High Modulus Polypropylene for Technical Textile Applications

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Abstract--- High-modulus–high tenacity PP filaments have found various uses in industrial applications/technical textiles on the basis of their superior properties and inert nature. The feed parameters as well as the processing variables, all have an important impact on the ultimate properties of PP filament, as has been observed by various researchers. This article critically reviews the production of high-modulus–high-tenacity PP filament along with proposed changes in microstructure leading to the superior mechanical properties. The contributions of crystallite and amorphous orientations, amorphous modulus, crystallinity, and flaws in the shaping of mechanical properties of such filaments have been discussed in this paper.

Keywords--- High Modulus, Metalocene, Zigler-Natta, Drawing, Gradient Heater

I. INTRODUCTION

Polypropylene (PP) filaments have become one of the most important industrial filaments. Fibers from advanced Ziegler-Natta and metallocene catalyst based polypropylene have made inroads in technical textiles. The relation between practical and theoretical values in modulus and tenacity values are still large and a great deal of challenge involved in achieving high draw ratios. In most of the cases, high draw ratios have been achieved with single or multiple steps but with low strain rates and low processing speeds. Majority of the processes are batch processes and limits productivity. Since the introduction of filament-forming, melt-spinnable, synthetic polymers – filament manufacturers have looked for ways to increase the strength and stability properties of the fibers made from those polymers. The additional strength and stability of the fibers are needed so that applications beyond textile uses could be opened for their products. Such non textile uses (also known as ''Technical Textiles'') include: tire cord, sewing thread, sail cloth, webs or mats used for road bed construction or other geo-textile applications, industrial belts, composite materials, architectural fabrics, reinforcement in hoses, laminated fabrics, ropes, etc. High-modulus–high-tenacity fibers have thus offered an interesting arena to a filament scientist. Production of high-modulus fibers has been tried through various routes [1–3]. The commercial polypropylene fibers remain in the modulus and tenacity range of 4–8 GPa and 0.35–0.6 GPa respectively whereas the theoretical modulus of PP has been found to be 35–42GPa when measured by the X-ray techniques [4,5] and the theoretical strength 3.9 GPa [6] which is also much higher as compared to the maximum tenacity achieved through any of the existing process. It is however worth mentioning that the maximum modulus values determined by X-ray assumes the applied macroscopic stress to be uniformly distributed throughout the crystallite and amorphous phases. Fanconi and Rabolt [7] presented higher values of modulus (88 GPa) determined by longitudinal acoustic modes observed from Raman spectroscopy and by neutron-scattering techniques.

Controlling either the molecular design or the morphological features can produce ultrahigh-modulus fibers. Altering the molecular design is associated with

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changing the average length of the molecular chains, the regularity of packing, and the chain stiffness. The morphological way to utilize fibers is to take aid of the intrinsic mechanical anisotropy present in the fibers and to further align them in the direction of the filament axis. There are two routes to align molecules parallel to the filament axis. In the first route, they are prealigned in a mechanical field and crystallization takes place in an extended state as in Gel Spinning. In the other route, flexible molecules are allowed to get folded and crystallized from melt or solution and then unfolded by solid state deformation. One good example of the second route is drawing where fibers are stretched as a result of their passage between a set of rollers having a positive speed differential. In this review article, the different parameters which affect the properties of high-modulus polypropylene filaments are discussed.

II. FACTORS AFFECTING ON PROPERTIES OF POLYPROPYLENE FIBER

It has been observed that the properties of the spun yarns are influenced by various factors like molecular weight, polydispersity, nature of extrusion, extrusion temperature, extrusion velocity, airflow rate, take-up velocity, and temperature.

A. Molecular Weight (MW) of the Sample

Svetec [8] found that a medium weight polymer with narrow molecular weight distribution was the most suitable for producing high-modulus–high-tenacity PP fibers. It has been generally observed that drawability increases with MW up to a certain value after which it decreases. As reported by Ahmed, drawability becomes maximum at 6.7-7.8*104 after which it deteriorates [9]. Generally a higher molecular weight implies a higher elongational viscosity, higher degree of crystallinity and a higher strength and modulus. The nucleation rate varies inversely with MW which implies that a filament spun from high MW would be of lower degree of crystallinity [10].

It has been observed by Kamezawa [11] that for samples with higher molecular weight with larger molecular chains, unfolding of chains during drawing becomes more difficult. They had shown that modulus depends on molecular weight especially in the range of higher draw ratios. They justified that the ends of extended chains, which are formed by being unfolded from the crystallites, form defects which form micro cracks in the sample when it is stretched. In higher molecular weight samples, such defective points are fewer and therefore extension of the original sample of a higher molecular weight to unfold to a greater extent without the formation of micro cracks is more likely. Kamezawa et al. [12] also observed that below a molecular weight (Mv) of 510,000, the higher the molecular weight, the higher the maximum modulus. The importance of the molecular weight can be appreciated from the gel spinning technique. Kavesh et al. [13] described in a US Patent production of high-tenacity–high-modulus polypropylene fibers. Solutions of ultra high molecular weight polypropylene in a relatively nonvolatile solvent are extruded through an aperture at constant concentration throughout and cooled to form a first gel of indefinite length. The first gels are extracted with a volatile solvent to form a second gel and the second gel is dried to form a low-porosity xerogel. The first gel, second gel or xerogel, or a combination, are stretched. The weight average molecular weight of polypropylene used in the process was around 2,000,000 (11 IV), where the IV numbers represent intrinsic viscosity of the polymer in decalin at 1350C. Ultrahigh-modulus polypropylene gel (Mw>10, 00,000) was prepared by dissolving it in a hot solvent with concentration of 0.5–1% w/w. The gel was spun, dried, and the films subsequently drawn to very high draw ratio at high temperature with low strain rate. The filaments/films exhibited excellent mechanical properties [14, 15]. Like any other process, the gel spinning process has its share of problems. This method is slow, requires specific molecular weights and distributions and extensive solvent removal schemes.

B. Initial Morphology

Isotactic polypropylene is a semicrystallite polymer containing monoclinic α-crystallites, hexagonal β-structures, orthorhombicγ-polymorphs and ''smectic'' meso-phase [16]. At rapid cooling of the melt, α-crystallites and smectic meso-phase are mainly developed, whereas β- and γ-polymorphs are observed as minority components [17]. The hexagonal β-form, together with the α-crystallites, occurs mostly on adding special nucleators [18]. The content of β-crystallites depends on conditions of crystallization and on the kind of nucleator and its concentration [19–22]. An unique feature of α-spherulites in iPP is the lamellar cross-hatching development of transverse lamellae oriented in the direction perpendicular to the direction of radial lamellae [23]. It has been seen [24] that materials with smectic structure (paracrystallite) and low crystallinity can be drawn to a higher degree than the monoclinic (β-crystallite) form. Similar observations have been confirmed by Jambrick and Diacik [25] who studied the deformation behavior of PP fibers at room temperature as well as at higher temperatures by measuring the drawing forces. According to them the filament with monoclinic structure required considerably more force for deformation than a filament of smectic structure. As explained by the authors, the stable monoclinic crystal has a three-dimensional crystallite order with a large number of tie links and so it offers much more resistance to deformation than that offered by the less-ordered smectic structure. Restricted crystallization in the spin line facilitates further drawing. As summarized by Wang, from the X-ray diffractograms, the structure of the as-spun fibers can be of three types (i) a para crystallite structure of low orientation, (ii) an α-monoclinic structure of low orientation, and (iii) an oriented α-monoclinic structure with distinct c+a axis orientation of crystallites. During rapid cooling from melt, mainly the smectic phase is formed with bit α-crystallites. It has been seen [26] that materials with smectic structure (paracrystallite) can be drawn to a higher degree than the monoclinic (α-crystallite) form. The feed filament should have low crystallinity values.

C. Polydispersity

A higher polydispersity implies deteriorating mechanical properties but enhanced processing ease. Low-molecular weight species act as a plasticizer and drawability is enhanced with broader molecular weight distribution. The effect of polydispersity on the drawing behavior is studied at length by Andreassen et al. [27]. He studied the effect of molecular weight distribution on modulus. He inferred that tensile modulus was higher for broad MW distribution at low draw ratio while the same observation was for low MW at high draw ratio. The tensile strength however increased for a decrease in the molecular weight distribution for all combinations of processing parameters.

D. Presence of Entanglements

The basic difference between the melt crystallized and gel-spun material is in the level of entanglements in the starting material. The higher level of entanglements is the reason behind the lower achievable amorphous orientation in the drawn material. There is a limit to which these entanglements can act as effective ''cross-links'' [28] and beyond a certain limit the drawability decreases. With a low level of entanglement good mechanical properties are obtained.

III. PROCESSING PARAMETERS

A. Spin Line Stress

Low spin line stress results in reduced stress-induced crystallization. The spin line stress is a function of the take-up velocity and the jet stretch defined as amount of attenuation imparted to molten polymers between the spinneret and before solidification.

B. Spinning Temperature

For 35 MFI material, as elaborated by Wang et al. [29], temperature above 240^0C results in a para crystallite structure. At lower spinning temperatures (220 and 200^0C) the α-monoclinic structure is also present. For lower MFI

material, higher spinning temperature could not suppress the formation of the α-monoclinic crystallites. They had found that for both series of as-spun fibers the values of specific secant modulus, tenacity, and specific work of rupture tend to decrease with increasing spinning temperature, while the reverse results were observed for natural draw ratio and the extension at break.

C. Cooling Procedure

The polymer, after leaving the spinneret, is cooled by air or a liquid. The rate of cooling in air is far in excess of 15^0C per minute and by quenching in a liquid, very high rates of cooling may be obtained. The high rate of cooling prevents excessive crystallization of the polymer which affects the subsequent drawing of the spun filaments.

D. Take-up Velocity

Lower take-up velocity has been seen to inhibit crystallization. A higher take-up velocity induces higher stress, which in turn induces higher crystallinity. Tension depends on the draw ratio and the takeup speed applied. The tension in the spinning zone is a function of the jet stretch. As Broda et al. have observed, for fibers spun [30] at low and medium take-up velocities, mesophase peaks occur. Mesophase peaks with similar intensity were obtained for fibers spun at take-up velocity from 1050 m/min. For fibers spun at higher take-up velocity 1200 m/min, the intensity of mesophase peaks decreases. For fibers spun at take-up velocity 1350 m/min the mesophase peaks disappear, and the X-ray diffraction pattern takes a shape characteristic for α-form.

E. Post-Spinning Parameters

The single most important post-spinning parameter is drawing. Drawing aims at producing long-chain molecules whose theoretical modulus is only limited by the extensibility and deformability of the covalent bonds along the fully extended chains. Many authors reported different deformation mechanisms during uniaxial drawing of polymers [31–34]. The maximum draw ratio, ease of drawing, and elastic modulus depends upon molecular weight, molecular weight distribution, initial morphology, drawing temperature, and strain rate.

The morphological changes occurring in semicrystallite polymers as a result of drawing have been extensively investigated. Samuels [35–37] studied the uniaxial deformation of both melt cast sheet and melt spun filament. He found that the deformation proceeds in two stages. In the first stage, there is lamellar slip, leading to c-axis orientation until the lamella becomes fully oriented. The substructure after this stage is no longer spherulitic but has transferred into a fibrillar structure. Once this point is reached, any further extension of the material results in a new deformed mechanism; crystal cleavage which forms the second stage of deformation. At this state to accommodate further extension, the lamellae break-off in blocks and the helical axis of the non crystallite molecules become more oriented in the direction of deformation. Finally, the structure as a whole cannot support the stress, flaws develop, and the sample breaks.

Peterlin [38,39] suggested that the basic structural unit in drawn PP is micro fibril, about 10 mm long and 10–20nm in diameter formed from destruction during drawing of the lamellae present in the original micro spherulitic materials. Each stack of parallel lamellae is broken down at a micro neck to give a bundle of micro fibrils. Cohesion within each fibril is enhanced by a limited number of tie molecules bridging the micro fibril boundaries, whereas cohesion between fibrils is poor because of the different orientations of the original parent lamella, which result in each fibril having a different draw history. Once a fully micro fibrillar structure has been developed, continued plastic deformation is thought to take place by slippage of the fibrils past one another and the resistance to deformation is provided both by friction and by the unfolding of lamellae on the fibril surface.

Jambrick and Diacik [40] have studied the deformation behavior of PP fibers at room temperature as well as at higher temperatures by measuring the drawing forces.

According to them the filament with monoclinic structure required considerably more force for deformation than that required to deform a filament of smectic structure. These authors have explained this behavior on the basis of crystal morphology. The stable monoclinic crystal has a three-dimensional crystallite order with a large number of tie links and so it offers much more resistance to deformation than that offered by the less-ordered smectic structure. An increase in drawing temperature causes a decrease in drawing tension because of higher chain mobility at higher temperature and leads to increase in drawability.

On drawing, there is more influence on the long periodicity. The increase of the long period as well as the crystal thickness is responsible for the increase of melting temperature. On the other hand, the increasing of the draw ratios to very high values leaves significant amount of imperfections in the form of voids in PP samples.

Generally there is an increase in tenacity and modulus on drawing. Gill and Banjamin [41] observed the crystallite orientation reached a constant level at the stretch ratio above 4 : 1 while strength continued to increase with further increase in draw ratio presumably due to continued improvement in amorphous orientation with stretch.

Though the deformation mechanisms [42,43] have been studied in detail, the plastic deformation of semicrystallite polymers is a complex process. Many competing phenomena are likely to occur simultaneously when a polymer is plastically deformed. Crystallite lamellae, separated by amorphous layers and connected by tie molecules, are arranged spatially to form higher level morphological forms, e.g. spherulites.

It has been proposed that stretching of iPP results in chain slip through crystals, sliding and breakage of tie chains [44,45], and activation of constrained amorphous regions driven by lamellar disintegration. In the post-yield region, these alternations of the microstructure result in cavitation, formation of fibrils, and stress-induced crystallization [46]. As proposed by Drozdov [47],

deformation of PP above their glass transition induces slip of junctions with respect to their position. Sliding of junctions reflects slippage of tie molecules along the lamellae and fine slip of lamellar blocks.

Wang et al. [48] concluded that single-stage drawing was not a feasible way to attain high tenacity. High draw ratio in a single stage results in the formation of defects, which affect adversely other properties of the fibers like their abrasion resistance. Their experiments showed that a first-stage drawing at relatively lower temperature of around 60^0C ensured that the fibers remain para crystallite. At the second stage however, these fibers are drawn at a higher temperature resulting in fibers of high tenacity.

Filaments of polypropylene of remarkably high-modulus and strength have been prepared by Clark and Scott [49] using the two-stage drawing process. The authors have remarked that the filaments have amorphous regions that are distributed at random within a continuous crystal matrix.

Time is also an important factor affecting the drawability, which depends on the drawing speeds. Drawing should take place allowing a time whereby the filament can take up the heater temperature. The time of deformation induced crystallization is dependent on the rate of drawing and higher rates raise the internal temperature of the polymer thus affecting the rate of crystallization.

IV.   DRAWING TECHNIQUES

There have been several drawing techniques and the successful ones are described as follows:

A.   Tensile Drawing

Tensile drawing is a process in which spun filaments/ films are drawn at high temperature with low strain rate to very high draw ratio. Taylor and Clark [50] had drawn polypropylene of molecular weight (MW) 2,77,000 to very high draw ratio of 22x by two-stage tensile drawing. Candia et al. [51] had drawn polypropylene sheet of MW 2,29,000 in two stage tensile drawing. The first-stage drawing was with a strain rate of 57% per minute to a draw ratio of 9x

and the second stage at a strain rate of 40% per minute to a total draw ratio of 44x.

B. *Zone Drawing and Zone Annealing*

The procedure of zone drawing [52] and zone annealing [53] has been successfully carried out by Kunugi and other scientists for various fibers [54] including polypropylene. In general, the apparatus is a reconstructed tensile tester. A band heater of a suitable width is attached to the crosshead. The process is different from the existing drawing because the deformation is restricted only in the heating zone. The sample is drawn by the tensile tester and at the same time the ensemble of the heater/cooler is shifted at an appropriate rate so that the deformed region is confined to the heating zone.

The draw ratio is controlled by the ratio of the drawing rate of the tensile tester to the shifting rate of the heater/cooler ensemble. The zone drawing, as reported by Kunugi, was done by moving the band heater from the lower part of the filament to the upper part while under tension. The zone-drawn filament was zone-annealed using the same apparatus except that the temperature and tension applied were much higher.

The zone drawing is done to produce highly oriented amorphous filament while the zone-annealing process produces highly oriented crystalline fibers as explained in below Figure. The CZD treatment was carried out five times [55] at a drawing temperature of 150_C stepwise with increasing applied tension from 14.8MPa for the first treatment (CZD-1) to 207.0 MPa for the fifth (CZD-5) at a running speed of 500 mm/min. The CZD-5 filament has Young's modulus of 14.7 GPa and a tensile strength of 1.08 GPa.
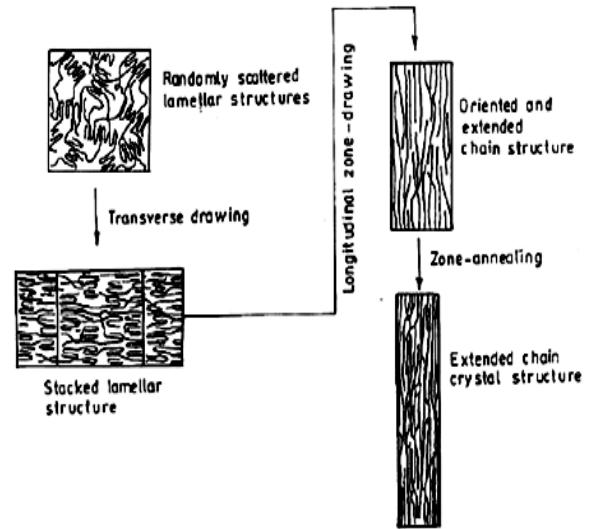
The superior properties of polypropylene obtained through the process were due to high orientation as confirmed by a birefringence of 0.0348 and a high crystallinity of 67.3%. The evidence for the existence of α-form in the CZD fibers was provided by WAXD and DSC measurements. The authors claimed the following advantages of the process: (a) prevention of formation of several nuclei, (b) elimination of internal distortion of crystallites, (c) prevention of thermal degradation of fibers due to short heating time, and (d) high dimensional stability of annealed fibers.

Kamezawa et al. [56] suggested an improvement in the zone drawing technique and introduced cooling elements by which the sample is cooled to a temperature lower than the room temperature immediately after being drawn over the heater.

C. *Constant Load Oven Drawing*

In this technique, [57] spun filament is drawn under constant tension in an oven. The oven temperature is slowly increased from ambient temperature to a suitable high temperature during the first stage of drawing. The second stage of drawing is carried out under the same tension at the elevated temperature to the final draw ratio.

D. Die Drawing

It is a technique where the solid polymer is charged into a conical die and the material is drawn through the die neck by some take-up mechanism with constant speed, where die is maintained at a high temperature. Figure explains the principle of die-drawing.

The unit essentially consists of three zones, i.e. the conical die flow zone, isothermal tensile flow zone, and nonisothermal tensile flow zone. Most studies reported on solid state extrusion or die drawing are related to the production of filamentary products exhibiting monoaxial orientation. More recently it has been shown that higher draw ratios are obtained in die drawing processes by adding an elongational axial component to shear deformations in the die. According to Shaw this results from the reduction in the velocity gradient across the axial direction, which alters the balance of forces in favor of the elongational components [58]. Coates and Ward [59] on the other hand, have attributed the achievement of higher production rates in the combined extrusion die-drawing process to the ability of the polymer to deform at an optimal strain rate which allows it to neck away from the die walls before it reaches the die exit.

E. Hot Nip Drawing

In this drawing technique, the extruded polypropylene sheet is gripped in a bottom gripper where a heating device with two sharp edges touches the opposite sides of the sheet. The upper tip of the thinned sheet is gripped and stretched with low constant strain rate. The neck produced travel downward because of the weight of the heating device, which stayed in contact with the newly forming neck. The drawing process was repeated several times for ultra drawing.

F. Temperature of Drawing

The temperature of drawing limits the drawing performance. Sufficient heat needs to be supplied to enable drawing without break although in certain cases heat needs to be removed in cases of high work of drawing. Ziabicki

[60] observed that a filament behaved like a brittle solid when drawn below the temperature of glass transition but increased temperature affected enhanced flow. The necking tendency also decreased, as reported by Spruiell, when the draw temperature approached the melting temperature.

It has been seen that the drawability of smectic structure was maximum at around 60^0C but for monoclinic structures, as reported by Wang [61] higher temperature was required.
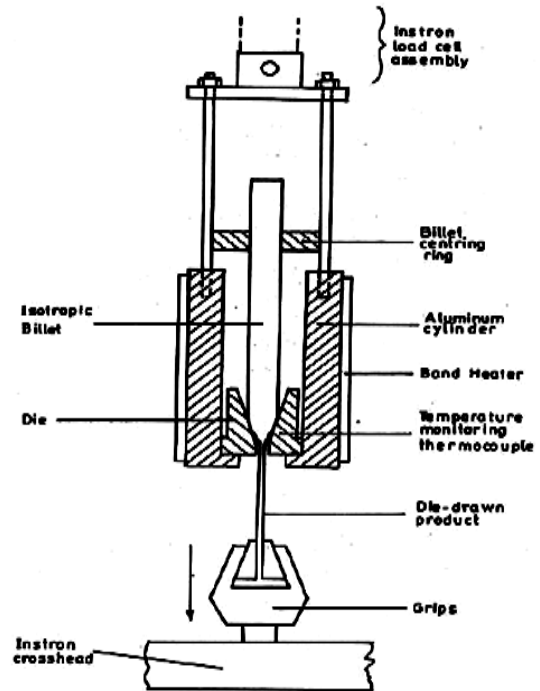
Die drawing

Generally homogeneous drawing can only occur at higher temperatures, while in cold drawing the sample stretches through a neck. Drawing is generally done in between the Tg and the Tm of the fibers. The increase in temperature lowers the temperature necessary for the initiation of the drawing and also the tension in the flow zone. The natural draw ratio decreases while the maximal draw ratio becomes greater. In the case of PP, a two-stage drawing with the first stage at 60^0C and the second stage at $120–140^0$C provided good results. Extensive work by Wang et al. [62] showed that heat treatment of para crystallite spun fibers of low orientation get transformed into the α-monoclinic form at a temperature of more than 80^0C. Their experiments also showed that conversion into the α-

monoclinic form before drawing reduces the maximum achievable draw ratio. Increased temperature of drawing upto 100^0C resulted in an increased optical birefringence. The authors ascribed the observation to preferential formation of crystallites aligned along the filament axis. They performed a series of heat treatment experiments, and observed that there is a gradual increase of the α-monoclinic form between temperatures of 80–120^0C.

Wang et al. [63] showed that single-stage drawn fibers at a temperature of 60^0C remained para crystallite inspite of being oriented. An increase of temperature to 80^0C resulted in fibers of alpha monoclinic crystallites with c-axis orientation. Fibers which were produced beyond 100^0C were mainly monoclinic with a small fraction of crystallites showing a-axis orientation.

Taylor et al. [64] observed that below 130^0C, micro fibrillar slippage was less which resulted in higher unfolding and orientation of chains with increase of draw ratio and a simultaneous increase in modulus. But temperature higher than 130^0C and higher molecular mobility between micro fibrils caused faster micro fibrillar slippage under stress without any effective molecular unfolding within micro fibrils. This resulted in lower values of modulus and tenacity beyond 130^0C.

Kamezawa et al. [65] commented that the optimum temperature to prepare the sample of the maximum modulus was between 120 and 130^0C. What they suggested was that at this temperature, crystals of isotactic PP become viscoelastic since the crystallite relaxation temperature is located at about 117^0C (138 Hz). However, the drawing temperature at which Ward and Capaccio [66] prepared oriented isotactic PP through cold drawing was around 110^0C.

V. HEAT SETTING/ANNEALING

Drawing and heat setting behavior of melt-spun PP fibers were also investigated by Samuels [67]. According to him two draw regions characterized by different deformation behaviors can be identified. In the low draw region, (with a draw ratio less than 2.25) the crystal lamellae-resisted orientation of the noncrystallite region controlled the deformation. On heat setting, orientation in the non crystallite regions does not change much. In the high draw region, structural changes are largely controlled by non crystallite molecules. During drawing, the highly developed crystals resist cleavage and the noncrystallite regions orient to relive the stress. On heat setting, noncrystallite region relaxes slightly, allowing the lamellae to become fully oriented by crystal cleavage and slip process and any further drawing leads to fracture by fibrillation.

Yamada et al. [68] experimented on the effect of annealing temperatures on high-modulus polypropylene and reported a decrease in modulus with high annealing temperatures. They explained the observation as a result of decrease of orientation function of the amorphous chains fa. The decrease in fa corresponds to a loosening of taut-tie molecules, which gradually occurs with annealing to 420 K.

Annealing at elevated temperature results in (i) secondary crystallization of a part of the amorphous phase, (ii) thickening of radial lamellae, (iii) development of subsidiary lamellae, and (iv) growth of the crystal perfection [69]. There has been a debate regarding the other change in structures on annealing. Some researchers opine [70, 71] that the fraction of β-spherulites increases on annealing in the interval of temperatures between 110 and 130^0C. Other authors strongly opine that at high annealing temperatures, the smectic mesophase is transformed into an α-phase without noticeable development of β-structures.

There has been several structural models suggested to describe the observed relation between β-phase concentration and the toughness of isotactic polypropylene. Karger Kocsis [72] explained the higher toughness of the β-phase by a phase transformation, i.e. by a mechanism similar to that which improves the toughness of the zirconium ceramics. It is also suggested that the higher toughness of the β-phase of isotactic polypropylene,

compared with the alpha modification, is an inherent property of the β-phase. As suggested by Elyashevich et al., [73] the β- phase essentially consists of extended chain crystallites with a high content of continuous chains which results in better continuity in the amorphous region.

VI. CHANGE IN SUPERSTRUCTURE OF HIGH-MODULUS AND HIGH-TENACITY PP FIBERS

There have been various processes employing drawing in one form or another. High-modulus–high-tenacity fibers can be achieved by drawing fibers in several stages with low strain rates to a very high draw ratio. A summary of the processes, temperature, speed, and final properties of the fibers so produced is given in Table. All the researchers mentioned have explained the reason of obtaining such high tensile properties in terms of the superstructure of the polymer which are categorized below

A. Crystallite and Amorphous Orientation

The most important parameters influencing the properties of high-modulus–high-tenacity fibers as found by different researchers seems to be the crystallite and amorphous orientation of the samples. The crystallite orientation values in all the cases have been calculated from orientation functions f_{110} and f_{040} determined from two experimentally accessible diffraction planes. Desper calculated amorphous orientation values, based on the calculation of Samuels, from Sonic Modulus measurements. Samuels formulated that the sonic modulus E_{or} of an oriented semi-crystallite polymer is related to the orientation functions f_c and f_{am}, the degree of crystallinity X_c, intrinsic transverse moduli $E_{t,c}$ and $E_{t,am}$ of the crystallite and amorphous phases calculated as $3.96*10^{10}$ and $1.06*10^{10}$ respectively.

Desper concluded from the experiments that amorphous orientation functions measured by the birefringence corroborate with the sonic modulus results, but according to him, were less accurate. From an error analysis, he determined that there was appreciable fluctuation of the local values of f_a which was not observed from the sonic modulus values. He further argued that sonic modulus is also sensitive to amorphous orientation, whereas birefringence was a measure of both the crystallite and amorphous orientations.

Yamada et al. [81] observed that the crystal c axis orientation leveled off after a draw ratio of 9. Above this draw ratio, the modulus was seen to be a function of amorphous orientation function. Kunugi et al. [82] observed an increase of both the crystallite orientation function (fc) from 0.97 to 0.99 and amorphous orientation function (fa) from 0.605 to 0.957 though fc reached a high value after zone drawing and fa values improved with zone annealing.

Different orientation functions for polypropylene obtained by researchers show that highest crystallite orientation values achieved were quite high. Kunugi et al. however have reported the highest amorphous orientation values in recent times.

The use of multiple techniques to characterize the effects of the deformation in terms of orientation development has been the principal trend except a few cases. Mirabella et al. [94] used an infrared dichroic method to calculate the orientation functions for gel-spun and drawn polypropylene films with calculations detailed in the paper. Even in the gel-spun polypropylene, the major reorientation at very high draw ratio between 8.3x and 47.5x occur in the amorphous phase. The ability of the amorphous phase to achieve high orientation perfection in the gel-crystallized specimens was mainly ascribed to the fact that entanglements in the gel were minimized. Mirabella also justified the high value of crystallite modulus obtained by Fanconi and Rabolt [95] with his experiments where he got a very high modulus of 36 GPa with an amorphous orientation function of 0.8.

It is a general observation that fc easily reaches a high value during drawing, but the improvement of fa is much slower and easily correlated with the improvement in modulus which suggests that the amorphous orientation

greatly contribute to the improvement of mechanical properties.

It has however to be noted that the birefringence and the sonic modulus values give only the average value of $\cos^2 q$, $(\cos^2 q)$, where q is the angle between the filament axis and the local polymer chain axis. An infinite number of configurations can have the same value of $(\cos^2 q)$. The modulus depends on the entire orientation distribution function (ODF), not just $(\cos^2 q)$ [96]. X-ray can provide the additional needed orientation distributions for the crystallite phase while both solid-state NMR [97] and Raman spectroscopy [98] can provide the orientation distribution functions for the crystallite and non crystallite phases.

It has been pointed out by Michielson et al. [99] that in highly crystallite materials, the birefringence is determined primarily by the orientation of the crystallite material. In lower crystallinity material, the average orientation is a combination of the usually highly oriented crystallite material and the lowly oriented non crystallite one. Since birefringence measures only $(\cos^2 q)$, very little is actually known about the orientation distribution within the non crystallite region, even when the non crystallite region makes up 40–60% of the material. They opine that additional measures like Polarized Raman Spectroscopy can be used for better analysis.

VII.   AMORPHOUS MODULUS VALUES

Peterlin clearly opined that tensile properties of oriented crystallite polymers having alternate regions of crystallite and amorphous regions along the molecular axis and therefore the latter with the lower modulus contributes to the decrease in modulus values. Kunugi et al. [100] calculated that the amorphous modulus of high modulus polypropylene prepared through zone annealing is significantly lower than polyethylene. The multizone-drawn, multizone-annealed filament had a high amorphous modulus of 8.82×10^{10} dyn/cm^2. They suggested that the helical conformation of polypropylene promotes unfolding

of the lamellae because of weak intermolecular forces but is not effective in producing a high-modulus as compared to the planar zig zag conformation of polyethylene molecular chains.

VIII.   DEGREE OF CRYSTALLINITY

The changes in the ''degree of crystallinity'' of PP fibers on drawing are a point of interest for many investigators. Conflicting results have been reported [101]. Nadella et al. [102] has observed a small increase in the degree of crystallinity of hot drawn, cold drawn, and annealed fibers measured by density than those of the as-melt spun filaments. On the other hand, Capuccio demonstrated a decrease in crystallinity with increasing draw ratio during cold drawing (100^0C).

However, lowering of crystallinity is less on drawing at higher temperature. Gill and Benjamin [103] observed for PP that the crystallinity increased initially with increase in draw ratio tended to peak at round ratios of 2:1; above this level the crystallinity showed a significant decrease. The amorphous layer thickness, however, showed a continuous rise. As observed by Cannon [104], the DSC crystallinity increased from 69 to 96% due to ultra drawing. It has been shown that the high DSC and X-ray crystallinity values are obtained with low-density crystallinity values. This is due to the presence of voids in the drawn samples.

IX.   CONCLUSIONS

Efforts to produce high-modulus–high-tenacity polypropylene fibers have met with success and very high-modulus (~51% of the crystal modulus) has been achieved through the melt spinning – drawing route, though the tenacity values achieved have been comparatively low. Thus there is lot of scope in the area of high-modulus fibers to minimize the gap between practical and theoretical values in modulus and tenacity and a great deal of challenge involved in achieving high draw ratios in the melt spinning – drawing route towards tailor making high-modulus fibers. In most of the cases, high draw ratios have been achieved

with single or multiple steps but with low strain rates and low processing speeds. Another limitation is that most of the processes are batch processes and limits productivity. Thus in the field of high-modulus–high-tenacity filaments, there is scope for further research in evolving processes which are fast and continuous in nature.

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