

Thermal Conductivity of Semi-Crystalline Polymers and Effect of Extrusion

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ABSTRACT: In this review we have concentrated on the interpretation of three essential aspects of the thermal conductivity K of polymers: the temperature dependence, the crystallinity dependence and the orientation effect. K for all amorphous polymers is approximately equal in magnitude and characterized by a T^2 dependence below 0.5K, a plateau region between 5 and 15K and a slow increase at yet higher temperatures. While a number of models involving different phonon scattering mechanisms are capable of explaining these features, further corroborating evidence would be needed to explain the ad hoc assumptions involved. For semicrystalline polymers K shows both strong crystallinity and temperature dependence, with a distinctive cross-over point at about 10K. These marked features can now be understood as the result of the interplay between two competing factors: the intrinsically higher conductivity in the crystalline regions, and the reduction in K due to an additional phonon scattering mechanism which becomes important at low temperature. This scattering could arise from either the correlation in the spatial fluctuation of the sound velocity in the polymer or the acoustic mismatch at the interfaces between the crystallites and the amorphous matrix.

KEYWORDS-thermal, conductivity, semi-crystalline, extrusion, polymers, matrix

I. INTRODUCTION

Orientation produces a very large anisotropy in semicrystalline polymers, which however decreases at low temperature and becomes insignificant below 10K. This feature can again be understood in terms of the same competing mechanisms if one realizes that the molecular chains in the crystallites are essentially lined up along the direction of orientation thus offering very little thermal resistance along this direction. For polyethylene with an extrusion ratio of 25 the thermal conductivity at 100K along the extrusion direction is 91 mW/cm K, a value extremely high for polymers and close to that of stainless steel. At this temperature the anisotropy is only about 20, yet because of the different temperature dependence of the thermal conductivity along and perpendicular to the extrusion direction, we predict an anisotropy as high as 60 at room temperature.

The thermal conductivity of five semi-crystalline and four amorphous polymers was determined within a wide range of temperature, starting at room temperature and going up to temperatures above the polymer melting point (T_m) for semi-crystalline polymers or above the glass transition temperature (T_g) for amorphous polymers. Two transient techniques were employed in the experimental investigation: the hot wire technique for the group of amorphous polymers, and the laser flash technique for the semicrystalline polymers. As expected, the experimental results show that T_g exerts a measureable influence on the thermal conductivity of amorphous polymers. In the case of semi-crystalline polymers, a singular behaviour of the thermal conductivity is observed within the T_m range. In order to explain the anomalous behaviour, the influence of these transition temperatures on the thermal conductivity behaviour with temperature has been analysed in terms of a phonon conduction process and temperature variations of specific heat and modulus of elasticity of the analyzed polymers.

Modelling heat-energy transfer problems under steady state or transient conditions is of fundamental importance in engineering design as well as for tailoring of thermal and mechanical behaviour of materials. Thermal conductivity, diffusivity and specific heat capacity are three important thermo-physical properties of a material that are needed for heat transfer calculations. Detailed knowledge of such properties becomes crucial in many situations when heat is added or removed from a material.[1,2,3]

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Thermal conductivity (k) is the property that determines the working temperature levels of a material, determining the temperature gradient inside this material, and so it is an important parameter in problems involving steady state heat transfer. This property assumes a critical role in the performance of materials in high temperature applications. Low thermal conductivity values are required when the purpose is to minimize heat losses. On the other hand, when heat transfer from one site to another is desirable, materials with higher thermal conductivities must be chosen. Therefore, reliable thermal conductivity values are essential for material selection criteria in order to get the best performance of the material in a specific application. However, it is one of the physical quantities that is difficult to measure and requires high precision in the determination of the parameters involved in its calculation. Moreover, many factors can affect the thermal conductivity of a material [1], [2], [3]: temperature, density, porosity, moisture, degree of crystallinity, orientation of grains, size of molecules, impurities, etc.

Thermal diffusivity (α) is a measure of the rate of heat propagation through a material. It is an important property in all problems involving non-steady state heat conduction. In the extrusion and injection moulding processes, knowledge of the precise values of both the thermal conductivity and diffusivity and their temperature dependence is essential for heat-energy transfer calculations in both heating and cooling cycles of polymer processing operations. In cooling operations, thermal conductivity variations can induce non-uniform cooling and shrinkage problems and, thereby, cause frozen-in stresses, delamination, shrink voids in extrudate profiles and injection mouldings [2], [3].

The specific heat (c_p - heat capacity per unit mass) is a thermodynamic quantity that determines the amount of heat necessary to raise by one degree the temperature of a unit mass of a material and is, therefore, associated with the energy consumption in heating processes. In the polymer melting process, the value of c_p increases substantially due to the fact that the high heat absorbed by the semi-crystalline material is used up as latent heat of fusion and does not contribute towards a temperature variation.

The anomalous thermal conductivity variations verified for both crystalline and amorphous thermoplastics in the temperature range around both T_g and T_m of these polymers, although well documented in published polymer processing literature [1], [2], [3], has seldom been analyzed in terms of the actual phonon heat conduction theory used for ceramic materials [4]. Hence in this work, the influence of thermal transition temperatures (T_g and T_m) on the behaviour of the thermal conductivity with temperature is determined and analysed in terms of the phonon conduction process. The thermal conductivity of five semi-crystalline and four amorphous polymers was determined within a wide range of temperature, starting at room temperature. Two transient techniques were employed in the experimental investigation: the hot wire technique for the group of amorphous polymers and the laser flash technique for the semicrystalline polymers.

II. DISCUSSION

The thermal behaviour of discontinuous carbon fibre reinforced polyphenylene sulphide (CF/PPS), additively manufactured by material extrusion, with a focus on the effects of thermal process conditions on the degree of crystallinity, oxidation crosslinking and mechanical properties of CF/PPS from filament fabrication, material extrusion to annealing treatment. The screw extrusion parameters are optimised by performing a thermal analysis of the fabricated filaments. The effect of crosslinking reactions on the crystallinity process in determining the mechanical properties of the printed samples is illustrated by investigating the influence of the printing conditions. Furthermore, the effect of annealing treatment on the semi-crystalline polyphenylene sulphide (PPS) is studied by measuring the degree of crystallinity and viscoelasticity behaviours. Results demonstrate that the flexural properties of the printed CF/PPS composites at elevated processing temperatures are determined by the oxidation crosslinking between PPS chains. These enhance the crystallisation process of semi-crystalline polymers by acting as the nucleating agent first but negatively affect the mechanical properties at higher temperatures because of the detrimental effects of the polymer inter-chain bonding. The maximum flexural strength of printed CF/PPS reached 164.65 MPa when processing at an extrusion temperature of 280°C, a printing temperature of 320°C, and an annealing temperature of 130°C for 6 h. By adjusting the thermal treatment conditions, the degree of the crystallinity and the mechanical properties of the printed CF/PPS composites can be designed, controlled and tailored.[4,5,6]

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Thermoplastic composites have increasing applications due to their advantages of rapid cycle time, improved impact strength, recyclability, and unlimited shelf life as compared to thermoset composites.¹ For instance, the G650 business jet from Gulfstream adopts the lightweight carbon fibre/polyphenylene sulphide (CF/PPS) to form the tail section, which reduces 10% of the structural weight and 20% of the cost.² Polyphenylene sulphide (PPS) is a semi-crystalline matrix with a relatively high service temperature, exceptional mechanical strength, great chemical resistance, and good flame retardation,³ and it is less expensive than other high-performance semi-crystalline polymers like polyether ether ketone (PEEK).⁴ Thermoplastic composites manufactured by additive manufacturing (AM) such as material extrusion technique recently emerged due to their high flexibility in geometry, cost-effectiveness, and being free of multiple processing tools.^{5,6} The most common polymers used in material extrusion based printing are acrylonitrile butadiene styrene (ABS),⁷ polylactic acid (PLA),⁸ polyamide (PA),⁹ and polyethylene terephthalate (PETG).¹⁰ Short carbon fibre reinforced polymers offer the most accessible pathway toward large-scale, affordable and functional AM composites.¹¹ Mixing short carbon fibres in the PPS feedstock can increase the thermal conductivity and mechanical strength and stiffness while reducing the thermal expansion and residual stress in the printed composites.¹² Furthermore, short carbon fibres can improve friction and wear resistance, even compared with their continuous carbon fibre counterparts.¹³ In general, higher fibre content and better-aligned short fibres in additive manufacturing lead to improved mechanical properties of printed composites.¹⁴ Therefore, material extrusion of discontinuous CF/PPS composites with a high fibre volume is likely to grow in the automotive, electronics, and aerospace industries as well as other fields, due to its relatively low cost, accessible printing process, and feasible recycling process.

As a typical heat crosslinking, semi-crystalline polymer, the degree of crystallinity of PPS in the extruding and printing processes is affected by the complex thermal conditions including melting and deposition, which subsequently influence the tensile strength, fracture toughness, impact properties and other mechanical properties.¹⁵ Previous studies on material extrusion of PPS focused on the printing parameters,¹⁶ heat transfer,¹⁷ layer adhesion,^{18,19} rheological and thermal properties^{20,21} of CF/PPS composites.²² They found that the 3D printed composites could present a comparable property to extrusion-compression moulding due to highly aligned fibres but a poorer mechanical property to the injection moulding. Material extrusion additive manufacturing still faces challenges, however, to produce high-performance short CF/PPS composite parts for high-end applications because of the formation of the densely packed and ordered crystalline regions as well as thermal and oxidative responses.²³ Although there is limited literature on the thermal history in material extrusion of CF/PPS, several studies have been reported on pure PPS^{24,25} and other semi-crystalline polymers such as PEEK²⁶ and PET.²⁷ Results show that printed parts with different degrees of crystallinity or different crystallinity regions in the same part can be designed and realized by controlling the heat treatment process. The above literature demonstrated that it is essential to analyse the thermal conditions on the performance of 3D printed semi-crystalline composites.

Previous studies have focused on various aspects of CF/PPS composites in material extrusion, including printing parameters, rheological and thermal properties, and mechanical performance. However, there is a need for further research to specifically investigate the thermal conditions and their effects on the degree of crystallinity and mechanical properties of CF/PPS composites. The present study, therefore, addresses this gap by investigating the thermal conditions, optimizing the mechanical properties, and exploring potential applications of CF/PPS composites in material extrusion. Firstly, this study aims to understand how the thermal history influences the resulting composites performance by examining the impact of different thermal processing conditions on the degree of crystallinity and mechanical properties of CF/PPS composites. Secondly, by systematically varying these conditions, we aim to optimize the mechanical properties of CF/PPS composites. By controlling the thermal parameters, such as filament fabrication temperature and annealing treatment parameters, we seek to tailor the degree of crystallinity and enhance the mechanical performance of printed parts. Lastly, this study is to identify potential applications for CF/PPS composites in high-end industries, such as aerospace, automotive, and electronics. By demonstrating the enhanced mechanical properties achieved through thermal optimization, we aim to display the suitability of CF/PPS composites for lightweight and high-performance components in these industries. Overall, the study contributes to the knowledge and understanding of the thermal behaviour and performance of CF/PPS composites in material extrusion additive manufacturing, which can have implications or optimizing processing parameters and improving the mechanical properties of printed parts. The aerospace, automotive, electronics and general manufacturing properties can benefit

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from the optimized CF/PPS composites produced through material extrusion, while the recyclability aspect aligns with sustainable manufacturing practices.

III. RESULTS

Over the past few years we have studied in detail the influence of (i) crystallinity and (ii) crystallite orientation in determining the thermal conductivity, κ , of semicrystalline polymers.¹⁻³ Between about 2K and room temperature the variations in κ with these two parameters are completely different above and below about 25K. At the higher end of the range the conductivity increases both with crystallinity and with orientation, the latter being brought about by drawing or extruding the isotropic polymer. At low temperatures, on the other hand, the specimens with the greatest crystallinity have the lowest conductivity with values in a 50% crystalline specimen at ~ 1.5 K roughly an order of magnitude lower than those found “universally” for amorphous solids.⁴ These low values, furthermore, are found to be more or less independent of crystallite orientation. [7,8,9]

Optical transparency is an important property for a material, especially in certain fields like packaging, glazing, and displays. Existing commercial transparent polymeric materials are mostly amorphous. Semicrystalline polymers have often superior chemical resistance and mechanical properties particularly at elevated temperatures or after solid-state drawing but they appear opaque or white in most cases. This review describes the present state-of-the-art of methodologies of fabricating optically transparent materials from semicrystalline polymers. A distinction is made between isotropic, biaxially stretched, and uniaxially stretched semicrystalline polymers. Furthermore, some functionalities of transparent nanocomposites based on semicrystalline polymers are also discussed. This review aims to provide guidelines regarding the principles of manufacturing transparent high-performance semicrystalline polymers and their nanocomposites for potential applications in fields like packaging, building, and construction, aerospace, automotive, and opto-electronics.

Generally, optical properties of a polymeric material involve transparency, gloss, clarity, haze, absorption of light, fluorescence, and so forth.^[1] In optics, transparency is the physical property of allowing light to pass through a material without scattering. Translucency allows light to pass through, but photons can still scatter at interfaces, or whenever there is a change in refractive index as in the case of a material made up of components with different refractive indices. A transparent material is typically made up of components with uniform refractive indices. Transparent materials appear clear, with the overall appearance of one color, or any combination leading up to a brilliant spectrum of every color. The opposite property of translucency is opacity.

Transparency is hugely important in the field of glass substitution, optical appliances, and packaging. Gloss is mainly determined by light reflection and a smooth surface usually means high gloss. The gloss of polymers is generally determined by their surface texture, which can originate from extrinsic as well as intrinsic factors. Extrinsic factors like a dusty environment, catalyst residues, or surface textures in molds or calenders can often be minimized during processing. Intrinsic factors, however, like the refractive index of the material that creates gloss are often more difficult to circumvent. Clarity is a measure of the direct transmission in relation to scattering at low angles ($< 2.5^\circ$). A high level of clarity indicates a good resolution of the details of an object when seen through the material. Haze, on the other hand, is defined as the part of the transmitted light which is scattered at larger angles ($> 2.5^\circ$). It denotes the milkiness of a sample. If haze is greater than 30%, materials will appear translucent, which is still useful though for many packaging applications. For non-conjugated systems, the material usually does not absorb fluorescence or phosphorescence, while conjugated systems like functional polymers consisting of graphene or carbon nanotube (CNT) nanoparticles do. In this review, the emphasis is however mainly on transparency.

In most studies reported in the literature related to optical transparency, a sample is usually placed at a very close proximity to an object or even directly on top of a background image, while transmittance spectra are normally measured at a short sample-to-detector distance (below 5 cm) in a UV-vis machine.^[2,3] Nevertheless, actual transmittance generally refers to a property commonly known as “see-through,” which involves an observer’s ability to distinguish clearly a relatively distant object through the material according to ASTM D1746-15, similar to the

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visibility of a faraway scenery seen through a window. Visibility and transmittance values in the visible light wavelength range, involving specimens positioned at a far distance from an object (or detector), are typically lower than when placed close to an object (or detector), and these differences become even larger in the case of translucent or opaque specimens.^[4] Therefore, optical transparency in the far field and transmittance spectra measured using a large sample-to-detector distance have a much greater practical significance for applications like windows and glazing. However, most of today's studies reported in literature only refer to near or very near field transparency and/or transmittance values and hence, unfortunately, examples listed in this review mostly concern near field transparency unless otherwise indicated. In addition, the thickness of the specimen affects its optical performance. Thinner films usually possess higher transparency since they contain fewer defects or particles that can scatter light. Light scattering by particles can either be Mie scattering when particles are similar to, or larger than the wavelength, or Rayleigh scattering when particles are small with respect to wavelengths of light and exhibit a refractive index close to 1.^[6, 5]

Common highly transparent materials include inorganic glasses or amorphous polymers and are extensively used in areas requiring a high clarity like optical devices, buildings, and automotive glazing. Inorganic glass combines a high clarity with scratch resistance and rigidity with a Young's modulus of 50-90 GPa. However, glass is also brittle with a low strength (< 50 MPa), strain at break and impact resistance. This results in safety issues when using glass in structural applications such as car windshields and glazing elements as fracture typically involves shattering into multiple fragments, potentially causing injuries to occupants.^[7] The brittle fracture behavior, poor impact resistance and post-failure behavior can be improved through the use of laminated glass by introducing transparent flexible polymeric interlayers in between glass layers,^[8] with the main purpose to preserve the integrity of glazing and to prevent it from scattering into multiple fragments. However, ultimately upon impact the glass layers in laminated glass will still fracture due to their intrinsic brittle nature, although the inner protective polymeric layer may give the glass some structural integrity and prevents it from being scattered around, thus qualifying it as safety glazing, security glass, car glass, bulletproof glass, and so forth.^[7, 9] However, strength and impact resistance of laminated glass is still rather low especially when compared with those of some metals or high performance composites.^[8, 10-12]

Isotropic transparent polymeric materials can reach similar optical properties as transparent inorganic materials like glass but with significant advantages in other properties such as low density, good impact resistance, flexibility, and rapid processing of complex shaped parts, and so forth. On the other hand, mechanical properties of polymeric materials such as Young's modulus (< 3 GPa) and tensile strength (< 70 MPa)^[13] are typically relatively low as a consequence of weak intermolecular interactions.

Based on the degree of crystallinity (X_c), polymers can be classified into two main categories: amorphous polymers (non-crystalline or low-crystalline structures with small amount of crystalline phase) and semicrystalline polymers.^[10,11,12]

Amorphous polymers represent the largest group of transparent plastics with major representatives such as polycarbonate (PC), poly(methyl methacrylate) (PMMA), polystyrene (PS), thermoplastic polyurethanes (TPU), polyvinyl butyral (PVB), and copolymer ethylene vinyl acetate (EVA). In general, these amorphous polymers tend to be atactic as in the case of atactic PS, while some polymers like Bisphenol A PC remain in their amorphous state upon cooling because of their extremely slow crystallization kinetics. In addition, polyvinyl chloride (PVC) can crystallize but typically has a crystallinity of only 10% and is therefore often classified as an amorphous polymer. Transparency can also be achieved in plasticized PVC as long as additives are selected carefully. In amorphous polymers, the absence (or limited size) of the crystalline regions contributes to their high optical transparency, while it also leads to the absence of a melting temperature and comparatively limited elastic moduli (2-3 GPa) and tensile strengths (~ 60 MPa) in the case of PC, PMMA and PS.^[13]

Semicrystalline polymers are composed of both crystalline and amorphous phases. Their high-temperature mechanical performance is often superior to amorphous polymers due to the presence of crystalline regions. However, because the refractive indices of these crystallites along a-axis, b-axis and c-axis are usually different due to anisotropy especially for orthorhombic unit cells like polyethylene (PE),^[14] and because they are usually higher than that of the amorphous

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phase, visible light can scatter at the numerous boundaries between these crystalline and amorphous regions. This light scattering leads to less light being transmitted through the polymer, resulting in opacity of most semicrystalline polymer products.

The dimensions of the crystals or other domains will greatly affect the transparency of a semicrystalline material. If the size of crystallites or inclusions is similar or larger than the wavelength of visible light, these aggregates will scatter the light, leading to poor transparency. Under these circumstances, a higher crystallinity usually means reduced clarity. If the dimensions of voids, crystallites or foreign inclusions are well below the wavelength of visible light (around $1/15$ of the light wavelength or roughly $600/15 = 40$ nm) light scattering will be largely eliminated, resulting in a translucent or transparent material even at higher crystallinity levels. In most semicrystalline polymers, especially those with a fast crystallization rate such as PE and polyamides like PA-6, the sizes of the crystals are generally larger than the wavelength of visible light, leading to a large amount of light scattering and an opaque appearance.

This paper will review the current state-of-the-art in producing transparent products from semicrystalline polymers including some of their nanocomposites. The review is organized according to the methodologies to produce transparent products like films consisting of isotropic, biaxially oriented, or uniaxially oriented semicrystalline polymers. Apart from molecular structure and processing history, the use of additives also greatly affects the optical properties of semicrystalline polymers.

There are a few ways to reduce the dimensions of crystals so as to produce transparent semicrystalline polymer products. Adding nucleation agents to isotropic semicrystalline polymers can effectively decrease the dimensions of crystals by accelerating the rate of nucleation and regulating the time scale of crystallization by initiating the crystallization of the polymer at higher temperatures during cooling of the melt. Nucleation agents are inorganic compounds, such as benzoic acid, kaolin, clay and talc, of high melting temperature and small average particle size ($\ll 100$ nm). The nucleation agents remain solid in the polymer melt and act as heterogeneous nuclei, decreasing the free energy for forming nuclei larger than the critical size.^[17] They provide numerous nucleating sites effectively decreasing the average size of the spherulites.

Clarifying agents, a subcategory of nucleating agents, are organic compounds that have a melting temperature within the processing window of the clarified polymer. Sorbitol and its derivatives such as 1,3:2,4-dibenzylidene sorbitol (DBS),^[24, 25] and 1,3:2,4-bis(3,4-dimethylidibenzylidene) sorbitol (DMDBS),^[21, 26] salts of rosin acid,^[27, 28] organic phosphates^[29] and trisamides (like N,N',N''-tris-isopentyl-1,3,5-benzene-tricarboxamide)^[20] are typically used as clarifying agents to fabricate transparent iPP products. Clarifiers like DBS can also enhance the transparency of PET products.^[30, 31] Low molar mass compounds like DBS dissolve in the molten polymer and self-assemble or crystallize upon cooling into a three-dimensional fibrous network of nanosized dimensions. Due to this nano-fibrillar network and its associated large surface area, it creates numerous nucleation points and leads to a strongly reduced average crystal size below the wavelengths of visible light (< 50 nm). This not only leads to increased clarity and reduced haze but also to enhanced stiffness and shorter cycle times during molding.

IV. CONCLUSION

Generally, there are three main routes to create transparent products from semicrystalline polymers: (a) suppressing crystallization and preventing the formation of large crystals by adjusting chemical structure, tacticity or rapid quenching; (b) reducing crystal or domain size to below the visible-light wavelength (usually < 50 nm) by adding nucleating or clarifying agents or by copolymerization; (c) matching of refractive indices between two semicrystalline polymers to produce transparent polymer blends. In many cases, a combination of (a), (b), and (c) is used to generate a high optical transmittance.

Stereoregular polymers like isotactic or syndiotactic polymers are spatially ordered and can potentially crystallize upon cooling from the melt (thermally induced crystallization), upon mechanical stretching or deformation (strain or stress induced crystallization, SIC) or upon crystallization from solution. During crystallization, the molecular chains will

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fold and form ordered regions called lamellae. Crystallization rate depends on various parameters including chain stiffness, molecular weight, temperature, and so on. For instance, PE will easily crystallize and normally achieve a crystallinity above 35% and an opaque appearance, while PC with its very slow crystallization rate will remain in its amorphous state upon regular cooling and exhibits a transparent appearance.

If the cooling rate of a polymer melt is greater than the crystallization rate like in the case of quenching, a crystallizable polymer can mostly remain in its amorphous state, preventing the formation of large crystals and spherulites. Amorphous polyethylene terephthalate (APET) films or sheets are transparent with good toughness and can be obtained by quickly cooling the molten PET to below T_g after cast film extrusion from a slot die. PET exhibits moderate crystallization rates and upon rapid cooling, chains do not have adequate time to reorganize themselves into an ordered crystalline structure and the PET will mostly remain in its amorphous state.[13,14,15]

Controlling chemical structures and tacticity can influence the crystallization process and the formation of large crystals. A high degree of polymer chain tacticity can facilitate the crystallization process since it is easier for regular chains to pack closely and form ordered crystalline structures. Usually, isotactic or syndiotactic structures result in a certain degree of crystallization, while most atactic polymers do not crystallize and remain in their amorphous state due to the absence of chain regularity. Polypropylene (PP) has different stereochemical configurations based on the relative position of adjacent methyl groups as it is polymerized from asymmetric propene monomers. Isotactic PP (iPP) and syndiotactic PP (sPP) are semicrystalline polymers and their relatively low crystallization speed under homogeneous nucleation leads to the formation of micron-sized crystals, accounting for their poor transparency, whereas atactic PP (aPP) is an amorphous polymer due to the irregular arrangement of its side groups, which prevents the formation of crystals. Thus, aPP possesses good transparency but also has a low heat deflection temperature (HDT) due to its low T_g . One exception is poly(vinyl alcohol) (PVA). PVA is an atactic polymer that can crystallize because its OH-groups are sufficiently small not to disturb the crystal lattice. PVA has good optical transparency and is used as linear polarizers applied in sunglasses, displays, cameras, and projection systems.

In terms of chain branching, branch content influences both crystallization kinetics and final morphology of lamellae crystals, with increasing branch content resulting in a decrease in crystallization rate as well as crystallinity. Branch length will also affect the final crystal morphology.^[15] Homo- or co-polyamides (PA) polymerized by asymmetric (co-)monomers possessing side chains or ring structures can achieve transparent amorphous PA products by disturbing the regularity of aliphatic PA chains, leading to a reduced formation of hydrogen bonds in combination with a lower crystallinity. For instance, the substituent methyl groups of poly(trimethyl hexamethylene terephthalamide) (PA 6-3-T) inhibit crystallization, and it remains amorphous at all temperatures with around 90% light transmittance.^[16]

However, the creation of transparent polymers by suppressing crystallization of intrinsically crystallizable polymers may lead to improved clarity but at a significant expense of their high temperature mechanical properties.

Adjusting the rate of crystallization is helpful in reducing the size of crystals in semicrystalline polymers. Poly(4,4'-aminocyclohexyl methylene dodecanedicarboxylamide), named PA PACM12,^[32] is a transparent microcrystalline cycloaliphatic polyamide and its chemical structure is shown in Figure 1E. The crystallization speed of PA PACM12 is relatively slow and as a result, fine crystalline structures with microcrystalline dimensions smaller than the wavelength of visible light can be formed. As a result, these materials are transparent with about 92% light transmittance. Meanwhile, these microcrystalline structures offer also excellent processibility, high thermostability as well as good scratch and abrasion resistance, making them suitable for applications like goggles and sunglasses.

Introducing comonomers for copolymerization helps to destroy the original continuous polymer chain structure and impedes crystal growth, leading to a decrease in crystalline dimensions and overall crystallinity. In the case of polyethylenes, nucleating and clarifying agents do not work because the crystallization rate is too high. Reducing their crystal size is usually done by copolymerization with low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and/or very low-density polyethylene (VLDPE). PP copolymerized with ethylene or higher α -

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olefins can reach good optical clarity. Ethylene-propylene random copolymers (EP-RACO) exhibit better transparency (up to 84.6%), higher toughness, lower processing temperatures, broader softening range and improved low-temperature impact strength in comparison to PP homopolymers, where the ethylene units act as disturbances in the EP-RACO chains and thus impede the crystal growth.^[33, 34] The increasing amount of ethylene units helps to shift PP's crystal arrangement from the predominant monoclinic α phase to an orthorhombic γ phase, and this modification is favorable for achieving a higher transparency.^[35] In addition, random isotactic copolymers of propylene and 1-butene can achieve a transparency of 90% together with a crystallinity of 30% to 50% after quenching, followed by aging at ambient temperature. This high transparency is explained by the absence of spherulites and/or the changes of crystal structure and morphology from nonisometric monoclinic lamellae to isometric mesomorphic nodules, with a structure optically less heterogeneous than a spherulitic structure, leading to less light scattering and hence increased light transmission.^[36] The copolymerization with diester-diamide and diester-tetra-amide segments such as polyether(ester amide)s (PEEAs) with poly(propylene oxide) (PPO) and monodisperse poly(hexamethylene terephthalamide) segments (PA-6,T) also results in transparent copolymers.^[37, 38] Some other copolymers such as poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)]^[39] and poly(N-methylmaleimide-alt-isobutene) [poly(MeMI-IB)]^[40] lead to optically transparent products as well.

Blends of some semicrystalline polymers can also achieve good clarity by decreasing the domain size of the dispersed phase to below the wavelength of visible light. For this purpose, these semicrystalline polymer blends need to have excellent compatibility while the presence of another polymer phase promotes heterogeneous nucleation, leading to a finer morphology. Modifying blending conditions as through intensive high speed mixing can reduce the dimensions of the dispersed phase.^[41] In addition, reactive compatibilization with suitable catalysts is helpful in making originally opaque incompatible polymer blends transparent by stabilizing the dispersed phases to smaller dimensions and lowering interfacial stresses. For instance, the light transmittance of poly(L-lactic acid)/ethylene vinyl alcohol (PLA/EVOH) blends was improved from 9.3% to 83.5% after reactive compatibilization with zinc stearate (ZnSt_2) as a catalyst. The introduction of EVOH with excellent water vapor barrier properties broadens the application of transparent PLA/EVOH especially in the packaging field[16]

REFERENCES

1. Bird, Stewart & Lightfoot 2006, p. 266.
2. ^ Bird, Stewart & Lightfoot 2006, pp. 266–267.
3. ^ Holman, J.P. (1997), Heat Transfer (8th ed.), McGraw Hill, p. 2, ISBN 0-07-844785-2
4. ^ Bejan, Adrian (1993), Heat Transfer, John Wiley & Sons, pp. 10–11, ISBN 0-471-50290-1
5. ^ Bird, Stewart & Lightfoot 2006, p. 267.
6. ^ a b Bejan, p. 34
7. ^ Bird, Stewart & Lightfoot 2006, p. 305.
8. ^ Gray, H.J.; Isaacs, Alan (1975). A New Dictionary of Physics (2nd ed.). Longman Group Limited. p. 251. ISBN 0582322421.
9. ^ ASTM C168 – 15a Standard Terminology Relating to Thermal Insulation.
10. ^ "Thermal Performance: Thermal Mass in Buildings". greenspec.co.uk. Retrieved 2014-09-13.
11. ^ Bird, Stewart & Lightfoot 2006, p. 268.
12. ^ Incropera, Frank P.; DeWitt, David P. (1996), Fundamentals of heat and mass transfer (4th ed.), Wiley, pp. 50–51, ISBN 0-471-30460-3
13. ^ Ashcroft, N. W.; Mermin, N. D. (1976). Solid State Physics. Saunders College. chapter 2. ISBN 0-03-049346-3.
14. ^ Perry, R. H.; Green, D. W., eds. (1997). Perry's Chemical Engineers' Handbook (7th ed.). McGraw-Hill. Table 1–4. ISBN 978-0-07-049841-9.
15. ^ Daniel V. Schroeder (2000), An Introduction to Thermal Physics, Addison Wesley, p. 39, ISBN 0-201-38027-7
16. ^ Chapman, Sydney; Cowling, T.G. (1970), The Mathematical Theory of Non-Uniform Gases (3rd ed.), Cambridge University Press, p. 248