Delta Form, Smectic)
Crystal System	Monoclinic	Hexagonal	Triclinic	Smectic (Metastable)
Chain Conformation	3/1 Helix	3/1 Helix	3/1 Helix	Disordered 3/1 Helix
Stability	Most Stable Thermodynamic Form	Metastable	Stable, occurs under specific conditions	Metastable, transforms readily

Main Formation Conditions	Conventional cooling from melt	Specific nucleating agents (e.g., γ-quinacridone) or temperature gradient fields	Low MW iPP, High-pressure conditions	Rapid Quenching, Cold Drawing
Typical Morphology	Spherulites, Bundle Crystals, "Kebab" Lamellae in Shish-Kebab	Spherical or Polygonal Structures	Crossed Lamellar Structure	Initial Ordered Structure in Amorphous Regions
Mechanical Properties	High Rigidity and Strength, Good Overall Mechanical Properties	Typically better toughness than α form, but lower stiffness and strength	Hardness and stiffness between α and β	Poor mechanical properties, soft and easily deformed
Thermal Behavior	Melting Point: 160-165°C	Melting Point: 140-155°C, lower than α form	Melting Point: ~150°C	Transforms to α form upon heating (~70°C+)

2.2 Crystallization Kinetics and Thermodynamics

The polymer crystallization process includes two stages: nucleation and growth. From Figure 3, the two stages of polymer nucleation and growth under polarized light microscopy can be seen.

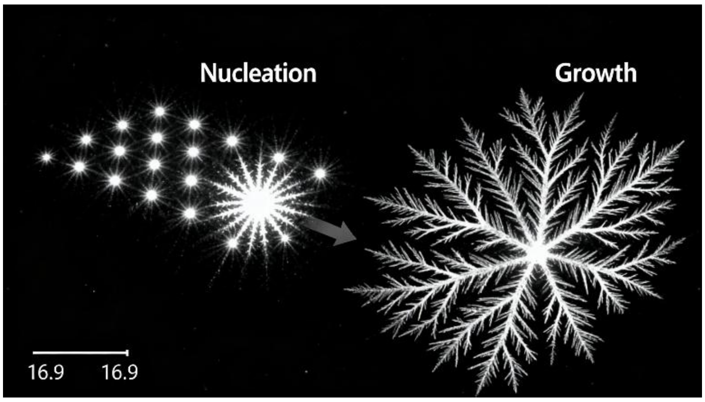

Figure 3 Process of nucleation and growth in polymer crystallization

Nucleation: Divided into homogeneous nucleation and heterogeneous nucleation. In fiber spinning, due to the presence of foreign impurities, heterogeneous nucleation dominates. However, under strong flow or stretch fields, unique flow-induced nucleation occurs. Stretched and oriented molecular chain bundles can act as nucleation sites, greatly increasing the nucleation density. [13]

Growth: The crystal growth rate is closely related to temperature, with a maximum crystallization temperature. The Avrami equation is often used to describe the kinetics of the isothermal crystallization process.

On the spin line, crystallization occurs under non-isothermal, non-equilibrium conditions with velocity and temperature gradients, making the kinetic process more complex. Figure 4 shows a schematic diagram of polymer crystallization under non-isothermal conditions with rising temperature changes. Research by Lu Fumin clearly shows that the molecular weight of the resin directly affects the viscoelasticity of the melt, thereby influencing the deformation history and crystallization rate on the spin line. [14] The low molecular weight portion usually plays a "plasticizing" role, facilitating chain segment movement and crystallization, while the ultra-high molecular weight portion is crucial for forming stable oriented structures.

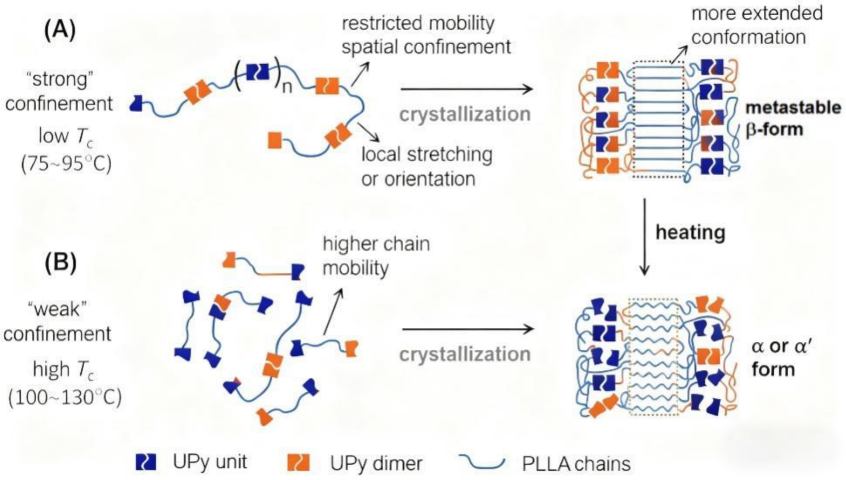

Figure 4 Process of polymer crystallization under non-isothermal, non-equilibrium conditions with velocity and temperature gradients

2.3 Coupling Effect of Orientation and Crystallization

"Orientation" in this context specifically refers to the preferential arrangement of molecular chains or crystallites in space. Under quiescent conditions, iPP melt crystallization usually forms isotropic spherulites. However, during the spinning process, the melt or solution is subjected to shear within the spinneret channels and subsequent stretch deformation, leading to the disentanglement and extension-orientation of molecular chains along the flow direction (fiber axis). [15]This oriented state has two crucial effects on crystallization:

Reducing the nucleation barrier: Highly extended molecular chain segments reduce the critical size required to form stable crystal nuclei, thereby significantly increasing the nucleation rate and density.

Guiding crystal growth: Crystals tend to grow epitaxially on the oriented molecular chains ("Shish"), forming a "shish-kebab" structure where lamellae attach laterally centered on the fiber axis. This structure is a typical feature of highly oriented crystallization and can transfer stress extremely effectively.

The induced crystallization phenomenon observed by Liu Shuangyang et al. in electrospun iPP fibers is essentially due to the pre-formed fibers (with higher orientation) providing a heterogeneous nucleation template for the subsequently crystallizing matrix, guiding the matrix molecules to undergo epitaxial crystallization on them, forming a strong and tough structure penetrating the interface. [16]

3. Orientation Crystallization Technology for Polypropylene Fibers

Orientation crystallization technology is not an independent process but runs through specific fiber preparation processes. This chapter will focus on two key technologies that can effectively induce polypropylene orientation crystallization: high-speed melt spinning and electrospinning.

3.1 High-Speed Melt Spinning Technology

High-speed melt spinning is the most mainstream technology for the industrial production of high-strength polypropylene fibers. The process is as follows: Polypropylene chips are melted, precisely conveyed by a metering pump, extruded through a spinneret to form melt streams, which are rapidly cooled and solidified under the flow field generated by high-speed winding (usually speeds above 3000 m/min), forming as-spun fibers.

3.1.1 Process Principle and Orientation Crystallization Process

In high-speed spinning, orientation crystallization occurs mainly in two regions:

Shear zone inside the spinneret channel: The melt undergoes intense shear flow inside the channel, causing preliminary molecular chain orientation. However, this shear orientation partially recovers at the die swell due to relaxation effects.

Stretch zone on the spin line: This is the key region for forming stable oriented structures. High-speed winding creates a continuous uniaxia flow field on the not yet fully solidified melt streams. This flow field further extends and orients the molecular chains on one hand, and greatly promotes the occurrence of Flow-Induced Crystallization (FIC) on the other hand. As the temperature drops, the melt rapidly nucleates and crystallizes in a highly oriented state, "freezing" the oriented "liquid" or "semi-solid" structure, forming fibers containing a large number of shish-kebab structures. [17]

Lu Fumin's research profoundly revealed the complexity of this process. He pointed out that the crystallization behavior on the spin line is the result of the coupling of temperature, velocity, and stress fields. For resins with a wide molecular weight distribution, the low molecular weight portion crystallizes first, potentially hindering the full orientation of the high molecular weight chain segments, while the high molecular weight portion, due to its long-chain entanglement network, is crucial for withstanding high spinning stress and forming stable oriented structures. Therefore, optimizing the molecular weight distribution is one of the cores for achieving high-strength spinning.

3.1.2 Influence of Process Parameters on Orientation Crystallization

Spinning speed: This is the most critical factor. As the spinning speed increases, the tensile stress and strain rate on the spin line increase, the molecular chain orientation degree significantly improves, the crystallization rate accelerates, and crystallinity also increases. [18]When the speed exceeds a certain critical value, the crystalline structure and morphology of the fiber undergo a qualitative leap, transitioning from being dominated by spherulites to being dominated by shish-kebab.

Cooling conditions: The cooling rate affects the crystallization temperature and process. Too fast cooling may lead to the formation of imperfect smectic crystals, while too slow cooling allows more time for molecular chain relaxation, which is not conducive to maintaining high orientation. Precise control of cooling air temperature, velocity, and position is needed to balance high-speed orientation and sufficient crystallization.

Melt temperature: A higher melt temperature means a lower initial entanglement degree of molecular chains at the exit and a longer relaxation time, which is beneficial for subsequent orientation. But excessively high temperatures can cause degradation.

3.2 Electrospinning Technology

Electrospinning is a technology that uses high-voltage electrostatic force to prepare micro-nano scale fibers. Although its output is low, it has unique advantages in preparing ultrafine fibers, special structure fibers, and studying fundamental crystallization behavior.

3.2.1 Process Principle and Characteristics

The process is as follows: The polypropylene solution or melt becomes charged under a high-voltage electrostatic field (usually several kV to tens of kV), forming a jet at the Taylor cone at the end of the spinneret.

[19]This jet undergoes severe whipping instability in the electric field, is rapidly stretched to the nanoscale, while the solvent evaporates or the melt cools, finally forming a non-woven fiber mat on the collecting device.

3.2.2 Orientation Crystallization Mechanism in Electrospinning

In electrospinning, the strain rate experienced by the jet is extremely high (can reach 10^4 ~ 10^6 s^-1), much higher than traditional melt spinning. This extreme stretching condition provides an ideal environment for high orientation of molecular chains and flow-induced crystallization.

Strong electric field stretching: The extremely high strain rate causes molecular chains to be strongly stretched in a very short time, with almost no time for relaxation, thus being "frozen" in a highly oriented state.

Rapid solvent evaporation/cooling: The rapidity of the process inhibits the formation of large-sized spherulites, forcing crystallization to occur in highly confined nano spaces, usually forming oriented microcrystals or shish-kebab structures.

The research by Liu Shuangyang et al., "Electrospun Isotactic Polypropylene Fibers Inducing Crystallization of Homogeneous Matrix," precisely utilized this high orientation and surface characteristic of electrospun fibers. They found that electrospun iPP fibers could act as efficient nucleating agents, inducing the surrounding unoriented iPP matrix to undergo epitaxial crystallization on their surface, forming a transcrystalline structure. This "self-induced" crystallization effect from fiber to matrix achieves strong bonding between fiber and matrix at the micro scale, is an effective strategy for preparing self-reinforced polypropylene composites, and significantly improves the overall mechanical properties of the material. [20]

3.3 Other Auxiliary Orientation Techniques

In addition to the two main techniques mentioned above, there are some post-treatment or auxiliary methods that can further enhance orientation crystallization:

Hot Drawing: Subjecting the as-spun fiber to multi-stage hot drawing above the glass transition temperature and below the melting point can further orient the molecular chains in the amorphous regions and promote the slip, rotation, and reorganization of existing microcrystals, forming more perfect, higher orientation degree crystal structures. [21] This is a key post-process for improving fiber strength and modulus.

Solid State Extrusion: Extruding the polymer solid from a die at a temperature below the melting point under great pressure, forcing molecular chains and crystals to undergo high orientation in the solid state.

4. Characterization of Oriented Crystalline Structure and Performance Correlation

To establish the structure-property relationship between the orientation crystallization process and the final fiber strength properties, precise characterization of the fiber's microstructure is essential.

4.1 Characterization Methods for Crystallinity

Crystallinity is an important parameter measuring the proportion of the crystalline part in a polymer. For polypropylene fibers, researchers have developed and applied various methods.

Density Gradient Column Method: Wu Jinhui studied this method in detail. Its principle is based on the different densities of crystalline and amorphous regions (crystalline density of iPP is about 0.936 g/cm^3, amorphous density is about 0.856 g/cm^3). By measuring the suspension position of the fiber in the density gradient column, its density can be calculated, and then the crystallinity can be calculated according to the two-phase model formula. This method has simple equipment, but the accuracy is affected by the stability of the gradient column and sample porosity. [22]

Inverse Gas Chromatography (IGC): Fang Shubin, Cai Zhengying and others were pioneers in applying this method to PP fiber research. IGC is a technique for characterizing the physical and chemical properties of solid surfaces. They used polypropylene fiber as the chromatographic stationary phase, and through the adsorption and dissolution behavior of probe molecules in it, calculated the crystallinity of the fiber. Its unique advantage is the ability to probe the crystallinity of the fiber surface, which is the key area for interaction with the external environment (such as interfacial bonding). Cai Zhengying and others also specifically studied the influence of experimental conditions such as carrier gas velocity and probe molecule type on the determination results, establishing the reliability of the method.

Differential Scanning Calorimetry (DSC): By measuring the melting enthalpy of the fiber during heating, and comparing it with the theoretical melting enthalpy of 100% crystalline polypropylene, the crystallinity can be obtained. This method is fast and convenient and is one of the most commonly used methods today. [23] It can simultaneously provide information such as melting temperature and crystallization temperature.

Wide-Angle X-Ray Diffraction (WAXD): WAXD is an authoritative method for studying crystal structure. The diffraction pattern can not only be used to calculate crystallinity but, more importantly, can distinguish different crystal forms and quantitatively analyze the crystal orientation degree.

4.2 Characterization of Crystal Morphology and Orientation

Wide-Angle X-Ray Diffraction (WAXD): By rotating the fiber sample perpendicular to the X-ray beam, a two-dimensional diffraction pattern can be obtained. The crystal orientation factor (Hermans orientation factor) along the fiber axis direction can be accurately calculated based on the azimuthal width of the diffraction arcs; the closer its value is to 1, the higher the orientation degree.

Small-Angle X-Ray Scattering (SAXS): SAXS is used to study structures on the scale of tens to hundreds of nanometers and is an ideal tool for observing the long-period structure of "Shish" (fibrillar crystals) and "Kebab" (lamellae) in the shish-kebab structure. By analyzing the shape and intensity of the scattering pattern, the arrangement, thickness, and long period of the lamellae can be inferred.

Polarized Light Microscopy (PLM) and Scanning Electron Microscopy (SEM): PLM can visually observe large-scale crystal morphologies such as spherulites. SEM, especially after etching the fiber (e.g., using potassium permanganate to etch away the amorphous regions), can directly observe fine crystal topological structures such as shish-kebab.

Table 2 Summary of Features for Common Crystalline Morphology Testing Techniques

Testing Technique	Core Testing Method	Main Research Content / Application Scenario	Key Analysis Results / Judgment Basis
Wide-Angle X-Ray Diffraction (WAXD)	Rotate fiber sample perpendicular to X-ray beam, obtain 2D diffraction pattern	Orientation characteristics of fiber crystals along the fiber axis	Calculate Hermans orientation factor; value closer to 1 indicates higher crystal orientation degree
Small-Angle X-Ray Scattering (SAXS)	Irradiate sample with small-angle X-rays, capture scattering signals	Structures at tens to hundreds of nanometers scale; observing long-period structure of "Shish" (fibril) and "Kebab" (lamellae) in shish-kebab	Analyze scattering pattern shape and intensity; infer lamellae arrangement, thickness, and long period

Polarized Light Microscopy (PLM)	Directly observe sample using polarized light imaging	Morphological features of large-sized crystals like spherulites	Intuitively presents the macroscopic morphology of large-sized crystals
Scanning Electron Microscopy (SEM)	Image via electron beam scanning after etching fiber (e.g., using $KMnO_4$ to etch amorphous regions)	Fine crystal topological structures such as shish-kebab	Directly observe the micro fine structure of etched fiber; clearly reveals the topological morphology of crystals

4.3 Mechanical Property Testing

The strength properties of fibers are mainly evaluated through single filament or multifilament tensile tests, obtaining key indicators including:

Tensile Strength: The maximum stress borne by the fiber at break, commonly in units of cN/dtex or GPa.

Initial Modulus: The slope of the initial linear part of the stress-strain curve, reflecting the fiber's ability to resist deformation, a measure of stiffness.

Elongation at Break: The strain at which the fiber breaks.

4.4 Structure-Property Relationship between Oriented Crystalline Structure and Strength Properties

A large number of studies, including all the references mentioned above, clearly point to a core rule: a highly developed oriented crystalline structure is the fundamental guarantee for obtaining high-strength, high-modulus polypropylene fibers.

Role of Crystallinity: Increased crystallinity means that molecular chains form strong lattice structures through regular arrangement, which can bear loads more effectively. The goal of "ultra-high crystallinity" in reports from Sinopec is precisely to pursue higher mechanical properties. [24] Qian Li's research on the evolution of the microstructure during the deformation of impact polypropylene also showed that the evolution of the crystalline phase directly affects the material's yield and hardening behavior.

Decisive Role of Crystal Orientation: This is the essence of orientation crystallization technology. When crystals (especially their molecular chain axes) are highly aligned along the fiber axis, external loads can directly act on the strong covalent bond backbone, rather than first breaking the weaker van der Waals forces or disentangling entanglements. This causes the fiber to exhibit extremely high strength and modulus in the axial direction.

Strengthening Mechanism of Shish-Kebab Structure: The shish-kebab structure is an ideal micro-model for high-performance fibers. The "Shish" (fibrillar crystal) is formed by highly extended molecular chain bundles, which run through along the fiber axis direction, providing extremely high axial modulus and strength. The "Kebab" (lamellae) act like piers, connecting and stabilizing adjacent Shish, and bearing part of the load. This "rigid yet flexible" hierarchical structure gives the fiber high strength while also possessing certain toughness. The perfection and density of the internal shish-kebab structure formed by high-speed spinning or electrospinning directly determine the upper limit of its final mechanical properties.

Comprehensive Influence: Research by Shangguan Yonggang on polypropylene alloys and Quan Yannan on the induced crystallization behavior of isotactic polypropylene both show that crystallization behavior (including nucleation, growth, and final morphology) is a complex process affected by multiple synergistic factors. [25] The optimized orientation crystallization process, under the premise of determining the molecular chain structure, precisely controls the external fields (flow field, temperature field) to synergistically improve the fiber's crystallinity, crystal perfection, and orientation degree, thereby maximizing the intrinsic mechanical potential of polypropylene. Experiments have proven that through such technologies, the strength of polypropylene fibers can be increased from the conventional 3-5 cN/dtex to over 10 cN/dtex, and the modulus can even achieve orders of magnitude growth.

5. Conclusion and Outlook

5.1 Main Conclusions

This paper systematically reviews the orientation crystallization technology of polypropylene fibers and its impact on strength properties. Based on existing literature research, the following main conclusions can be drawn:

Orientation crystallization is the core pathway to enhance the strength of polypropylene fibers. By inducing molecular chain orientation through the flow and stretch fields during the spinning process and facilitating crystallization in this state, the mechanical limitations of conventional spherulitic structures can be overcome. This enables the formation of highly ordered crystal structures, such as shish-kebab, thereby translating the high intrinsic strength along the molecular chain direction into superior macroscopic fiber performance.

High-speed melt spinning and electrospinning are two effective orientation crystallization technologies. High-speed spinning achieves macro-scale orientation and crystallization of molecular chains through the elongational flow field generated by high winding speeds, making it suitable for the industrial production of high-performance fibers. In contrast, electrospinning utilizes high-voltage electrostatic fields to generate extremely high stretching strain rates, enabling extreme molecular orientation at the nanoscale. This method is particularly suitable for producing ultrafine fibers and conducting fundamental research, while its resulting products can effectively induce matrix crystallization, enabling the fabrication of self-reinforced composites.

The polymer's own structure and process parameters jointly determine the orientation crystallization effect. The resin's molecular weight and its distribution, and tacticity are intrinsic determining factors. External process parameters such as spinning speed, cooling conditions, and draw ratio, through coupling with intrinsic factors, finely regulate the kinetics of orientation crystallization and the final formed microstructure.

Characterization techniques are the bridge connecting structure and performance. Density gradient column, DSC, and IGC can be used for crystallinity analysis, while WAXD/SAXS are indispensable tools for studying crystal orientation and shish-kebab structure. Mechanical property testing ultimately quantifies the performance improvement brought by orientation crystallization. Research shows that the increase in crystallinity and, especially, the great improvement in crystal orientation degree are the fundamental reasons for fibers to obtain high strength and high modulus.

The formation and perfection of the shish-kebab structure is the key to obtaining ultra-high strength properties. This special structure generated by flow-induced crystallization achieves efficient stress transfer in the direction of the covalent bond backbone, and is the microstructural blueprint for developing the next generation of ultra-high strength polypropylene fibers in the future.

5.2 Future Outlook

Although research on orientation crystallization of polypropylene fibers has achieved fruitful results, there are still many areas worthy of in-depth exploration:

Orientation Crystallization in Multi-component and Composite Systems: Future research can pay more attention to the crystallization behavior of polypropylene blended with other polymers (such as polyethylene, polyamide) or composite systems with nano-fillers (such as carbon nanotubes, graphene, nano-cellulose) under orientation fields. These heterogeneous components may act as efficient heterogeneous nucleating agents, or even participate in constructing more complex hybrid oriented structures (such as using CNTs as templates for "Shish"), potentially synergistically enhancing both the strength and functionality (e.g., electrical and thermal conductivity) of the fibers.

Green and Sustainable Processing Technologies: Current electrospinning still largely uses organic solvents. Developing environmentally friendly polypropylene melt electrospinning technology, or water-based electrospinning using green solvents, is an important future direction. Meanwhile, the recycling and reuse of processed waste polypropylene products, and restoring or even enhancing their mechanical properties through orientation crystallization technology, have huge environmental and economic value.

Deepening Application of In-situ and Multi-scale Characterization Techniques: Using advanced methods such as synchrotron radiation X-ray sources to conduct in-situ, real-time characterization of the orientation crystallization process on the spin line will be able to directly capture the formation moment of "Shish" and the growth kinetics of "Kebab," providing the most direct experimental evidence for establishing more accurate theoretical models. Combined with molecular simulation, the mechanism of orientation nucleation can be understood from the atomic/molecular scale.

Intelligent Structure Design for Specific Applications: Based on the precise control of orientation crystallization, intelligent polypropylene fibers with gradient structures, skin-core structures, or stimulus-responsive crystal form transitions can be designed. For example, utilizing the volume change accompanying the transition from β form to α form may lead to the development of new sensing or actuating fibers.

In summary, the orientation crystallization technology of polypropylene fibers is a vibrant and promising research field. Through multidisciplinary integration and continuously deepening the understanding of the structure-property relationship between process, structure, and performance, it will surely promote polypropylene fibers towards a new stage of higher performance and functionality, expanding their broader application space in the national economy and high-tech fields.

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