Creating Complex Polymer Systems
From Polyethylene *Al Dente* to Polystyrene *Mille-Feuille*

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Summary

Polymers have improved the quality of our everyday life ever since their discovery and, in many aspects, have made our current living standard possible. By now, these materials have proven to be economical, lightweight and durable, leading to a vast number of applications ranging from demanding, highly specialized products to low-tech mass-produced goods. Polymers often earn the quality mark high-performance due to the possibility of orienting the macromolecular chains of which they consist, thereby transforming these materials from being relatively weak to being strong, stiff and tough in a given direction of orientation. Also, by using appropriate processing routes it is possible to create, besides one- and two-dimensional macromolecular arrangements, three-dimensional complex, hierarchical or multi-layer polymer structures.

Polymers are versatile materials which, depending on their exact molecular structure and processing conditions, can be amorphous, crystalline, or even liquid-crystalline. In each case, different strategies to achieve chain orientation are required. It is, therefore, not surprising that there is still a vivid interest in new processing methods by which polymers can be oriented or structured to further tailor their properties. It is the objective of this thesis to specifically explore different routes to macromolecular manipulation in polymeric materials, with the aim of enhancing or achieving novel material properties.

The first study concerns a critical re-examination of the role of solvent quality in the established “gel-spinning” technique of ultra-high molecular weight polyethylene (UHMW PE) towards “green-fabricated” high-performance fibers. It is shown that at a given polymer concentration, replacing the conventionally-used good solvents with relatively poor solvents (including, but not limited to, natural oils), increases the maximum draw ratio by a factor of two, with corresponding increases of ~100% and ~75% in Young’s modulus and tensile strength, respectively.

The second processing route addresses the so-called “foil-spintrusion” of self-reinforced, high-performance liquid-crystalline polymer (LCP) films for recyclable monolithic “composites”. The combination of 100% “fiber” content and
the absence of an adhesive or matrix yields a material with attractive specific mechanical properties for thin laminate structures, which outperform even aramid/-epoxy composites.

In contrast to the uniaxial orientation common to both of the above processing approaches, the third approach explores a new method for simultaneous, continuous biaxial orientation. The applicability of this alternative laboratory-scale route is first demonstrated by reproducing the well-known biaxially oriented isotactic-polypropylene (i-PP), generating films with mechanical properties that approach those of commercially available materials. Subsequently, biaxial orientation is used to enable fast processing of alumina-platelet-reinforced i-PP films. During the biaxial solid-state deformation, the polymer matrix forces the platelets into a planar alignment. These films can be subsequently stacked and consolidated into laminates.

Finally, the fourth method is based on creating polymer products with complex and/or hierarchically ordered cross-sections. For the first time, static mixers were employed for polymer systems with high molecular weights using polyamide (PA), polystyrene (PS) and polyurethane (PUR). Besides manufacturing tree-like structures with trunks, branches and leaflets, an interesting – and, notably, bioinspired – approach is presented via manufacturing PS/PUR multi-layers, wherein the alternating soft, thin layers improve the crack resistance of normally brittle PS.

This thesis describes versatile processing methods for a diverse range of polymer systems. Fibers and films are addressed, as well as laminates and complex arrangements made of amorphous, crystalline or liquid-crystalline polymers.
Zusammenfassung


Die erste Studie beschäftigt sich mit der kritischen Evaluation der Lösungsmittelqualität im etablierten „Gel-Spinn“ Verfahren von ultrahochmolekularem Polyethylen (UHMW PE) mit dem Ziel, umweltfreundliche Hochleistungsfasern zu produzieren. Es wird gezeigt, dass bei einer gegebenen Polymerkonzentration in Lösung statt des Einsatzes von *guten* Lösungsmitteln relativ *schlechte* verwendet werden können (einschliesslich, aber nicht
beschränkt auf natürliche Öle), was eine Verdoppelung des maximalen Verstreckungsgrades hervorbringen kann. Dies geht mit einer entsprechenden Zunahme des Elastizitätsmoduls und der Zugfestigkeit dieser Fasern um jeweils ~100% beziehungsweise ~75% einher.

Das zweite hier vorgestellte Verfahren ist die sogenannte „Folien-Spintrusion“, mit dem selbstverstärkende, hochleistungsfähige flüssigkristalline Polymer (LCP) Folien für wiederverwertbare monolithische Verbundwerkstoffe produziert werden können. Die Kombination von 100% Fasergehalt und die Abwesenheit eines Klebstoffes oder einer Matrix ergibt ein Material mit attraktiven spezifischen mechanischen Eigenschaften für dünne Laminatstrukturen, welche sogar Aramid-/Epoxid-Verbundwerkstoffe übertreffen.


Das vierte Verfahren befasst sich mit der Herstellung von polymeren Produkten mit komplexen und/oder hierarchisch geordneten Strukturen. Statische Mischer werden für Polymere wie zum Beispiel Polyamid (PA), Polystyrol (PS) und Polyurethan (PUR) verwendet. Neben der Herstellung von baumartigen Strukturen mit Stamm, Ästen und Blättern wird ein anderer interessanter – und besonders hervorzuheben, bioinspirierter – Ansatz zur Fertigung von PS/PUR Vielfachschichten vorgestellt. Dünne PUR Schichten verbessern die Rissbeständigkeit von sprödem PS.

Chapter 1

Introduction
1 Background

The following sections will present a brief overview of the current state-of-the-art in the fields of high-performance polymer-based fibers, films and systems, as well as products made therewith. In particular, the focus is on the remaining macromolecular processing and production issues that hamper further development of this important area of material science and engineering.

During the last fifty years, the academic and industrial communities have been exposed to, and increasingly employed, what are generally referred to as “high-performance” (organic) polymer fibers. Well-known examples are those based on the relatively rigid polyaramids (e.g. Kevlar®, Twaron®) and those manufactured with ultra-high molecular weight polyethylene (UHMW PE: Dyneema®, Spectra®), which is an intrinsically flexible chain molecule. The above-mentioned fibers exhibit tensile (Young’s) moduli and tensile strengths on the order of, respectively, ~100 GPa and ~3 GPa.[1,2] When expressed in terms of “specific” characteristics, due to their low density (~1 g cm⁻³) – as opposed to that of steel (~7.9 g cm⁻³) – the phrase “10×stronger and stiffer than steel” has frequently been used.

1.1 Oriented Polymer Fibers

In most cases, the common feature in such high-performance polymer structures is the high degree of extension and orientation of the macromolecules that constitute these materials. However, in the absence of an external field, such as elongational flow or uniaxial mechanical stress, polymers do not spontaneously form the desired highly oriented structures and tend to assemble into isotropic solids of very modest mechanical performance.[3-6] Remarkably, already in the early 1930s, scientists were contemplating the required macromolecular arrangement for such strong and stiff polymer systems. For instance, Carothers and Hill advanced a “crystal lattice” (Figure 1), formed by parallel-aligned (semi-)crystalline polymer chains of unequal length, and their first attempt to realize such a structure, with markedly improved mechanical properties, yielded
fibers obtained by uniaxial solid-state plastic deformation (so-called “cold drawing”) of melt-spun polyesters and polyamides.\cite{7}

![Figure 1. Lattice of molecules of unequal length and randomly distributed chain ends. The concept was advanced by Carothers and Hill for parallel-aligned polymer chains in a useful man-made fiber (cf. ref. [7]).](image)

The first successful large-scale effort towards unusually stiff and strong polymeric structures was initiated in the mid-1960s by Stephanie Kwolek and Herbert Blades. Working at E. I. du Pont de Nemours & Company, Inc., they discovered that the highly extended poly(p-phenylene terephthalamide) (PPTA), a so-called rigid-rod polymer, could be spun by dry-jet-wet-spinning from concentrated sulfuric acid into high-performance fibers.\cite{8-11} This invention took advantage of the fact that above a certain polymer concentration, PPTA and sulfuric acid form a liquid-crystalline (lyotropic) solution, in which (mainly for entropic reasons) the rigid macromolecular chains align themselves into nematic, ordered domains. These domains, in turn, could be subsequently aligned by application of an elongational flow field (Figure 2a), achieved by a high ratio between windup and extrusion speed, yielding, after consolidation by removal of the sulfuric acid in water, high macromolecular orientation in the fibers.

As previously mentioned, flexible macromolecules have also been used for manufacturing high-performance fibers. The issue here is that (semi-)crystalline flexible-chain polymers typically solidify in an entangled form, with partly folded-chain crystals that most often group into three-dimensional ordered entities termed “spherulites”. Motivated by theoretical estimations that certain extended (semi-)crystalline polymer chains could attain an axial tensile modulus of ~300 GPa and an axial tensile strength up to 20 GPa,\cite{12-15} researchers began to
perform basic experiments to force these three-dimensional “folded”-chain crystal morphologies into highly extended and uniaxially oriented structures.

In the 1970s, Capaccio and Ward succeeded in carrying out uniaxial solid-state deformation of melt-processed polyethylene (PE) in a temperature range close to, but marginally below, its melting temperature to draw ratios (i.e. the ratio between final and initial sample lengths) of above 20. The resulting fibers featured Young’s moduli of up to 70 GPa and tensile strengths of ~1 GPa. These studies indicated that the Young’s modulus of drawn fibers is determined by the draw ratio, whereas the maximally obtained draw ratio of melt-crystallized material was shown to decrease with increasing weight-average molecular weight ($M_w$). Owing to the relatively low molecular weight of the PE used, the tensile strength of these melt-spun and drawn – to ultimate levels of extension, which are limited by $M_w$ – fibers was low compared to PPTA fibers and, therefore, subsequent studies focused on increasing the breaking stress. Attempts to stretch melt-processed ultra-high molecular weight polyethylene (UHMW PE; $M_w \geq 3.0 \times 10^6$), to draw ratios above six, failed. Subsequently, it was recognized by Smith et al. that for flexible-chain polymers with relatively weak inter-chain interactions (such as PE), entanglements between polymer chains are the primary factor limiting the maximum draw ratio and that a reduction of the density of entanglements could be achieved by crystallizing PE from (semi-)dilute solutions, leading to the (inaccurately-termed) “gel-spinning” route for producing high-performance PE fibers (Figure 2b). In contrast to melt-crystallized PE, ultra-drawing up to draw ratios of 30 and more of solution-processed (solutions containing 2% w/w polymer) higher molecular weight PE grades ($M_w = 1.5 \times 10^6$) results in stiff and strong fibers with a Young’s modulus and a tensile strength in excess of 100 GPa and 3 GPa, respectively.

Despite the commercial success of the above-processed fibers, issues remain, such as the unattractively and uneconomically low concentrations of polymer solutions, requiring elaborate solvent removal and recovery procedures, as well as the environmental concerns associated with the solvents and extraction means themselves.
Figure 2. a) Alignment of the rigid PPTA macromolecules during dry-jet-wet-spinning. Above a certain polymer concentration in sulfuric acid, PPTA macromolecules form a liquid-crystalline solution. This liquid-crystalline solution is spun and oriented in an elongational flow field, and quenched in water. b) By dilution in a solvent at elevated temperatures, the flexible UHMW PE macromolecules start to disentangle. (Semi-)dilute solutions can be spun and quenched into fibers with reduced polymer entanglement density and can be subsequently drawn to high levels of extension during or after removal of the solvent.

1.2 Uniaxially Oriented Polymer Films

A common technique for improving the mechanical properties of a polymer material is to strengthen it with strong and stiff fibers, as in fiber-reinforced composites, in which, for instance, the previously described high-performance fibers are employed in the form of continuous yarns and woven fabrics or as short fibers. Many mechanical properties would improve with increasing fiber content; however, standard impregnation techniques limit the fiber content to about ~60% v/v, requiring ~40% v/v of matrix material with modest mechanical characteristics.\[24,25\]
Recently, in an attempt to increase the effective fiber content, new processing methods have emerged that allow the production of thin laminates by spreading and parallel aligning of high-performance yarns – even down to that of single filaments – followed by impregnation and curing. This fiber-spreading technique to make thin-ply laminate composites allows for a higher fiber volume content, enhanced fiber alignment as well as improved fracture and fatigue characteristics.[26,27] Eye-catching commercial examples of this kind of technology are the racing sails produced by the North Sails Group, the Cuben® fiber laminates and Createx Amalgame sheets.[28–30] However, the cumbersome, expensive and elaborate spreading and impregnation of the fibers without inflicting damage, is an obvious disadvantage of this technology.

Other efforts have been made to produce cost-effective self-reinforced polymer films by avoiding the need of impregnation, where matrix and reinforcement consist of a single chemical species, notably with isotactic-polypropylene (i-PP).[31] An example of this is the so-called “all-polypropylene” (all-PP) tapes which are designed to compete with traditional thermoplastic composites.[32,33] After extrusion, these tapes are uniaxially stretched and subsequently sandwiched for instance by two unoriented i-PP layers. These all-PP tapes can be fused in a hot press into single-polymer monoliths that hold the promise of high “fiber” volume content and facile recyclability.[34] However, their relatively low stiffness, about 15 GPa for uniaxially oriented polymer structures, is a major drawback for demanding applications.[35]

A new method for the production of self-reinforced material has been introduced recently, *i.e.* the so-called “foil-spintrusion” of highly oriented films of enhanced performance.[36] In this technique, uniaxially oriented films were produced from a thermotropic liquid-crystalline polymer (LCP), poly(p-hydroxybenzoic acid-co-2-hydroxy-6-naphthoic acid), Vectra® A950, using a newly-designed multi-filament-fusing die. These *semi-rigid* macromolecules are spun and aligned through a filament-fusing die from an ordered, thermotropic melt (Figure 3). It was shown that the thus manufactured unidirectional films exhibit promising mechanical properties, combining a Young’s modulus of 70 GPa and a tensile strength exceeding 2 GPa.[37] It was found that the manufactured
4–12 µm thick films could be fused together at elevated temperatures by a solid-state post-polymerization reaction\[^{38,39}\] into monolithic structures, retaining their mechanical performance without any adhesives or matrix material.

**Figure 3.** Below a specific temperature the semi-rigid LCP macromolecules form an ordered, thermotropic melt which can be extruded and oriented into films, in the fashion of dry-jet-wet-spinning of PPTA fibers (cf. Figure 2a), in an elongational flow field. The key element in the filament-fusing die is the half-cylindrical plate comprising arrays of cylindrical orifices, each representing a single spinneret. Schematic drawing of a) cross-section, b) top view and c) photograph of the filament-forming part as well as d) side, e) overall view and f) photograph of the filament-fusing part of the LCP film die. Schematic drawings from ref. [5].

Unexplored, however, are the issues concerning the production and properties of monolithic structures of these films, including reproducible and reliable methods of generating such new materials.
1.3 Biaxially Oriented Polymer Films

In most applications, the highly anisotropic uniaxially oriented polymer structures described in Sections 1.1 and 1.2 are often not loaded exactly along the direction of their macromolecular orientation, leading to a severe reduction of the mechanical performance of the final product in which they are incorporated.\cite{40,41} Therefore, attempts have been made to manufacture high-performance polymer films by biaxial orientation, using, for instance, PPTA or UHMW PE.\cite{42,43} However, calculations by Bastiaansen et al.\cite{44} have shown that biaxial orientation of polymers results in structures that rather resemble an aggregate of crystalline entities in which the condition of constant overall stress results in poor in-plane stiffness, on the order of only 10 GPa (Figure 4a). \[N.B. Interestingly, an example of films with a higher in-plane stiffness are in-situ grown planar-oriented bacterial cellulose films, with a stiffness and tensile strength of 18 GPa and 230 MPa, respectively.\cite{45} The preferred structure for generating high in-plane stiffness – maximum theoretical values of about 110 GPa – was shown to be a quasi-isotropic assembly of stiff, uniaxially oriented films (Figure 4b) which, most unfortunately, cannot be generated by biaxial stretching.\cite{44}

![Figure 4. a) Schematic illustration of an aggregate of crystalline entities which is typically found in biaxially deformed polymer films. b) A laminate, made of unidirectionally oriented sheets (cf. ref. [44]).](image)

Although, to this day, high-performance polymer structures have not been produced by biaxial orientation, this technique is still widely used for enhancing certain in-plane mechanical properties, as well as gas-barrier properties.\cite{46-50}
which are highly important in food and beverage packaging applications. For instance, biaxially oriented isotactic-polypropylene (BOPP) provides a major contribution to this industry segment. Unfortunately, further advancement of and innovation in this important area are impeded, since current laboratory methods for exploratory biaxial drawing do not allow for continuous drawing and often result in inhomogeneous samples.\textsuperscript{[51,52]} Furthermore, the industrial processes for biaxial deformation, such as the double and triple bubble\textsuperscript{[53]} and tenter frame\textsuperscript{[54]} methods, require large and expensive equipment which remains an impeding issue for the development of biaxially oriented films of novel polymers, polymer blends and composites.

### 1.4 Bi- and Triaxially Arranged Polymer Systems

After the above short review of uni- and biaxially oriented polymers, possessing one- and two-dimensional orientation respectively, this section introduces complex structured two- and three-dimensional polymer systems created by static mixers. Here the goal is not to orient the macromolecules, but rather to arrange them in two- and, finally, three-dimensionally directed layers.

A static mixer is a device for the continuous mixing by flow division of two or more fluid materials. The working principle of static mixers is based on the application of the baker’s transformation: a repetitive action of stretching – i.e. creating new interface – and folding or stacking (Figure 5a) or stretching, cutting and stacking (Figure 5b).\textsuperscript{[55–57]}

![Figure 5](image.png)

**Figure 5.** The fundamental working principle of static mixers, applying the baker’s transformation. Repetitive a) stretching and folding or b) stretching, cutting and stacking.
Static mixers, like the Sulzer SMX mixer\cite{58} and the Kenics mixer,\cite{59} are frequently used in the food- and process-technology industry. Downscaling to microfluidics has recently resulted in new geometries that can also be realized on small scales,\cite{60-63} with one of the most interesting designs being the splitting serpentine mixer.\cite{64-66} If an initial two-layer system is fed into such a mixer, a stratified, alternating multiple layer structure results. By processing combined fluxes of different melt flows of, e.g., polyamide (PA), polystyrene (PS) or polyurethane (PUR), essentially any number of alternating layers can be obtained. By combining hard and soft polymers, potentially interesting mechanical properties can be obtained. Modifying the technique to multiply structures, rather than layers, allows three-dimensionally arranged polymer structures to be obtained. Interestingly, every initial structure can be multiplied, and no restrictions exist regarding the number of polymers fed, their flux ratio and initial configuration. For the purpose of illustrating the potential of these new processing techniques, a series of recently-developed static mixers, so-called Dentinxc and Peelincx mixers,\cite{67} were employed.

2 Objective and Scope of Thesis

The principal objective of the work presented in this thesis is to develop and evaluate new processing methods for advanced, structured high-performance polymer systems.

Part A of this thesis is directed to uniaxially oriented polymer structures.

In Chapter 2, the role of solvent quality in the established solution-processing route of UHMW PE is examined. Solution-crystallized UHMW PE precursor films are produced using a broad range of organic solvents, including the current-standard solvent decalin, mineral oil and a variety of saturated fatty acids, as well as vegetable oils. The main objective is to manufacture UHMW PE fibers and films employing a “green” solvent technology, combining more efficient processing with comparable or even better mechanical properties than for current commercially available products.
The aim of Chapter 3 is an in-depth evaluation of the anisotropic (visco-)elastic and fracture properties, as well as strain-rate dependent characteristics of high-performance LCP films, produced via foil-spintrusion. These films are stacked and consolidated, without any use of adhesives or matrix, at elevated temperatures, into monoliths with the promise also of improved recyclability for these “composite” materials.

Part B of the thesis will address biaxially oriented polymer-based films.

In Chapter 4 an alternative, laboratory-scale processing method for obtaining biaxially oriented films is presented. The new approach involves continuous, simultaneous biaxial solid-state deformation of polymer-based precursor tubes over a heated V-shaped metal mandrel. i-PP is used as an illustrative example throughout, although this study shows that the same technique can also be applied to other polymers, polymer blends and composites.

Part C of this thesis addresses the continuous creation of structured films with complex or hierarchical three-dimensional arrangements, using static mixers.

In Chapter 5, the aim is to improve the recently developed static mixers to be able to deal with polymer combinations possessing different viscosities. Ultimately, a modified version of the so-called Peelincx mixer allows realizing 10, 120, 1’440, 17’280 and 207’360 alternating polymer layers. The system is tested first with an equal viscosity system, blue-dyed and transparent PA:PA, and with a combination of a brittle, thermoplastic polymer with a soft, rubbery one, PS:PUR. Flux ratios were varied from 1:1 up to 1:60.

The objective of Chapter 6 is to investigate a “one step” manufacturing process of complex, hierarchically-arranged polymer systems. Hierarchy level 0 corresponds to the two dimensionally arranged structures of Chapter 5. Hierarchy level 1 orients the layers vertically, and combines them with horizontal top- and bottom layers, yielding a structure resembling “bare tree trunks standing on the horizontal ground and pointing towards the sky”. The next hierarchy level 2 adds branches to the trunks. Hierarchy level 3 further adds leaflets to both sides of the branches that are connected to the trunks. Basically a variety of structures are realized, characterized by the designed co-continuity of both constituent
components. This method for continuous creation of films with hierarchical cross-sections could find applications in photovoltaics and selectively transporting membranes.

Finally, in Chapter 7 general conclusions and an outlook are presented.

This dissertation is based on the following manuscripts:


References


Part A

Uniaxially Oriented Polymers
Chapter 2

Gel-Processing Revisited:
*The Worse, the Better*
Chapter 2

Gel-Processing Revisited

1 Introduction

The solution-spinning/drawing process, which came to be known as “gel-spinning”, allows the fabrication of ultra-high modulus and ultra-high strength polyethylene (PE) fibers and films. Following the classical paper on the mechanism of aforementioned process,[1] Booij et al.[2] investigated the use of uniaxial tensile deformation for achieving the ultimate levels of chain extension and alignment for weakly-interacting macromolecules. It was demonstrated that uniaxial alignment and, therewith, enhancement of the associated mechanical properties of (semi-)crystalline polymers such as PE, is limited primarily by the degree of entanglement for the constituent macromolecules, rather than the shape, size or order of crystalline entities. In these experimental studies, the degree of entanglement was varied by dissolving ultra-high molecular weight polyethylene (UHMW PE) at different concentrations and consolidation through gelation of the spacing between macromolecular entanglements ($M_e$), following the well-established concept that the $M_e$ in solution, $M_e^{sol}$, varies as:[3]

$$M_e^{sol} = \frac{M_e^{melt}}{\Phi}$$  \hspace{1cm} (1)

where $M_e^{melt}$ is the molecular weight between entanglements in the (undiluted) polymer melt and $\Phi$ is the polymer volume fraction in the solution. Subsequent quenching-induced gelation of the solutions followed by solvent removal – an approach commonly referred to as gel-processing – allowed to preserve the degree of entanglement in the solid-state polymer films.

The classical theory of rubber elasticity[4] states that the maximum draw ratio $\lambda_{\text{max}}$ (i.e. the ratio between final and initial sample lengths) of a permanent network varies with the statistical length of chain segments between crosslinks, as quantified by $M_e$. Assuming that the entanglements of macromolecular chains, whether in the melt or gel, act as (semi-)permanent crosslinks, $\lambda_{\text{max}}$ can be expressed as:

$$\lambda_{\text{max}} \propto M_e^{1.5}$$  \hspace{1cm} (2)
Consequently, Booij et al.\cite{2} proposed a simple expression for the concentration-dependence of the maximum draw ratio $\lambda_{\text{max}}$ of UHMW PE fibers and films prepared by the gel-processing route:

$$ \lambda_{\text{max}} = \frac{\lambda_{\text{melt}}}{\Phi^{0.5}} $$

(3)

Here $\lambda_{\text{melt}}$ is the maximum draw ratio of a melt-quenched solid and, as above, $\Phi$ is the starting polymer volume fraction in solution. For UHMW PE (typical weight-average molecular weight $\bar{M}_w \geq 3.0 \times 10^6$), which in the melt-crystallized state has $\lambda_{\text{melt}} \approx 6$, the generation of stiffness levels in excess of 150 GPa and tensile strength greater than 2.5 GPa requires molecular draw ratios of around 40.\cite{5} According to relation (3), to enhance the “drawability” and thus improve the mechanical properties of UHMW PE, polymer concentrations in solutions as low as $\Phi \approx 0.03$ would be required in the case of, for instance, decahydronaphthalene ("decalin") – a good solvent for UHMW PE – being used as a diluent.\cite{5,6} [N.B. This assumes that all entanglements present in the melt or solution are trapped.]

Despite this seemingly uneconomical and complicated process, ultra-high modulus and ultra-high strength UHMW PE fibers have been successfully developed on a significant commercial scale, albeit exhibiting a somewhat lower level of mechanical properties due to the higher polymer solution concentrations used (typically $\sim 10\%$ v/v). These materials, which are sold under various trade names including Dyneema® and Spectra®, have found widespread use in a broad range of demanding applications that include personal armor, sails, ropes and surgical sutures.\cite{7,8}

Recognizing the above-described concentration issue with the solution-spinning/drawing process, Rotzinger et al.\cite{9} subsequently set out to control the entanglement density in solid-state UHMW PE by physicochemical means during polymer synthesis, rather than the semi-dilute solution-based gel-processing route described above. In their approach, the conditions of ethylene polymerization were modified to reduce the length of the growing macromolecular chain in the fluid phase to well below the spacing between
macromolecular entanglements found in an unperturbed PE melt ($M_e \approx 1.25 \times 10^3$, cf. ref. [10]), in order to impede their formation. This was achieved by employing low polymerization temperatures, low monomer pressure and/or low catalyst activity.\textsuperscript{11,12} The polymers thus produced underwent solid-state compression-molding, yielding macroscopically-coherent films. With compression-molding being carried out below their melting temperature, hence the designation “virgin”, \textit{i.e.} not previously molten or dissolved, low entanglement density is preserved in the resulting films. The films were subsequently drawn into ultra-high modulus and strength materials by employing the usual tensile deformation techniques. Today, more than two decades after its invention,\textsuperscript{13} this solvent-free process is also being commercialized for the production of high-performance films.\textsuperscript{14}

Although both the “semi-dilute solution”- and “virgin polymer”-based UHMW PE processing routes that were developed have, as mentioned above, proven to be a practical and economic success, there are several remaining difficulties associated with these two technologies:

i) The “gel-processing” method, despite having several advantages regarding production control, has a significant drawback, namely the need to recover and purify large amounts of flammable solvent (typically 90 kg per 10 kg fiber), such as decalin by evaporation\textsuperscript{15} or mineral oil extracted with, for instance, hexane or fluorocarbon compounds.\textsuperscript{16} Furthermore, it has been reported that the solvents and means of extraction employed carry significant health hazards (\textit{cf.} refs. [26–36] in ref. [17]).

ii) Although the virgin polymer-based processing route has the advantage that no solvent is utilized in the film or fiber production process, it nevertheless requires delicate control over several key aspects of the film or fiber production process. For instance, this pertains to both the polymerization, which involves non-trivial catalyst systems, as well as to the production of solid-state compression-molded precursor films which subsequently require relatively low tensile deformation rates.
Accordingly, technologically attractive production of ultra-high modulus and strength PE fibers and films presents ample room for improvement, especially given that the number of beneficial applications, and the market as a whole, are continuing to expand.

With this background in mind, we have attempted to address the above issues by controlling the density of chain entanglements in solution-processed, solid UHMW PE not only by varying the concentration of the polymer in solution, as in the gel-processing technique described above, but also by optimizing the “quality” of the solvent. As will be demonstrated below, this approach was successful in allowing a dramatic reduction in the amount of diluent required and trivializing its recovery and purification while, at the same time, maintaining the flexibility of solution processing and providing undisputable environmental benefits.

It should of course be mentioned that exploration of diluents other than, for instance, decalin and mineral oil has been reported. Examples include Motooka et al.\cite{18} who described the use of aliphatic carboxylic acids, alcohols, acid amides, carboxylic acid esters, aliphatic mercaptanes, aliphatic aldehydes and aliphatic ketones in gel-processing of UHMW PE from solutions of relatively high polymer concentrations. However, the mechanical properties of the resulting fibers were disappointingly low, with Young’s moduli invariably below 65 GPa. In addition, extraction was carried out using highly flammable and toxic solvents such as hexane, heptane, heated ethanol, chloroform and benzene, which have well-known adverse environmental and health issues. Elsewhere, Rajput et al.\cite{17} attempted to dissolve 5% w/w UHMW PE in selected vegetable oils, such as sunflower and palm oil, but without success. In hindsight, this was due to the relatively low polymer concentration in these solutions, which yielded films of macroscopically poor mechanical coherence (\textit{vide infra}).
2 Background

Virtually since the birth of polymer science it has been realized that fully extended and oriented macromolecular chains offer greatly enhanced mechanical properties in the orientation direction.\cite{19} In case of flexible polymers, the most common orientation method is uniaxial solid-state plastic deformation, also known as “cold-drawing”. It has been established for various polymer systems, that under optimum drawing conditions (no chain-slip), the development of both Young’s modulus and strength directly correlates with the applied plastic deformation.\cite{20-22} Assuming pseudo-affine deformation of strongly anisotropic structural “units”, Irvine and Smith\cite{5} were able to capture this dependence in an analytical two-parameter model, relating the Young’s modulus of the oriented polymer to the plastic draw ratio $\lambda$ as:

$$E = \frac{1}{E_u} - \frac{3\lambda^2}{2(\lambda^3 - 1)} \left(1 - \frac{\arctan(\sqrt{\lambda^3 - 1})}{\sqrt{\lambda^3 - 1}}\right) - \frac{1}{2} \left(\frac{1}{E_u} - \frac{1}{E_h}\right)^{-1}$$

(4)

In this equation, the fitting parameters $E_u$ and $E_h$ represent the moduli of the unoriented and fully oriented polymer, respectively. Using this equation, the experimental “$E$-$\lambda$-curve” for PE was accurately described using values of $E_u$ of about 1 GPa and $E_h$ of about 300 GPa. From the experimental $E$-$\lambda$-curve and its description using equation (4), it follows that attractive levels of stiffness in excess of 150 GPa require plastic draw ratios of more than 40. Unfortunately, the plastic draw ratio for UHMW PE, crystallized from the melt, is limited to ~6. The reason for this is that, in flexible polymers with weak inter-chain interactions such as PE, the plastic draw ratio is believed to be limited by the same entanglements that dominate the flow behavior of polymer melts and polymer solutions, and that are trapped during solidification of the polymer system.\cite{2} During gel-spinning, the entanglement density is reduced by crystallization of UHMW PE from semi-dilute solutions, thereby increasing the molecular weight between entanglements and the maximum plastic draw ratio, as described by equations (1)–(3).
However, equations (1)–(3) assume that the macromolecular chains in solution adopt their unperturbed dimensions (θ-condition). In addition, equations (1)–(3) disregard the influence of the crystallization process on $M_e$. With respect to the first assumption, it is well established that the spatial arrangement of (flexible) macromolecules is strongly influenced by their surroundings.[23] For instance, at low polymer concentrations, in fluids that strongly interact with the polymer (“good solvents”) the radius of gyration of a coiled macromolecule is expanded, whilst in a θ-solvent it is equal to the state found in its molten form. Upon further reducing the solvent quality, the chains will collapse even more, accompanied by macroscopic phase separation.

The issue of chain expansion or contraction naturally impacts the entanglement density in solutions of macromolecules, as well as the so-called chain “overlap” concentration, $Φ^*$. In polymer solutions of volume fractions below this concentration – generally referred to as “dilute” solutions – the macromolecules do not intertwine and exist as individual objects in the fluid phase. Cooling down such dilute solutions to induce polymer crystallization does not yield coherent solids or gels due to the non-interconnected nature of macromolecules in this phase; instead, separate crystalline entities (often single crystals) are formed. Solutions containing amounts of polymer above $Φ^*$, when cooled, generally solidify in the form of gels, in which the density of entanglements that existed in solution is largely preserved in the condensed phase if solidification is induced rapidly. Whilst, intuitively, the quality of the solvent is of importance, it has been established that in the so-called “concentrated” regime, i.e. well above $Φ^*$, in polymer solutions of concentrations $Φ > \sim 10\% \text{ v/v}$ the macromolecules adopt conformations as in the melt and in θ-solvents – also in good solvents.[24] That regime is, of course, precisely our object of interest, and, hence the dependence of macromolecular conformation on solvent quality may be of lesser concern.

With respect to the second assumption behind equations (1)–(3), i.e. neglecting the influence of crystallization on $M_e$, it has been found that when the process of gelation of a solution of a given polymer concentration (or solidification of a polymer melt for that matter) occurs at elevated temperatures
(lower undercooling), the maximum draw ratio of the resulting polymer solid can be drastically enhanced, likely due to (additional) disentanglement due to a macromolecular process known as “reeling-in” of the polymer chains during the formation of the crystalline entities.\textsuperscript{[2,21,25]} In what follows, “undercooling” is defined in a dynamic setting as the difference between endset dissolution temperature of UHMW PE in a solvent, $T_d$, obtained by heating the solution at a given rate, typically $20 \, ^\circ\text{C} \min^{-1}$, and the equilibrium endset dissolution temperature of UHMW PE in the same solvent, $T_d^0$, obtained by a Hoffman-Weeks plot,\textsuperscript{[26]} as is also commonly performed in polymer blends.\textsuperscript{[27]} Unfortunately, there is no theoretical expression for the “undercooling”, $T_d^0 - T_d$, as a function of solvent quality, as the dissolution temperature $T_d$ is a dynamic quantity that depends on the heating rate. Only the equilibrium dissolution temperature of the polymer in solution, $T_d^0$, follows directly from the melting point depression, the latter being the difference between $T_d^0$ and the equilibrium melting point of the pure polymer, $T_m$, governed by the well-known equation:\textsuperscript{[28]}

$$\frac{1}{T_d^0} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{v_u}{v_1} \left( (1 - \Phi) - \chi (1 - \Phi)^2 \right)$$

(5)

Here, $R$ is the molar gas constant, $\Delta H_u$ is the heat of fusion per repeat unit of the polymer, $v_u/v_1$ is the ratio of the molar volumes of the polymer repeat unit and the solvent, $(1 - \Phi)$ is the volume fraction of the diluent and $\chi$ is the Flory-Huggins interaction parameter. From this equation, it follows that the melting point depression for a given polymer at a given volume fraction of the solvent, depends on the ratio of the molar volumes of the repeating unit and the solvent, and the quality of the solvent, given by $\chi$. Therefore, for polymer crystallized from solutions with “poor” solvents, \textit{i.e.} those characterized by values of $\chi$ close to 0.5 ($\chi > 0.5$ leads to liquid-liquid demixing), a low melting point depression is observed. Here it should be noted that solvents that are perceived as good solvents for UHMW PE, such as decalin and xylene, giving rise to a more substantial melting point depression, are “athermal” at best (\textit{i.e.} $\chi = 0$) due to the absence of specific interactions, but typically have values of $\chi$ upwards of 0.3.\textsuperscript{[29]}
Based on the above, we selected the undercooling, which follows from the depression of the crystallization temperature of the polymer from solution as measured by differential scanning calorimetry (DSC) as well as solution viscosity measurements, which directly reflect coil expansion. The viscosity was measured in terms of melt-flow rate (MFR) as a simple, but effective tool to evaluate the physico-chemical interactions between the polymer and the small-molecular compounds explored.

3 Experimental Section

Materials. Ultra-high molecular weight polyethylene GUR4120 (UHMW PE; $\bar{M}_w = 5.0 \times 10^6$) was obtained from Ticona and used as received. Decahydroraphthalene (decalin; mixture of cis- and trans-isomers, Acros Organics) was dried over molecular sieves prior to use. Additional solvents, namely mineral oil (EMCAplus 350, Oxiteno), paraffin oil (Sigma-Aldrich), 1-dodecanol (Sigma-Aldrich), lauric acid (ABCR), stearic acid (AppliChem), peanut oil (Qualité & Prix, COOP, Switzerland), olive oil (Filippo Berio, olio extra virgine di oliva il classico, COOP, Switzerland) were used as received. Irganox 1010 and Irgafos 168 (BASF) were used as antioxidants.

Sample Preparation. The required amounts of UHMW PE and solvent were added to a round-bottomed flask, together with 0.5% w/w (based on UHMW PE content) of both Irganox 1010 and Irgafos 168. The continuously-stirred mixture was heated to 90 °C to ensure full dissolution of the antioxidant in the solvent. Approximately 6 mL of slurry was collected with a syringe and fed into a laboratory recycling twin-screw micro-compounder (CPC Eindhoven, The Netherlands), operated at 120 rpm under a nitrogen blanket. The processing temperature was selected in the 160–230 °C range, depending on the diluent employed, and all solutions were mixed for at least 10 min prior to extrusion. Subsequently, the extruded strands were slowly cooled to room temperature and extensively washed to extract the diluent. Isopropanol and diethyl ether (among others) were used for extraction of the “green” solvents, while heptane was used for removal of paraffin oil, mineral oil and decalin.
**Tensile-Drawing.** The washed and dried strands (typical diameter ~1.5 mm) were tensile drawn on a Kofler bench at temperatures in the 125–150 °C range. Nominal draw ratios were calculated from the displacement of ink marks printed onto the undrawn samples at 1 cm intervals.

**Mechanical Properties.** A paper frame was made by cutting a 70×10 mm² window in a light cardstock-grade (160 g m⁻²) paper. The stretched samples were longitudinally glued to the frame, ensuring that variation in the initial sample length of 70 mm for tensile testing was kept to a minimum. Tensile measurements were carried out using an Instron 5864 static mechanical tester fitted with a 100 N load cell and equipped with mechanical clamps. A constant elongation rate of 20 mm min⁻¹, determined by the cross-head speed, was used throughout. All tests were performed at room temperature (~20 °C). The cross-sectional area of the samples was calculated from their respective length and weight, with the latter determined using an ultra-micro balance (UMT2, Mettler Toledo, Switzerland), assuming a density of 1 g cm⁻³. All reported values for the modulus, tensile strength and elongation at break correspond to an average of at least three separate measurements.

**Thermal Analysis.** Differential scanning calorimetry (DSC) was performed using a DSC 822e instrument (Mettler Toledo, Switzerland), routinely calibrated using indium standards. DSC thermograms were recorded under a nitrogen flow using 20 °C min⁻¹ heating/cooling rates. Samples were heated from 25 to 180 °C and then cooled to 25 °C (two cycles were executed per sample). Typical sample weight was ~5 mg. Crystallization/dissolution temperatures reported in Table 1 and 2 correspond, respectively, to the onset/endset temperatures for the thermal transitions recorded during first-cooling/second-heating scans.

Equilibrium melting temperatures, *i.e.* dissolution temperatures, $T_d^0$, of UHMW PE in 20% v/v solutions with selected solvents, were determined by DSC using the well-known Hoffman-Weeks analysis.[26] Briefly, the solutions were equilibrated at 160 °C (above $T_d^0$ of neat UHMW PE), followed by quenching to the chosen crystallization temperature, $T_c$, and holding for 45 min. The resulting isothermally-crystallized solutions were then reheated, recording the endset
dissolution temperature, $T_d$, for UHMW PE. Extrapolating the experimentally measured $T_d$ values as a function of $T_c$ to the $T_d = T_c$ line yielded the $T_d^0$ of UHMW PE in solution.

Melt-Flow Rate. Melt-flow rates (MFR) of solutions comprising 20% v/v UHMW PE were determined with a melt-flow index instrument (MeltFlow LT, Haake, Germany) according to the ISO1133 standard, using a weight of 10 kg at a temperature of 180 °C. All reported values correspond to an average of 7 measurements performed with 10 min collection time.

4 Results and Discussion

4.1 Thermal Analysis

In Figure 1, cooling DSC thermograms are presented of solutions comprising 20% v/v UHMW PE in a variety of solvents. Expectedly – based on entropic and enthalpic effects as described by equation (5), respectively, at increasing molecular size or polarity of the solvent, the onset temperature of crystallization increased, i.e. the quality of the small molecular compounds as solvent for UHMW PE decreased. Concomitantly, the temperature at which gelation occurred had increased. For instance, in the case of the commercially employed decalin and mineral oil, this process commenced around 88 °C and 112 °C respectively, whereas in relatively poor solvents such as peanut oil and olive oil, gelation already occurred at elevated temperatures as high as ~119 °C, which is only a few degrees below that for UHMW PE crystallized from the melt, 122 °C.

Also, of course, when a poor solvent, such as 1-dodecanol, was added to a good solvent like decalin, the temperature of the onset of crystallization/gelation rapidly increased, as illustratively shown here for 1:4 and 1:1 mixtures of those species.
Chapter 2  Gel-Processing Revisited

Figure 1. Cooling thermograms (not to absolute scale) of (●) neat UHMW PE; and of 20% v/v solutions of the polymer in different solvents: (△) peanut oil; (●) olive oil; (◇) peanut oil:stearic acid (1:1); (●) stearic acid; (○) lauric acid; (♦) paraffin oil; (◇) mineral oil; (■) decalin:dodecanol (1:1); (○) decalin:dodecanol (4:1); (▲) decalin.

Table 1. Crystallization temperatures $T_c$ of UHMW PE in neat form and dissolved at 20% v/v in various solvents, together with the corresponding lowering of the crystallization temperature, $\Delta T_c$, calculated as $\Delta T_c = T_{c}^{PE} - T_c$, with $T_{c}^{PE}$ being the crystallization temperature of pure UHMW PE (122 °C).

<table>
<thead>
<tr>
<th>Polymer/Solvent</th>
<th>$T_c$ / °C</th>
<th>$\Delta T_c$ / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHMW PE</td>
<td>122</td>
<td>-</td>
</tr>
<tr>
<td>Decalin</td>
<td>88</td>
<td>34</td>
</tr>
<tr>
<td>Decalin:Dodecanol (1:1)</td>
<td>107</td>
<td>15</td>
</tr>
<tr>
<td>Decalin:Dodecanol (4:1)</td>
<td>94</td>
<td>28</td>
</tr>
<tr>
<td>Paraffin Oil</td>
<td>112</td>
<td>10</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>112</td>
<td>10</td>
</tr>
<tr>
<td>Lauric Acid</td>
<td>114</td>
<td>8</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>115</td>
<td>7</td>
</tr>
<tr>
<td>Stearic Acid:Peanut Oil</td>
<td>117</td>
<td>5</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>119</td>
<td>3</td>
</tr>
<tr>
<td>Peanut Oil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1 collects an overview of the depression of the onset crystallization temperature ($T_c$) of reference neat UHMW PE, and when dissolved at 20% v/v in various liquids, indicative of the solvent quality of the different species. As will be shown below, elevated crystallization temperatures, indicative of crystallization at low undercooling, dramatically affected the tensile deformation behavior of the solid UHMW PE produced, in line with the results reported by Smith.[25]

Figure 2. Hoffman-Weeks plots of 20% v/v solutions UHMW PE in selected solvents: (◇) peanut oil:stearic acid (1:1); (●) stearic acid; (■) decalin:dodecanol (1:1); (○) decalin:dodecanol (4:1); (▲) decalin. The colored lines are linear extrapolations towards the line $T_d = T_c$.

To further quantify the undercooling at which UHMW PE crystallizes during cooling, the equilibrium endset dissolution temperatures $T_d^0$ of 20% v/v UHMW PE in selected solvents were determined using Hofmann-Weeks analysis as shown in Figure 2. Using these values, for each solvent system, the “undercooling” ($\Delta T = T_d^0 - T_d$) was calculated from the endset dissolution temperature $T_d$ of UHMW PE, measured by DSC of gels that were obtained by heating the 20% v/v UHMW PE solutions at a rate of 20 °C min$^{-1}$. A plot of the undercooling as a function of the equilibrium dissolution temperature is given in Figure 3, confirming the general finding listed in Table 1, namely that the
undercooling decreases with increasing crystallization/dissolution temperature of UHMW PE in solution. The corresponding maximum drawability $\lambda_{\text{max}}$ of fibers obtained from 20% v/v solutions of UHMW PE from the same solvents is listed in Table 2.

![Figure 3](image)

**Figure 3.** A plot of the undercooling $(T_d^0 - T_d)$ as a function of the equilibrium dissolution temperature $T_d^0$ of 20% v/v solutions of UHMW PE in selected solvents: (◇) peanut oil:stearic acid (1:1); (●) stearic acid; (■) decalin:dodecanol (1:1); (○) decalin:dodecanol (4:1); (▲) decalin. The dashed line is a guide for the eye only.

**Table 2.** Comparison of maximum drawability $\lambda_{\text{max}}$ of the fibers obtained from 20% v/v solutions of UHMW PE in selected solvents with the following thermal characteristics obtained from DSC analysis on the gels after extrusion: equilibrium dissolution temperature $T_d^0$ (determined using Hoffman-Weeks analysis, ref. [26], see Figure 2), endset dissolution temperature $T_d$ and undercooling $\Delta T = T_d^0 - T_d$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$T_d^0$ / °C</th>
<th>$T_d$ / °C</th>
<th>$\Delta T$ / °C</th>
<th>$\lambda_{\text{max}}$ / -</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decalin</td>
<td>126</td>
<td>102</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>Decalin:Dodecanol (4:1)</td>
<td>127</td>
<td>108</td>
<td>19</td>
<td>28</td>
</tr>
<tr>
<td>Decalin:Dodecanol (1:1)</td>
<td>132</td>
<td>117</td>
<td>15</td>
<td>34</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>135</td>
<td>126</td>
<td>9</td>
<td>40</td>
</tr>
<tr>
<td>Stearic Acid:Peanut Oil (1:1)</td>
<td>135</td>
<td>132</td>
<td>3</td>
<td>40</td>
</tr>
</tbody>
</table>
4.2 Melt-Flow Rate

In Table 3 are presented the results of melt-flow rate (MFR) tests, again of 20% v/v of UHMW PE solutions in a broad range of solvents. Evidently, the solution viscosity dramatically decreased with decreasing solvent quality – somewhat unexpectedly for such concentrated solutions (cf. ref. [30]). That latter result obviously is of potential advantage for more efficient gel-processing UHMW PE.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MFR / g (10 min)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decalin</td>
<td>0.1</td>
</tr>
<tr>
<td>Mineral Oil</td>
<td>2.6</td>
</tr>
<tr>
<td>Decalin:Dodecanol (1:1)</td>
<td>12.3</td>
</tr>
<tr>
<td>Peanut Oil</td>
<td>12.3</td>
</tr>
<tr>
<td>Olive Oil</td>
<td>13.5</td>
</tr>
<tr>
<td>Stearic Acid:Peanut Oil (1:1)</td>
<td>28.5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>30.2</td>
</tr>
</tbody>
</table>

4.3 Tensile Deformation

In the following section, the influence of the solvent quality upon the deformation behavior of gel-processed UHMW PE will be presented.

Figure 4 shows the maximum draw ratio, $\lambda_{\text{max}}$, realized under the present conditions, as function of the initial polymer concentration in a range of diluents, including the commercially employed decalin and mineral oil for reference purposes. As clearly demonstrated by the results presented, the familiar dramatic increase of $\lambda_{\text{max}}$ with decreasing value of $\Phi^{[1,2]}$ was found and, therewith, increased mechanical properties. More interesting, however, though is the finding that at every concentration a significant increase in maximum draw ratio was observed for UHMW PE processed from poor solvents.
Figure 4. Maximum draw ratios and the resulting tensile strength and Young’s modulus values for UHMW PE gel-processed from different solvents as a function of initial polymer volume fraction. (△) peanut oil; (◇) olive oil; (◇) peanut oil:stearic acid (1:1); (●) stearic acid; (〇) lauric acid; (◆) paraffin oil; (⊗) mineral oil; (■) decalin:dodecanol (1:1); (◇) decalin:dodecanol (4:1); (▲) decalin. (●) neat UHMW PE. Lines are guides for the eye only.
The systematic correlation between $\lambda_{\text{max}}$ and $\Phi$ observed for processing UHMW PE for all the solvent systems is most clearly revealed in the log-log plot presented in Figure 5. From this figure, it appears that for the range of polymer concentrations employed, all curves are parallel with the same slope, indicative of a multiplicative dependence of the maximum draw ratio on concentration and solvent quality, suggesting the following power-law behavior:

$$
\lambda_{\text{max}} = \frac{\lambda_{\text{solvent}}}{\Phi^{0.7}}
$$

Here, $\lambda_{\text{solvent}}$ is a constant that is different for each solvent system and that is found to increase with decreasing solvent quality. Thus it appears that the main influence of using different solvents in the gel-spinning process is the replacement of equation (3) with equation (6), as will be discussed in more detail in Section 4.5.

![Figure 5](image)

**Figure 5.** Log-log plot of the maximum draw ratio of UHMW PE as a function of polymer volume fraction, processed from different solvents, showing the consistent dependence of $\lambda_{\text{max}}$ on $\Phi$ due to reduction of entanglements. The lines are linear fits with a slope of $-0.7$. Symbols for different solvents as in Figure 4.
4.4 Mechanical Properties

While encouraged by the observed increase in drawability of UHMW PE processed from relatively poor solvents, the issue, of course, is whether or not this translates into similarly enhanced mechanical properties of the drawn material. That this was indeed the case indeed is already shown in Figure 4, and is elaborated upon in Figure 6 and Figure 7. Also shown in Figure 6 is a fit of the $E$-$\lambda$ data with equation (4), which assumes pseudoaffine deformation of the flexible PE chain molecules during cold drawing, resulting in realistic values for $E_u$ ($= 2.4$ GPa) and $E_h$ ($= 300$ GPa), demonstrating that this relation holds independent of the quality of the solvent employed. In Figure 7 are plotted the values recorded for the tensile strength versus those for the Young's modulus of UHMW PE processed from different solvents to various draw ratios. Also here, within experimental uncertainty, no influence of solvent quality on that correlation was observed.

![Graph showing mechanical properties development](image)

**Figure 6.** Development of Young’s modulus (maximum values obtained are reported) with draw ratio of UHMW PE processed from 10% v/v solutions in (♦) peanut oil:stearic acid (1:1), (●) stearic acid, (◇) mineral oil, (■) decalin:dodecanol (1:1) and (▲) decalin. The curve represents the development fitted with equation (4), resulting in similar parameters according to ref. [5].
The one-to-one correlations between polymer concentration and maximum draw ratio (left y-axis of Figure 4), maximum draw ratio and Young's modulus (Figure 6) and Young's modulus and tensile strength (Figure 7), have been condensed in Figure 4. In this figure, the corresponding Young's modulus and tensile strength for a given maximum draw ratio, are projected on the right y-axis. In this manner, Figure 4 clearly reveals the two major advantages of the use of relatively poor solvents for gel-processing UHMW PE. Those benefits are:

i) At a given polymer concentration, the material can be drawn further by as much as twice when processed from poor solvents compared to that obtained from good solvents, yielding products of correspondingly enhanced mechanical properties.

ii) When a certain set of mechanical properties is desired or sufficient for the envisaged applications, the efficiency of the solution-based gel-processing technology can be dramatically enhanced, since much higher concentrations of the polymer in poor solvents can be employed than in good solvents – by as much as 150%.

![Graph showing tensile strength versus Young's modulus](image)

**Figure 7.** Tensile strength versus Young’s modulus (maximum values obtained are reported) of UHMW PE processed from 10% v/v solutions in (○) peanut oil:stearic acid (1:1), (●) stearic acid, (◇) mineral oil, (■) decalin:dodecanol (1:1) and (▲) decalin. The line is a guide for the eye only.
4.5 Solvent Influence

As mentioned before, the main influence of solvent quality on the gel-spinning process is the improved maximum draw ratio upon crystallization from “poorer” solvents, embodied by replacing equation (3) with equation (6). Comparing these two equations, there are two differences: firstly, a change in power-law coefficient, from \( \lambda_{\text{max}} \propto \Phi^{-0.5} \) (Booij et al.,[2] equation (3)) to \( \lambda_{\text{max}} \propto \Phi^{-0.7} \) (Figure 5). Secondly, the replacement of the constant prefactor \( \lambda_{\text{melt}}^{\text{max}} \) (the maximum draw ratio of melt-crystallized UHMW PE in equation (3)) with a solvent-dependent maximum draw ratio, \( \lambda_{\text{solvent}}^{\text{max}} \) in equation (6).

The change in power-law coefficient from \(-0.5\) to \(-0.7\) is actually in line with experimental rheological studies by Colby et al.[30] who reported that the molecular weight between entanglements in solution is independent of solvent quality and scales as \( M_e^{\text{sol}} \propto \Phi^{-1.3} \) rather than the commonly used \( M_e^{\text{sol}} \propto \Phi^{-1} \).[3] Substitution of \( M_e^{\text{sol}} \propto \Phi^{-1.3} \) into equation (2) results in \( \lambda_{\text{max}} \propto \Phi^{-0.65} \), which is close to the experimentally observed scaling \( \lambda_{\text{max}} \propto \Phi^{-0.7} \) in Figure 5.

The origin of the change in the prefactor is less clear. The multiplicative dependence of the maximum draw ratio on solvent quality and concentration, suggests that an additional concentration-independent factor in enhanced draw ratio can be achieved by crystallization of UHMW PE from poorer solvents:

\[
\lambda_{\text{max}} = \frac{\lambda_{\text{solvent}}^{\text{max}}}{\Phi^{0.7}} = \frac{\lambda_{\text{solvent}}^{\text{max}}}{\lambda_{\text{melt}}^{\text{max}}} \frac{\lambda_{\text{melt}}^{\text{max}}}{\Phi^{0.7}}
\]  

(7)

The reason for the occurrence of the additional drawability factor \( \lambda_{\text{solvent}}^{\text{max}} / \lambda_{\text{melt}}^{\text{max}} \) could be an additional degree of disentanglement induced by the crystallization process, also known as reeling-in (cf. Appendix). Reeling-in is found to occur more prominently during crystallization at low undercooling.[2,21,25] Improved drawability by reeling-in can, thus, be induced in any solvent system, as was already demonstrated for crystallization of UHMW PE from decalin.[25] However, the rate of crystallization at low undercooling becomes increasingly slower when moving from “moderate” to good solvents. This is where crystallization from poor solvents appears to be advantageous, as the poor solvent quality induces
crystallization at low undercooling, as is demonstrated experimentally in Figure 3 and Table 3, where it is shown that at an identical (realistic) cooling rate of 20 °C min⁻¹, the undercooling needed to induce crystallization of UHMW PE in poor solvents (high \( T_d^0 \)), is lower than that for moderate solvents (low \( T_d^0 \)). Finally, it should be noted that the “constant” factor (\( \lambda_{\text{solvent}} / \lambda_{\text{melt}} \)) appears constant for the range of concentrations studied, but is expected to become unity near \( \Phi \approx 1 \), as then, by definition, \( \lambda_{\text{max}} \) becomes equal to the maximum draw ratio of melt-crystallized material, \( \lambda_{\text{melt}} \).

4.6 Solvent Recovery

Inherent to the solution-processing/drawing technique for producing high-performance PE fibers and films is, of course, the removal and recovery of the diluent that is employed to reduce the entanglement density in the solidified polymer precursor that is to be oriented by tensile deformation. In the case of the decalin-based process, this is realized by evaporating the solvent.[15] When employing mineral oils, as promoted in, for instance, the production of UHMW PE fibers by Honeywell (formerly Allied-Signal) sold under the trade name Spectra®, the diluents are removed by extraction with, among others, trichlorotrifluoroethane,[16] hexane and the like. All the above species are associated with highly questionable flammable, environmental and health issues (cf. refs. [26–36] in ref. [17]). In the here-described advancement of the process based on concentrated solutions in poor – as opposed to good – solvents, including, among others, fatty acids and natural oils omnipresent in, for example, fruits, nuts and seeds, are the major recovery and environmental advantages in addition to the above-described higher concentrations that can be employed to reach the required degree of disentanglement of UHMW PE, i.e. less diluent to recover. Furthermore, environmentally friendly extraction means can be employed to recover the solvent used in the process, which themselves can be selected to solidify for trivial recovery. An example of that case would be a mixture of stearic acid:peanut oil (1:1) as the solvent and isopropanol as extraction means, or, possibly, super-critical CO₂.[31,32]
5 Conclusions

The results presented here clearly indicate the major benefits of employing poor, rather than good, solvents in the gel-processing method, as they facilitate the use of substantially higher initial polymer concentrations, thereby drastically reducing the solvent recovery load and – most importantly – provide significant environmental gain. These advantages are illustrated in Figure 8, where mechanical properties are presented for drawn UHMW PE processed from selected poor solvents, such as stearic acid, compared to the current industrial standard (good) solvent decalin.

![Figure 8](image_url)

**Figure 8.** Maximum draw ratio with corresponding tensile strength and Young’s modulus of UHMW PE gel-processed from different solvents as a function of polymer volume fraction. (△) peanut oil; (♦) olive oil; (◇) peanut oil:stearic acid (1:1); (●) stearic acid; (◻) lauric acid; (▲) decalin. (●) neat UHMW PE. Lines are guides for the eye only.
Appendix

Reeling-in

Improved drawability via a promoted reeling-in process can be induced in any solvent system, as was demonstrated by Smith for UHMW PE crystallized from decalin solutions.[25] However, the rate of polymer crystallization from solutions in moderate/good solvents becomes increasingly slow at low undercooling. This is where crystallization from poor solvents appears to be advantageous, as the poor solvent quality induces crystallization at lower undercooling, as is demonstrated experimentally in Figure 1, and results in increased lamellar thickness of the polymer crystals.

In further support of this hypothesis, a DSC model study was carried out, in which the lamellar thickness $l_c$ of PE crystals obtained by crystallization from 20% v/v UHMW PE solutions in selected solvents was calculated using the Gibbs-Thomson equation (8):

$$l_c = \frac{2\sigma_e}{\Delta H_f} \frac{T_d^0}{(T_d^0 - T_d)}$$

Here $\sigma_e$ is the lamellar fold-surface free energy (a value of $9\times10^{-6}$ J cm$^{-2}$ as for neat PE was used, cf. ref. [26]), $\Delta H_f$ is the enthalpy of fusion per unit volume of crystal (= 293 J cm$^{-3}$, cf. ref. [33]), $T_d^0$ is the equilibrium melting/dissolution temperature of UHMW PE in 20% v/v solution with the selected solvent (determined by the Hoffman-Weeks analysis) and $T_d$ is the corresponding endset dissolution temperature. The resulting polymer crystals exhibit a higher lamellar thickness with the reducing quality of the solvent; notably $l_c = 9.0$ nm is obtained for stearic acid – a poor solvent – in comparison to 3.2 nm resulting from crystallization from a decalin solution of equivalent concentration.

In order to confirm the accuracy of the reported $l_c$ values, especially given the assumption of constant $\sigma_e$ in different solvents, a second control experiment was carried out in which 20% v/v UHMW PE solutions in selected solvents (for this experiment: with crucible blends and upon heating and cooling rates at 10 °C min$^{-1}$) were isothermally crystallized for 45 min at a range of
temperatures $T_c^{iso}$. Gratifyingly, a plot of $l_c$ values calculated by equation (8) versus undercooling ($i.e. T_d^0 - T_c^{iso}$) shown in Figure A1 displays a consistent increase of $l_c$ with reducing undercooling irrespective of the specific solvent used.

![Figure A1](image)

**Figure A1.** Dependence of lamellar thickness of undercooling ($T_d^0 - T_c^{iso}$) for UHMW PE crystallized from 20% v/v solutions in (●) stearic acid, (◇) mineral oil, (■) decalin:dodecanol (1:1), (○) decalin:dodecanol (4:1) and (▲) decalin. The solutions were isothermally crystallized for 45 min at the indicated undercoolings.

While it is beyond the scope of the present study, the calculated $l_c$ values can be confirmed by calculating the long period $L$, determined by small-angle X-ray scattering (SAXS), taking into account the degree of crystallinity for the polymer samples. [N.B. Previous reports have indicated excellent agreement between the lamellar thicknesses determined by DSC and SAXS; cf. ref. [34].] Additional experimental approaches to determining the lamellar thickness could be based on transmission electron microscopy (TEM)[35] or analysis of the spectroscopic signatures of the low-frequency Raman-active band for PE.[36]
References


Chapter 3

Liquid-Crystalline Polymer Films for Monolithic Composites
1 Introduction

Continuous fiber-reinforced composite materials exhibit desirable mechanical properties, such as high specific stiffness and high specific strength, combined with superior fatigue resistance and fracture toughness.\textsuperscript{[1]} Standard fabrication methods of such composites involve the immersion of fiber tows in a matrix material by a variety of impregnation techniques,\textsuperscript{[2]} resulting in transversely isotropic unidirectional (UD) lamina or prepregs having typical thicknesses on the order of 0.1–0.5 mm. These lamina are stacked in different orientations to achieve the desired mechanical performance of the final composite material object. This standard method of manufacturing composites suffers from a number of well-known issues that have been addressed in numerous studies and are listed hereafter.

Firstly, while the mechanical properties improve with increasing fiber content, standard impregnation techniques limit the fiber content to about 50–60\% $v/v$.\textsuperscript{[1]} Secondly, laminating plies in different directions introduce interlaminar normal and shear stresses at the ply boundaries leading to delamination, especially near the free edges of the laminated plies.\textsuperscript{[3]} Studies have shown, however, that the occurrence of this particular failure mode can be reduced by decreasing the layer thickness of the plies. Moreover, thin ply drops are advantageous for the production of smooth tapered laminated composites.\textsuperscript{[4,5]} However, despite the advantages of laminated composites the presence of different fiber and matrix materials hampers proper recycling strategies for composite components and waste.\textsuperscript{[6–8]}

Various processing methods for composites have been proposed that address one or more of the above issues. One such method is fiber-spreaing followed by impregnation, which allows for the production of thin laminates with improved fracture characteristics.\textsuperscript{[9]} This method is used commercially, for example, in the three-dimensional laminate technique ($3DL^\circledR$) applied by North Sails.\textsuperscript{[10]}

Another development that indeed offers the promise of improved recyclability is the use of self-reinforcing materials,\textsuperscript{[11]} such as solid-state uniaxially drawn polypropylene-polypropylene blends.\textsuperscript{[12–14]} These single-phase materials, termed
“monoliths” rather than composites, are typically produced in the form of consolidated tapes. The core, acting essentially as the “fiber” in these “composite” tapes, is highly oriented, exhibiting enhanced stiffness and strength in the tape direction as well as a superior melting temperature. The top and bottom layers consist of unoriented material that is used for melt-fusing, exploiting the difference in melting temperatures between oriented and unoriented material, optionally aided by the use of small amounts of co-monomer in the unoriented “matrix” polymer. However, the relatively low stiffness values of approximately 15 GPa of such oriented polypropylene tapes are a major drawback for many demanding applications.[13] Aside from full recyclability of these materials, the primary advantage of the use of melt-fusion or welding to consolidate tapes into laminates is that it does not rely on impregnation, which is known to be a major “bottle-neck” in most thermoplastic composite manufacturing processes.[2]

As an alternative approach to creating self-reinforced composites with enhanced mechanical properties, hot-compaction of liquid-crystalline polymer (LCP) fiber tows and surface-dissolution of aramid fibers have been used.[15–17] These self-reinforced materials typically exhibit longitudinal tensile moduli and tensile strengths of ~60 GPa and ~1 GPa, respectively.

A new method for the production of self-reinforced high-performance materials was recently introduced, referred to as “foil-spintrusion” of polymer films.[18] Via this technique, continuous high-performance UD films were extruded with, among other materials, a thermotropic LCP, poly(p-hydroxybenzoic acid-co-2-hydroxy-6-naphthoic acid), known as Vectra®, using a newly-designed multi-filament-fusing die.[19] It was reported that these uniaxially oriented tapes show promising mechanical properties, combining a Young’s modulus of 70 GPa and tensile strength of up to 2 GPa. In essence, the mechanical performance of these films matches that of the commercially available Vectran® fibers made of the same polymer produced by conventional melt-spinning of the same material,[20] often followed by a heat-treatment step to boost the tensile strength.[21,22] The foil-spintrusion process allows for the production of continuous films in a wide range of thicknesses: from > 20 μm to 4 μm or less. Furthermore, it was found that these films can be fused together at increased temperatures by a solid-state
post-condensation reaction into monolithic structures (Figure 1), while retaining their mechanical performance without the use of adhesives or matrix material.

Figure 1. a) Bobbin of an as-extruded LCP film (typical film thickness ~15 μm). b) UD LCP cuboid specimen for compression testing, consisting of 280 single films, hot-pressed into a monolith. UD tensile test specimen manufactured from c) 15 and d) 30 LCP layers, with material orientation axis at 0° and 90°, respectively.

These highly oriented LCP films address all four of the aforementioned obstacles:

i) The foil-spintrusion process allows for the production of extremely thin LCP films, which are advantageous for creating monolithic parts showing greater resistance to delamination and improved fracture characteristics.

ii) LCP monoliths fully consist of highly oriented polymers with 100% “fiber” volume fraction for creating high-performance monoliths.

iii) The LCP lamina can be fused together into monolithic laminates without the use of adhesive or matrix material, thus avoiding the usual impregnation issues of thermoplastic composites.

iv) The use of a single chemical species ensures full recyclability.
The objective of this study is to evaluate the use of these high-performance LCP films for “monolithic” composite applications. All tested monoliths are unidirectional (UD; i.e. all films were stacked and consolidated, having the same uniaxial orientation) and made of heat-treated LCP films. Both orientation-dependent elastic and fracture properties of the resulting monoliths will be discussed. Additionally, fusion of films into monoliths, based on a post-condensation reaction between the single layers under pressure and at elevated temperatures, is critically examined.

2 Experimental Section

Materials. The material used in this study is a thermotropic liquid-crystalline polymer (LCP), Vectra® A950 (Ticona, Germany), a random copolyester of 73% mol p-hydroxybenzoic acid (HBA) and 27% mol 2-hydroxy-6-naphtoic acid (HNA). The LCP was received in the form of pellets and dried at 120 °C in a vacuum oven for at least 12 hrs prior to processing.

Film Processing. Films were extruded following the so-called “foil-spintrusion” process using a single-screw extruder (Teach-Line® E20T SCD15, Collin, Germany) with a barrel diameter of 20 mm and a multi-filament-fusing die. The extrusion was performed at 300 °C and 50 rpm with a take-up speed of 0.6 m s⁻¹, resulting in films with a thickness of approximately 15 μm.

Heat-Treatment. For Vectran® fibers it is well known that their strength can be improved by a solid-state heat-treatment at elevated temperatures, most likely due to a post-curing reaction that increases the molecular weight. The same heat-treatment was applied to the as-extruded films, which were co-wound with glass fiber mats onto bobbins to allow for water removal during the solid-state post-condensation. The bobbins were first annealed in an oven under nitrogen atmosphere for 1 hr at 230 °C, followed by a second heating step for 24 hrs at 270 °C.
Production of Monoliths. Unless mentioned otherwise, in this study all unidirectional (UD; i.e. all films having the same uniaxial orientation) monoliths were produced by compacting a number of heat-treated films for 9 hrs at 270 °C and 7 bar using a hot press (Rondol, UK).

Tensile Testing. Elastic, fracture and relaxation properties were analyzed using a tensile-tester (Instron 5566, USA) at ambient temperature. As-extruded and heat-treated single LCP films, as well as UD LCP monoliths, were tested. All monoliths for tensile tests consisted of 15 or 30 layers of the heat-treated film fused together. Test specimens (dimensions summarized in Table 1) were cut from single films and monoliths using a utility knife. The cross-sectional area of a single films sample was calculated from its length and weight, using a density of 1.40 g cm\(^{-3}\) (supplier data). To avoid slip-out and damage due to clamping, aluminum tabs with a thickness of 0.5 mm were attached to the clamping area at both ends of every specimen, using Araldite® Standard (Huntsman Advanced Materials, Switzerland) as an adhesive (see Figure 1 (c, d)). Analysis of the elastic and fracture behavior of films and monoliths was performed in the orientation direction of the material as well as in off-axis directions, at an initial strain rate of \(10^{-3}\) s\(^{-1}\).

Relaxation experiments on films and monoliths were carried out only along the orientation axis of the material. The specimens were loaded to a strain of 1.0%, at an initial strain rate of \(10^{-3}\) s\(^{-1}\) and relaxation was recorded for 4000 s.

Table 1. Specimen dimensions for tensile testing: testing-angle \(\theta\), sample length \(l\), width \(w\), amount of layers \(x\), thickness \(h\) and gauge length \(GL\).

<table>
<thead>
<tr>
<th></th>
<th>(\theta / ^{\circ})</th>
<th>(l / \text{mm})</th>
<th>(w / \text{mm})</th>
<th>(x / -)</th>
<th>(h / \mu\text{m})</th>
<th>(GL / \text{mm})</th>
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<td>120</td>
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<tr>
<td></td>
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<td>1</td>
<td>15</td>
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</tr>
<tr>
<td>Monolith</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>0–10</td>
<td>200</td>
<td>12.5</td>
<td>15</td>
<td>225</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>15–90</td>
<td>140</td>
<td>25.0</td>
<td>30</td>
<td>450</td>
<td>100</td>
</tr>
</tbody>
</table>
**T-Peel Testing.** The level of adhesion between two individual films was examined by T-peel force testing. Two films, having the same uniaxial orientation, were fused in a press (Rondol, UK), using a thin Teflon® film as a starter crack at one edge. To determine the increasing adhesion with consolidation time, samples were prepared at 270 °C for 1 to 24 hrs at two different pressures: 1 and 7 bar. After quenching to room temperature, the specimens were cut into 15 mm wide UD strips. T-peel force testing was performed at room temperature with a tensile-tester (Instron 5566, USA), gauge length of 10 mm, recording the force at a constant cross-head speed of 100 mm min⁻¹.

**Shear Strength Testing.** A short-beam shear test was employed to measure the interlaminar shear strength (ILSS) of UD LCP monoliths, despite the fact that well-sintered monolithic samples appeared homogeneous, *i.e.* with individual layers no longer distinguishable.[24] Samples for shear strength measurements were cut from monoliths of 4 and 16 mm thickness, prepared by consolidating 280 and 1150 layers, respectively. The heat-treated films were fused in a hot press (Rondol, UK) at 270 °C for 3, 6, 9 and 24 hrs at a pressure of 7 bar. The machined short-beams for ILSS testing had a minimum thickness of 4 mm; widths and lengths were 4 and 10 times the sample thickness, respectively. Tests were performed at room temperature with a tensile-tester (Instron 5566, USA) using a 3-point bending widget at a constant downward cross-head speed of 1 mm min⁻¹. The span length was 5 times the thickness.

**Uniaxial Compression Testing.** For uniaxial compression testing, a 4 mm thick UD monolith was manufactured by fusing heat-treated films for 9 hrs in a hot press (Rondol, UK) at 270 °C and at a pressure of 7 bar. Samples with a cross-section of 4×4 mm² and a height of 8 mm were prepared with different orientations of 0°, 5°, 10°, 15°, 30°, 45°, 60° and 90°, where the orientation is specified by the angle between the sample axis and the material orientation axis. Compression tests were performed using a tensile-tester (Instron 5566, USA) at a constant cross-head speed of 0.5 mm min⁻¹, corresponding to an initial strain rate of 10⁻³ s⁻¹.
Manufacturing and Testing of Sandwich Panels. Sandwich structures used in this study consisted of a 20 mm thick Rohacell® IG-F foam core, made of poly(methacrylimide) (Evonik Industries, Germany) of a density of 75 kg m\(^{-3}\)\[25]\ covered on both sides with a face material. The employed face materials were commercially available UD E-glass- (SGL Carbon SE, Germany), UD flax- (Bcomp, Switzerland), UD Kevlar® 49- (ECC Engineered Cramer Composites, Germany) and UD T700S carbon (SGL Carbon SE, Germany) fabrics, as well as the UD LCP monoliths reported in this study. All fabrics had an area density of 300 g m\(^{-2}\) with the exception of Kevlar® 49, for which the corresponding value was 150 g m\(^{-2}\).

The monoliths used as face material were prepared by compacting 18 heat-treated films (resulting in a thickness of \(~250 \mu m\) at 270 °C and 7 bar for at least 9 hrs. The LCP monoliths were adhesively bonded to the structural foam core with a two-component epoxy resin (type HT 2, R&G Faserverbundwerkstoffe GmbH, Germany), followed by a curing procedure in a vacuum bag for 24 hrs at 60 °C. All UD fabrics were carefully impregnated and subsequently laminated with a given amount (approximately 40% w/w) of the epoxy resin on the foam core. Applying a vacuum bag technique allowed the impregnated fabrics to be cured for 24 hrs at 60 °C. All sandwich panels were produced with the same core-to-face weight ratio.

Test specimens with dimensions of 50×500 mm\(^2\) (perpendicular to and along the main orientation axis, respectively) were cut from these panels and tested with a tensile-tester (Zwick Z020, Germany) at ambient temperature using a 4-point bending test setup with a total span length of 450 mm and 225 mm between the two center pins, at a rate of 1 mm min\(^{-1}\).[26]

Scanning Electron Microscopy. After uniaxial compression testing, LCP monolith samples for scanning electron microscopy (SEM) were sputtered with a thin conductive layer of platinum and imaged using a LEO 1530 Gemini scanning electron microscope (Zeiss Elektronenmikroskopie GmbH, Germany) using secondary electron detection.
3 Results and Discussion

3.1 Elastic Behavior

Highly oriented polymer films and fibers typically exhibit transversely isotropic elastic behavior described by the stiffness matrix $\mathbf{C}$ with components $c_{ij}$, or by its inverse, the compliance matrix $\mathbf{S}$ with components $s_{ij}$. Choosing the 1-direction as the direction of orientation (that is, equivalent to the longitudinal or extrusion direction) and the 2,3-plane as the plane of isotropy, and assuming a plane stress condition perpendicular to the film surface in the 3-direction, transverse isotropy leads to four independent elastic constants. The latter are typically identified as: the longitudinal and transverse Young’s moduli, $E_1 = 1/s_{11}$ and $E_2 = 1/s_{22}$, respectively, the shear modulus, $G_{12} = 1/s_{66}$ and the Poisson number, $\nu_{12} = -s_{12}/s_{11}$.[1] In this case, the off-axis stiffness, $E_\theta$, measured in a uniaxial tensile test at an angle $\theta$ to the orientation direction, follows from the reciprocal value of the compliance in that direction:[27]

$$
\frac{E_\theta}{E_1} = \left( \cos^4 \theta + \frac{E_1}{G_{12}} \cos^2 \theta \sin^2 \theta + \frac{E_1}{E_2} \sin^4 \theta \right)^{-1}
$$

From this equation, it follows that uniaxial tensile testing of uniaxially oriented films in various directions and fitting the experimental Young’s moduli to equation (1) allows direct determination of $E_1$ and $E_2$, but not of $G_{12}$ and $\nu_{12}$. However, assuming the isotropic value of 0.4 for the Poisson’s ratio $\nu_{12}$, the shear modulus also follows from equation (1) and is straightforwardly calculated from the Young’s moduli $E_1$, $E_2$ and $E_{45^\circ}$ as:

$$
\frac{G_{12}}{E_1} = \left( 4 \frac{E_1}{E_{45^\circ}} - (1-2\nu_{12}) \frac{E_1}{E_2} \right)^{-1}
$$

The longitudinal Young’s modulus $E_1$ for as-extruded LCP films was $57 \pm 4$ GPa. After heat-treatment, this value increased to $68 \pm 3$ GPa, which is equivalent to that of Vectran® fibers.[20]

To evaluate the effect of heat-fusion on the elastic behavior, UD monoliths (depending on testing-angle, using 15- or 30-layers of heat-treated LCP film,
respectively) were produced. The modulus of these monoliths as a function of testing-angle is presented in Figure 2.

![Graph showing Young's modulus as a function of testing-angle for UD LCP monoliths.](image)

**Figure 2.** Young’s modulus as a function of testing-angle for UD LCP monoliths (○). The line represents a fit using equation (1). Monoliths were manufactured at 270 °C and 7 bar for 9 hrs.

The angle θ specifies the tensile test direction with respect to the orientation direction of the material (Figure 3). A longitudinal Young’s modulus value of 65 ± 3 GPa was obtained for the monoliths, which is slightly lower than the value of single heat-treated films of which they were composed. This loss of stiffness is possibly due to minor stacking faults and some loss of orientation during fusion. Figure 2 also shows that the UD monoliths are highly anisotropic. The off-axis stiffness of the monoliths was found to drop sharply to almost half of the initial longitudinal Young’s modulus already at θ = 5°. Using equation (2), the experimental shear modulus $G_{12}$ of an UD LCP monolith was found to be ~1 GPa. This value is relatively low compared to the typical values for the axial shear modulus of high-performance fibers such as aramid (Kevlar® 49) and high-strength carbon (T300), which are reported to be 2–3 and 12 GPa, respectively,[28–30] but is the same as for high-performance polyethylene (PE)
fibers ($G_{12} = 1$ GPa for Spectra® 900, cf. ref. [28]). The low shear modulus of oriented LCP is reflected in the observed strongly-reduced off-axis stiffness and is indicative of relatively weak inter-chain interactions.

Figure 3. Definition of the testing-angle $\theta$, specifying the material orientation axis of the LCP film or UD monolith (extrusion direction $ED = 1$-direction) with respect to the tensile test direction, $1'$. Direction 3 is perpendicular to the film surface. Background: actual sample.

3.2 Viscoelastic Behavior

A double-logarithmic plot of the relaxation modulus versus time of as-extruded and heat-treated single films, as well as 15-layer UD monoliths, results in parallel straight lines, as shown in Figure 4.

These results suggest that the viscoelastic behavior of the films and monoliths is governed by power-law relaxation. In that case, the relaxation modulus $E(t)$ is given by:

$$E(t) = C \left( \frac{t}{t_0} \right)^{-n}$$

(3)

Here, $t$ is the relaxation time in units of seconds, $C$ is the relaxation modulus at $t_0$ and $n$ is the power-law coefficient. The values of these parameters for the LCP
samples can be derived from a best fit of the data in Figure 4 with equation (3); these are summarized in Table 2.

![Figure 4](image)

**Figure 4.** Relaxation moduli of the as-extruded (■) and heat-treated (●) films as well as UD monoliths (○) measured at 1.0% strain. Lines are fits using equation (3).

Using the Boltzmann superposition principle it can be shown that for power-law materials, the stress as a function of time, \( \sigma(t) \), during tensile testing at a constant strain rate \( \dot{\varepsilon}_0 \) follows from equation (3) as:

\[
\sigma(t) = C \dot{\varepsilon}_0 t \left( \frac{t}{t_0} \right)^n = E(t) \varepsilon(t) = C \dot{\varepsilon}_0 (t/t_0)^{1-n}
\]

(4)

This leads to the following equation for the secant modulus, \( E_\varepsilon \), measured at a strain of \( \varepsilon = \dot{\varepsilon}_0 t \):

\[
E_\varepsilon = \frac{\sigma(\varepsilon/\dot{\varepsilon}_0)}{\varepsilon} = \frac{E(\varepsilon/\dot{\varepsilon}_0)}{1-n} = C \left( \frac{\varepsilon}{\dot{\varepsilon}_0} \right)^{1-n} (\dot{\varepsilon}_0 t_0)^n
\]

(5)

Experimental values of the secant modulus, measured at a strain of 1.0% at different strain rates, are presented in Figure 5. The linear correlations in this
Figure, calculated using equation (5) with the material parameters determined from relaxation experiments (Table 2), are in good agreement.

![Figure 5](image)

**Figure 5.** Young’s moduli of the as-extruded (■) and heat-treated (●) films as well as UD monoliths (○) at different strain rates. Lines represent fits using equation (5).

The power-law coefficient $n$ also determines the damping properties of the loss tangent, $\tan \delta$, which is the ratio of energy lost to energy stored in a cyclic deformation and follows from $n$ as:

$$
\tan \delta = \frac{\sin \left(\frac{(2-n)\pi}{2}\right)}{\sin \left(\frac{(1-n)\pi}{2}\right)} \approx \frac{n\pi}{2} \quad \text{for low values of } n
$$

In Table 2, the experimental power-law coefficients for heat-treated LCP films and their laminates are compared with literature values for aramid fibers and fiber-reinforced epoxy composites based on high-performance PE and high-strength carbon fibers. The LCP films and UD monoliths are found to feature damping properties as good as those of the commercially available Vectran® fibers.
Table 2. Parameters from the power-law relaxation modulus $C$, equation (3), for LCP films and UD monoliths (testing-angle $\theta = 0^\circ$), determined from a best fit to the relaxation data in Figure 4 and compared with literature values of aramid fibers (Twaron® HM), as well as composites based on high-performance PE (50% v/v Spectra® 1000) and high-strength carbon (50% v/v XA-S/3K) fibers. The power-law coefficient $n$ determines the damping properties of a power-law-obeying material.

<table>
<thead>
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<th>Material</th>
<th>$C$ / GPa</th>
<th>$n$ / -</th>
<th>ref.</th>
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<td>-</td>
</tr>
<tr>
<td>Heat-Treated LCP Film</td>
<td>79</td>
<td>0.044</td>
<td>-</td>
</tr>
<tr>
<td>UD LCP Monolith</td>
<td>71</td>
<td>0.044</td>
<td>-</td>
</tr>
<tr>
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<td>33</td>
</tr>
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<tr>
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<td>115</td>
<td>0.008</td>
<td>34</td>
</tr>
</tbody>
</table>

3.3 Tensile Failure

The orientation dependence of fracture strength of the heat-treated single LCP film and UD LCP monoliths measured at a constant strain rate of $10^{-3}$ s$^{-1}$ is presented in Figure 6. The off-axis tensile strength data for both the films and monoliths were found to be in excellent agreement with the well-known Tsai-Hill criterion for the failure of unidirectional composites. The Tsai-Hill model is based on the Hill criterion for plastic flow of transversely isotropic materials,[35] assuming that failure stress is initiated by, and immediately follows plastic flow,[1,36] and is given by the tensile strength $\sigma_\theta$ at an angle $\theta$ as:

$$\sigma_\theta = \left( \frac{\cos^2 \theta (\cos^2 \theta - \sin^2 \theta)}{\sigma_1^2} + \frac{\sin^4 \theta}{\sigma_2^2} + \frac{\cos^2 \theta \sin^2 \theta}{\tau_{12}} \right)^{-0.5}$$  \hspace{1cm} (7)

Here, $\sigma_1$ is the longitudinal and $\sigma_2$ the transverse tensile strength, respectively, and $\tau_{12}$ is the axial shear strength.
The longitudinal tensile strength of the as-extruded films was found to be $0.80 \pm 0.02$ GPa which, following heat-treatment, improved to $1.9 \pm 0.1$ GPa. This significant increase of tensile strength has been attributed to increased molecular weight resulting from the post-condensation reaction during heat-treatment.[21,22] Monoliths attained a slightly lower longitudinal tensile strength of $1.7 \pm 0.1$ GPa, again likely due to some misalignment of the constituent films. As was found for the stiffness values in Section 3.1, the tensile strength also decreases dramatically when tested off-axis (Figure 6). The transverse tensile strength of the films and the monoliths was determined to be ~10 MPa. A best fit of the off-axis experimental strength values to equation (7), using the measured values for the longitudinal and transverse strength, resulted in an axial shear strength $\tau_{12}$ of ~20 MPa for the single films and ~26 MPa for the UD monoliths.

![Graph showing tensile strength versus testing-angle of UD LCP monoliths.](image)

**Figure 6.** Tensile strength versus testing-angle of UD LCP monoliths (○). The line represents the Tsai-Hill fit using equation (7). Monoliths were manufactured at 270 °C and 7 bar for 9 hrs.
Again, these are relatively low values, indicative of weak inter-chain interactions, which is in agreement with the low value of the shear modulus $G_{12}$ reported in the previous section. The longitudinal and transverse strain at break of LCP monoliths was approximately 2.5 and 1.0%, respectively. The latter value is relatively high, which is advantageous since the mechanical properties of biaxial or quasi-isotropic laminates are often limited by the transverse fracture strain.

![Figure 7](image.png)

**Figure 7.** Tensile strength of as-extruded (■) and heat-treated (●) films as well as monoliths (○) recorded at different strain rates. Dotted lines are simple linear fits.

It should be noted that the tensile strength of the investigated material was strongly dependent on strain rate, with an increase at higher rates, for instance from $\sim$1.3 GPa at $10^{-5}$ s$^{-1}$ up to $\sim$2.2 GPa at $10^{-1}$ s$^{-1}$ for the heat-treated films and monoliths (Figure 7). This increase of tensile strength is clearly advantageous for applications that involve high velocity impacts.
3.4 Compressive Failure

The off-axis compressive strength of UD LCP monoliths is presented in Figure 8. It is also observed to follow the Tsai-Hill failure criterion (equation (7)), albeit with a substantially lower value for the longitudinal compression strength compared with the longitudinal tensile strength.

![Figure 8](image)

**Figure 8.** Compressive strength of UD LCP monoliths (○) with a cube size of 4×4×8 mm$^3$, fused at 270 °C and 7 bar for 9 hrs. Measured values are compared to the values predicted by the Tsai-Hill model (solid line; equation (7)).

The line in Figure 8 represents a fit of the Tsai-Hill criterion to the compressive strength data, using an identical value for the shear strength, $\tau = 26$ MPa, that was obtained from the off-axis tensile strength data. The data show a modest maximum compressive strength of 95 ± 1 MPa in the orientation direction, which is comparable to the low compressive strength of high-performance PE-based composites.[28] This low value, again, reflects the highly anisotropic character and poor shear properties of the LCP material, thus limiting somewhat the scope for structural applications of these monoliths.
3.5 Interfacial Properties

Figure 9 shows the variation of T-peel force for the as-extruded and heat-treated LCP films post-processed at different pressures and for different compaction times. The as-extruded and heat-treated samples consolidated at 1 and 7 bar both reached nearly identical T-peel force levels (of 2-layer laminates) of approximately 180 N m\(^{-1}\) after 9 hrs.

![T-peel force of two hot-compacted films at 270 °C as a function of manufacturing time. Heat-treated films pressed at 1 bar (♦) and 7 bar (♦); as-extruded films pressed at 1 bar (☉) and 7 bar (☉).](image)

Interestingly, but not entirely surprisingly, the as-extruded films featured a substantially more rapid development of the T-peel force than their heat-treated counterparts. We attribute this phenomenon to the presence of more reaction sites available for post-condensation in the former, untreated films. In addition to T-peel testing, the inter-layer adhesion was also evaluated with a short-beam shear test for measuring the interlaminar shear strength (ILSS) of UD monolithic laminates (where at least 280 layers were fused together), even though the material appears to be homogeneous, with the individual lamina no longer distinguishable.
The ILSS value was calculated as follows

\[ ILSS = \frac{3P_m}{4wh} \]  

(8)

where \( P_m \) is the maximum load observed during the 3-point bending test, \( w \) is the sample width and \( h \) is the sample thickness.[24] The maximum attainable ILSS for monoliths was 18 MPa after hot-compaction for 24 hrs at 270 °C and 7 bar (Figure 10). Both T-peel force and ILSS improved with compaction time but reached rather limited maximum values, possibly indicative of insufficient adhesion or limited cohesive strength within a single LCP film/layer.

![Figure 10. Interlaminar shear strength plotted against T-peel force. Monoliths were made by hot-compaction of heat-treated LCP films at 270 °C at i) 1 bar for 3 (►), 6 (▼), 9 (◀) and 24 hrs (▲) and at ii) 7 bar for 3 (►), 6 (▼), 9 (◀) and 24 hrs (▲).](image)

Therefore, further experiments were performed in an attempt to investigate and improve the interfacial adhesion. Unfortunately, using thinner films (down to ~5 μm) or applying an epoxy-based adhesive to impregnate the films (~0.5% w/w) had only a minimal effect on the ILSS.
Finally, scanning electron microscopy (SEM) micrographs of the fracture plane of specimens after compression testing (Figure 11) suggest that the poor T-peel force and ILSS values originate from the weak internal coherence within the LCP layer itself and not from the potentially weak adhesion between separate layers in the laminate. A typical crack through a LCP monolith is imaged in Figure 12. Vast amounts of fibrillation can be seen within the crack and near the edges, whereas the sample face appears monolith-like and homogeneous (Figure 12a). At larger magnifications near the edge (Figure 12b), it can be observed that these cracked areas and fibrils (Figure 12c) are much thinner than the original single film thickness of ~15 μm, indicating cohesive fibrillation failure.

All of these observations point towards the susceptibility of LCP monoliths to shear loadings due to weak internal coherence, resulting in the observed poor T-peel force, modest ILSS values and low compression strength. In fact, the ILSS value of a monolith appears to be limited by the shear strength of its building block—a single film—as determined from the off-axis test. Consequently, the ILSS of a LCP monolith cannot exceed a shear strength of 26 MPa, which is well below the value of 40 MPa that is generally obtained for composite systems based on aramid, glass or carbon fibers for use in structural composite applications.[28,37–41]

**Figure 11.** *UD LCP monolith a) before and b) after compression testing, indicating major fibrillation in the cracks.*
Figure 12. SEM image of a crack in a monolith that failed in compression. a) Along the edge of the crack, extensive fibrillation can be seen, whereas the sample face appears monolith-like. b) At higher magnification it can be observed that the cracked areas or “splinters” are much thinner than the single films (15 μm) which were used to manufacture the monoliths. c) The fracture plane of these areas features fibrils as thin as ~0.1 μm.
3.6 LCP Monoliths for Stiffness-Based Designs

As indicated above, it appears that the use of present LCP films for large monolithic structural components is inappropriate due to their intrinsically low compressive and shear strengths. On the contrary, the absence of matrix material in fused LCP films leads to 100% “fiber” content, resulting in oriented monoliths with attractively high specific stiffness and tensile strength. An application area where a high specific elastic performance is of paramount importance and poor shear and compression properties are less relevant, is composite sandwich panels.

Sandwich panels are common lightweight structural elements that consist of two thin faces of a stiff and strong material separated by a core of low density (Figure 13a and Figure 14). The deflection $\delta_f$ of a composite sandwich panel in a 4-point bending test is described by:[42]

$$\delta_f = \frac{PL}{96D} + \frac{PL}{8S} \tag{9}$$

Here, $P$ is the load on the panel and $L$ is its span length (Figure 13b). $S$ is the shear stiffness of the panel and can be calculated with

$$S = G_c w s \tag{10}$$

where $G_c$ represents the shear modulus of the core ($G_c = 29$ MPa for the poly(methacrylimide) foam, cf. ref. [25]), $w$ is the panel width and $s$ is the distance between the center of the faces. The flexural stiffness $D$ can then be experimentally evaluated using equation (9).[43]

The flexural stiffness of a panel can be calculated with a simplified model, equation (11):[44]

$$D_{cal} = \frac{E_f w h_f (h_c + h_f)^2}{2} \tag{11}$$

where $E_f$ is the Young’s modulus of the face materials and $h_f$ and $h_c$ are the thicknesses of the face and core, respectively (Figure 13a).
In Table 3, the measured and calculated flexural stiffness values for sandwich panels with glass-, flax-, aramide- and carbon/-epoxy faces, as well as the presented LCP monoliths are listed. The face material is UD throughout and all panels were produced with the same core-to-face weight ratio of ~2, which is the weight ratio for optimum bending stiffness. The measured and calculated flexural stiffness values are in gratifying agreement. The carbon fiber-based sandwich panel attained the best specific value of $52 \pm 1 \, (N \, m^2) \, cm^{-1}$ due to the high Young’s modulus of the T700S carbon fibers; however, the LCP-based panel had the second highest specific stiffness, measured to be $38 \pm 2 \, (N \, m^2) \, cm^{-1}$. This value exceeds that of the other materials studied, the next best of which was the aramide sandwich panel for which a flexural specific stiffness of $35 \pm 1 \, (N \, m^2) \, cm^{-1}$ was recorded. This promising result obtained with the LCP sandwich panels directly stems from the relatively low density of the LCP polymer and the high volume content of the reinforcing material in the monoliths.
Table 3. Measured flexural stiffness $D$ and calculated flexural stiffness $D_{\text{cal}}$ (equation (11)) per specimen width of composite sandwich panels with core-to-skin weight ratios of approximately 2. The core consists of a poly(methacrylimide) Rohacell® IG-F foam. Face materials were UD LCP monoliths, as well as glass, flax, aramid and carbon fabrics; all UD and impregnated with a standard epoxy resin (~40% w/w).

<table>
<thead>
<tr>
<th>Material</th>
<th>$D$ / (N m$^2$) cm$^{-1}$</th>
<th>$D_{\text{cal}}$ / (N m$^2$) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCP Monolith</td>
<td>38 ± 2</td>
<td>36</td>
</tr>
<tr>
<td>Glass/-Epoxy</td>
<td>17 ± 1</td>
<td>16</td>
</tr>
<tr>
<td>Flax/-Epoxy</td>
<td>25 ± 2</td>
<td>22</td>
</tr>
<tr>
<td>Aramid/-Epoxy</td>
<td>35 ± 1</td>
<td>37</td>
</tr>
<tr>
<td>Carbon/-Epoxy</td>
<td>52 ± 1</td>
<td>54</td>
</tr>
</tbody>
</table>

Figure 14. Composite sandwich panels based on different UD face materials: a) glass/-epoxy, b) flax/-epoxy, c) LCP monolith, d) aramid/-epoxy and e) carbon/-epoxy.
4 Conclusions

Free-standing LCP films and their UD monolithic laminates exhibited highly anisotropic behavior with good longitudinal specific stiffness and tensile strength of about 65 GPa and 1.7 GPa, respectively. It was found that both the single films and the monoliths exhibit power-law relaxation in the viscoelastic regime, with excellent damping behavior. In addition, high strain rate experiments indicated that the LCP materials have a high velocity impact strength. For instance at a strain rate of $10^{-1} \text{s}^{-1}$, tensile strengths of over 2.2 GPa were recorded.

Less favorably, the monoliths were found to exhibit poor compressive and shear properties, possibly limiting their use to semi-structural applications. It was shown that this is due to an inherent weakness of the highly oriented films rather than a limited adhesion between the individual layers. Fitting the off-axis strength with the Tsai-Hill equation, the axial shear strength of the investigated material was determined to be in the range 20–26 MPa for both tensile and compression experiments. This relatively low value should be regarded as an intrinsic material parameter that constitutes an upper limit of the shear strength of these UD monoliths. Should the adhesion due to the post-condensation reaction exceed the axial shear strength of a single lamina, the monolith will fail cohesively, within a single layer, despite the good adhesion between them. This was indeed confirmed by scanning electron microscopy of fracture surfaces of samples that failed in compression, which featured massive fibrillation on a scale much smaller than the thickness of a single LCP layer.

Nevertheless, the high “fiber” volume and low density of the LCP film do result in monoliths with excellent specific stiffness. Recognizing these advantageous properties, it was shown that LCP monoliths are appropriate for applications requiring these attributes, for example as face material for composite sandwich panels. The LCP-based panels were shown to outperform the specific stiffness of sandwich structures with various face materials including glass, flax and aramid UD laminates.
References


Part B

Biaxially Oriented Polymers
Chapter 4

Continuous, Simultaneous Biaxial Drawing
1 Introduction

Many attempts have been made to manufacture high-performance polymer structures by biaxial orientation, using, for instance, poly(p-phenylene terephthalamide) (PPTA), ultra-high molecular weight polyethylene (UHMW PE) or cellulose,[1–3] In a study of Bastiaansen et al., it was shown that biaxial orientation of macromolecules results in aggregates of crystalline entities in which the condition of constant overall stress ensures an in-plane stiffness that is reduced by at least one order of magnitude compared to a quasi-isotropic lamellar arrangement of uniaxially oriented polymer films (see Chapter 1 Figure 4).[4] Although, to this day, high-performance polymer structures have not been produced by biaxial orientation, this technique is still widely employed for enhancing the performance of polymer films in terms of, for instance, in-plane stiffness and strength, as well as gas-barrier properties.[5,6] These films, such as biaxially oriented isotactic-polypropylene (BOPP), poly(ethylene terephthalate) (BOPET) and polystyrene (BOPS), are used in the food and beverage packaging industry,[5] as well as in specialized products such as facings for high-performance fibers in sails or as microporous separators in batteries.[7–10]

The process for manufacturing biaxially orientated products was first applied in 1939 to cellulose-based films and was further developed by The Dow Chemical Company in the late 1940’s into a technique termed as the “double-bubble” process,[11,12] By employing a circular die, a tubular film is extruded and immediately quenched. This primary tube is then reheated to temperatures which are close to but still below the melting range, and subsequently inflated by compressed air, resulting in solid-state deformation to a thin film bubble to achieve not only a longitudinal but also transverse orientation. In order to increase the film toughness, a third bubble can be introduced for annealing.[13] This state-of-the-art technique is referred to as the “triple-bubble” and is typically employed for multi-layer packaging films, consisting of a certain sequence of poly(ethylene terephthalate) (PET), isotactic-polypropylene (i-PP), polyamide (PA), poly(vinyl-co-ethylene) (EVOH) or polyethylene (PE) layers.[14]

Another technique involves sheet extrusion followed by quenching and sequential or simultaneous biaxial solid-state deformation at elevated
temperatures with a tenter-frame.[15] Unfortunately, current laboratory methods for biaxial drawing do not allow for continuous drawing and often result in inhomogeneously oriented samples.[16–18] The aforementioned industrially applied techniques require large and expensive equipment which – until now – has hindered further innovation and further development of biaxial stretching as applied to new polymer-based systems, including composites, multi-layers and blends.

In this study we present a laboratory-scale method that involves biaxial solid-state deformation of “precursor” polymer tubes over a heated V-shaped metal mandrel, where the drawing rate is controlled by using the traverse of a tensile-tester or take-off rolls. This alternative method has several advantages over current industrial and laboratory techniques:

i) The technique is a controllable, small-scale method for semi-continuous, simultaneous biaxial solid-state deformation. In combination with a tensile-tester, both drawing rate and drawing force can be monitored, and films can be annealed directly in an environmental chamber.

ii) The processing conditions are similar to those adopted in, for example, the triple-bubble and tenter-frame processes, as well as injection-stretch-blow molding.

iii) Homogeneous thin films (~10 μm) can be produced with balanced biaxial properties, meaning in-plane properties are independent of angle or position.

iv) Only relatively small material quantities are needed (≤ 0.5 kg) and, therefore, the method may be suitable for exploration of new materials which are expensive and/or unavailable in large quantities.

i-PP is used as an illustrative example throughout, although the same technique might also be applicable to other polymers and polymer blends.
2 Experimental Section

Materials. The isotactic-polypropylene (i-PP) Hostalen PPH 1050 (Hoechst AG, Germany; now LyondellBasell) was used. Micrometer-sized alumina platelets, $\varnothing = 5\text{–}30 \mu\text{m}$ and thickness $\approx 200\text{–}300$ nm, Xirallic® T60-10 SW Crystal Silver (Merck KGaA, Germany), were used as received.

Compounds. Alumina platelets and i-PP pellets were premixed in a metal bucket for $\sim2$ minutes. The mixture was slowly fed into a co-rotating twin-screw extruder (Teach-Line® ZK 25 T, Collin, Germany). The blending process was performed at screw speeds of 80 rpm at 240 °C. In order to reduce damage to platelets, a “mild” screw design was chosen. Platelet concentration was increased for every compounding step in 10% w/w increments up to a maximum platelet content of 40% w/w. The emerging strand was quenched in a water bath and subsequently pelletized. The granulates were dried at 100 °C in a vacuum oven for at least 12 hrs prior to further processing.

Tube Extrusion. i-PP-based precursor tubes were manufactured using a single-screw extruder (Teach-Line® E20T SCD15, Collin, Germany) with a barrel diameter of 20 mm and a tube die (Figure 1a). Extrusion was performed at a screw speed of 10 rpm at 230 °C. In order to produce tubes of homogeneous wall thickness, an internal pressure of 2 bar and take-up speed of approximately 2 m min$^{-1}$ was applied. After quenching to $\sim10^\circ\text{C}$, the as-extruded tubes featured a diameter of 11 mm and a wall thickness of $\sim0.5$ mm (Figure 1b).

Figure 1. a) Production of i-PP precursor tubes employing a tube die with a cooling unit and take-off rolls. b) As-extruded tubes.
**Uniaxial Drawing.** Uniaxial drawing experiments were performed in the range of 25–170 °C to determine the optimum temperature for solid-state deformation. Tests were conducted with a tensile-tester (Instron 5864, USA) equipped with an environmental chamber and a 2 kN load cell. Dog-bone shaped samples of i-PP (punched out of a hot-pressed film) had a gauge length of 12 mm, width of 2 mm and thickness of 0.5 mm.

![Graph](image)

**Figure 2.** a) Yield stress (◇) and b) maximum draw ratio $\lambda_{\text{max}}$ (◆) versus drawing temperature for uniaxially drawn neat i-PP samples. The solid line at 160 °C corresponds to the biaxial deformation temperature chosen for the i-PP tubes.
The cross-head speed was set to 7.2 mm min⁻¹ (corresponding to an initial strain rate of 0.01 s⁻¹). The material was found to have a maximum uniaxial draw ratio \( \lambda_{\text{max}} \) (ratio of final to initial sample length) of \(~26\) in the range of 152–160 °C with a corresponding yield stress of roughly 4 MPa (Figure 2). All biaxial drawing experiments were subsequently conducted in this temperature range.

**Biaxial Drawing of i-PP Tubes.** Biaxially oriented films were produced by solid-state deformation of as-extruded i-PP tubes using a heated V-shaped metal mandrel (Figure 3) at elevated temperatures (152–160 °C). The internal heating cartridges were temperature controlled by a K-type thermocouple, both connected to a regulator (Jumo, Germany). The deformation rate was controlled by either a tensile-tester (Instron 5864, USA) fitted with a 2 kN load cell or by chill rolls (Teach-Line® CR 72T, Collin, Germany), allowing maximum drawing speeds of 2 m min⁻¹. The resulting biaxially oriented films were \(~10\) μm thick.

![Figure 3. Schematic of the V-shaped metal mandrel. The stretching in the transverse direction depends on the shape or, more specifically, the ratio of the initial and final width of the mandrel. The longitudinal drawing mainly depends on the wedge angle and the friction between the metal body and precursor tube.](image)

**Film-Blowing.** As a control experiment, films were also manufactured via film-blowing. Extrusion was performed with a single-screw extruder (Teach-Line® E20T SCD15, Collin, Germany), screw speed of 40 rpm at 240 °C, feeding a film-blowing die (Teach-Line® BL 50 T, Collin, Germany) maintained at 250 °C. The take-up speed was adjusted so that films with a thickness of 15 μm were produced.

**Mechanical Testing.** Tensile test measurements were conducted with a tensile-tester (Instron 5864, USA) fitted with a 100 N load cell and equipped with pneumatic clamps. To avoid slip-out, adhesive masking tape Scotch® (3M, USA) was used to cover the clamping area at both ends of every specimen. Dog-bone
shaped samples had a gauge length of 12 mm and a width of 2 mm. The film thickness was calculated from the weight of a circular sample (Ø = 5 mm) stamped out of the film area next to the dog-bone, using a density of 0.9 g cm\(^{-3}\). The cross-head speed was set to 7.2 mm min\(^{-1}\) (corresponding to an initial strain rate of 0.01 s\(^{-1}\)).

**Differential Scanning Calorimetry.** Melting temperatures were determined with a DSC822e differential scanning calorimeter (DSC) (Mettler, Switzerland), calibrated with indium. Samples of ≤ 5 mg weight were heated from 25 to 250 °C at a scanning rate of 10 °C min\(^{-1}\) under constant nitrogen flow.

**Optical Properties of Films.** Haze and clarity was determined using a Haze-Gard Plus® apparatus (BYK Gardner GmbH, Germany).

**Scanning Electron Microscopy.** Samples for scanning electron microscopy (SEM) were prepared by cryofracturing. After fracture, samples were sputtered with a thin conductive layer of platinum and imaged using a LEO 1530 Gemini scanning electron microscope (Zeiss Elektronenmikroskopie GmbH, Germany) using secondary electron detection.

**Wide-Angle X-Ray Diffraction.** Wide-angle X-ray diffraction (WAXD) was performed on an Xcalibur™ PX diffractometer (Oxford Diffraction, UK) using Mo-K\(\alpha\) radiation (0.71 Å wavelength), at room temperature.

### 3 Results and Discussion

#### 3.1 Alternative Method for Biaxial Drawing

The design concept for the biaxial solid-state deformation of tubes over a mandrel can be described as a process analogous to “putting on socks”. By means of an expanding metal body, a polymer-based tube is stretched at elevated temperatures in the transverse and longitudinal directions simultaneously (Figure 3). The draw ratio in the transverse direction depends on the shape or, more specifically, the ratio of the initial and final width of the mandrel. The longitudinal draw ratio mainly depends on the wedge angle and the friction between the metal body and the precursor tube.
The concept of using a heated metal object to apply a biaxial deformation to a tubular plastic object was already adopted by Ward and co-workers, wherein polymer pipes were stretched over a "conical mandrel die".\[19\] The pipes produced showed markedly improved mechanical properties.\[20,21\] Although successful in establishing a continuous, simultaneous biaxial deformation process, two major problems remained with Ward’s setup:

i) The laboratory setup was large, consisting of a 15 m drawing bench.

ii) The reported end products were not thin films but rather self-reinforced tubes (with resulting wall thicknesses \(\geq 0.2\) mm).

Figure 4. Two fundamentally different metal mandrels for biaxial deformation of polymer-based tubes. a) Initial experiments were carried out unsuccessfully with cones. b) After a refit of the mandrel, biaxial deformation of tubes was possible with a wedge.
The first drawing experiments in this study were also carried out with heated cones (Figure 4a) of different geometries over which an i-PP precursor tube was drawn. It was found that a reproducible and continuous stretching process was not possible due to the high drawing forces required to pull the precursor tube over the mandrel. Even with different surface modifications, e.g. notches or grooves for reducing the contact area and using lubricants such as silicon oil, film tearing during solid-state processing still occurred.

Consequently, a redesign of the mandrel was undertaken and semi-continuous processes were found to be possible using a set of V-shaped mandrels (Figures 4b and 5). It should be mentioned, however, that the homogeneity of the biaxially deformation of the precursor tube is sacrificed, and that stretching mainly takes place in the top and bottom parts of the wedge; see also Figure 17 (a, b).

**Figure 5.** Different wedges used for biaxial deformation. All have the same initial and final width, but different semi-opening angle \( \varphi \) of: **a**) 8°, **b**) 14° and **c**) 18°.
The advances associated with the new design originates from the notches milled along the sides of the wedges (Figure 6). Apart from being isolated from the main stretching regions of the wedge by frictional corners, the part of the i-PP tube that is recumbent along the notched side now has no contact with the heated metal body and remains thicker (~0.25 mm) as a result of the restricted heat transfer. These regions of preferentially uniaxially aligned material provide “leashes” that help transferring the tensile load from the tensile-tester or chill-rolls and prove to be essential in allowing drawing of the tubes over the mandrel, gratifyingly yielding balanced biaxially drawn films of ~10 μm thickness.

3.2 Friction

The total friction force during drawing is strongly influenced by the wedge angle. When the semi-opening angle $\varphi$ is small, e.g. $8^\circ$ in Figure 7a, the deformation of the i-PP tube occurs first in the longitudinal direction. However,
the large force required to draw the material over the wedge results in strain localization and severe necking, followed by inhomogeneous deformation. When \( \phi \) is large, 18° (see Figure 7c), a sequential drawing process results with transverse stretching followed by stretching in the machine direction. Intermediate semi-opening angles, like 14° in Figure 7b, yield properly balanced, simultaneous biaxial stretching. Strain hardening during deformation evidently assists in eliminating initial strain localizations.

The result of the transient drawing force for mandrels with different mandrel angles is shown in Figure 8. From this figure it is clear that for slender mandrels, the accumulated friction is so high that a steady-state drawing process cannot be achieved. The initial tube section is stretched until fracture occurs after necking. Stretching of i-PP tubes with a mandrel having a \( \phi = 14^\circ \), yields films with a biaxial draw ratio \( \lambda_{0^\circ/90^\circ} \) of ~7 × 7, see Figure 9.

![Figure 7](image.png)

**Figure 7.** Photographs of the critical solid-state deformation stage of i-PP tubes at 160 °C, using wedges with different semi-opening angles. A 5×5 mm² grid was drawn on the precursor tubes. **a)** A small wedge angle, \( \phi = 8^\circ \), results in strain localization and severe necking, followed by inhomogeneous deformation and film tearing. **b)** An intermediate angle, \( \phi = 14^\circ \), yields balanced, simultaneously biaxially stretched films, as indicated by the red squares. **c)** Larger wedge angles induce a sequential drawing process.
Figure 8. Transient drawing force as function of film extension (equivalent to time as the drawing speed is constant). For slender mandrels, $\varphi = 8^\circ$ (○), the accumulated friction is so large that early fracture occurs and no steady-state drawing process can be reached and film tearing occurs. Force-extension-curves obtained from tube drawing using mandrels with semi-opening angles $\varphi = 14^\circ$ (■) and $\varphi = 18^\circ$ (▲) illustrate that a steady-state semi-continuous drawing process can be achieved.

Figure 9. Unstretched (right side, initial grid size: 5×5 mm²) and stretched i-PP tube (left side, biaxial draw ratio $\lambda_{0^\circ/90^\circ}$ of ~7×7) after removal of the sample from the wedge. Biaxial deformation was performed at 160 °C and 1 m min⁻¹, using a mandrel with $\varphi = 14^\circ$.

Friction between the precursor tube and the mandrel is an important factor in the biaxial drawing process. If the friction is too high, steady-state drawing does not occur as observed employing a slender mandrel, e.g., $\varphi = 8^\circ$ (cf. Figure 7a).
Figure 10. Photographs of the initial solid-state deformation of i-PP tubes at 160 °C, using a mandrel with a φ of 14°. A 5×5 mm² grid was drawn on the precursor tubes prior to deformation. The tube in a) was stretched on the “dry” mandrel whereas in b) stretching was performed on the same mandrel lubricated with paraffin oil.

However, attempting to reduce friction by simple means – such as employing a lubricant – leads to a similar problem as using a mandrels with small or large semi-opening angles. Figure 10 shows the initial deformation pattern, produced by using a wedge with φ = 14°, “dry” (Figure 10a) and lubricated with paraffin oil (Figure 10b), respectively. When using a lubricant, the deformation of the i-PP tube occurs first on both sides in the transverse direction as in the case of large wedge angles, while the middle part of the precursor tube remains unstretched leading to inhomogeneous deformation as with mandrels with small angles. For drawing the tube further in longitudinal direction, a large force is required that results in strain localization, severe necking and film tearing. This experiment demonstrated that for creating balanced biaxial films the correct wedge angle should be combined with a right amount of friction between the precursor tube and the mandrel.
3.3 Mechanical Properties

All samples analyzed in the following sections were produced with the wedge mandrel design of $\varphi = 14^\circ$ (dry, no lubricant involved), at a temperature of 160 °C. The films exhibited a biaxial draw ratio $\lambda_{0^\circ/90^\circ}$ of approximately 7×7 and a thicknesses of ~10 μm. The influence of biaxial deformation speed on mechanical properties of these i-PP films was analyzed; the results are presented in Figure 11.
Chapter 4  

Encouragingly, a major improvement over the values of the unoriented polymer of both the Young's modulus and tensile strength \textit{in both directions}, reaching values of up to 400% or more, was achieved with the present deformation process – both at relatively low and at high deformation rates. Higher rates result in less relaxation and more affine deformation, resulting in enhanced properties.

The \textit{balanced} character of the mechanical properties of the biaxial films produced is further demonstrated by testing the angle-dependence of the Young’s modulus and tensile strength, see Figures 12 and 13.

\textbf{Figure 12.} Testing-angle dependence of the Young’s modulus of biaxially oriented i-PP (●). Solid line indicates the stiffness of the isotropic, unoriented precursor tube.

Virtually isotropic in-plane tensile properties are recorded for a \textit{balanced} biaxially oriented film, produced at 160 °C and 2 m min$^{-1}$ (corresponding to initial biaxial strain rates of $\sim$0.2 s$^{-1}$) over the V-shaped mandrel of $\varphi = 14^\circ$. The stiffness and tensile strength are approximately 2.2 GPa and 210 MPa, respectively, approaching the performance of commercial biaxially oriented i-PP films. The strain at break is 56 ± 9%. The corresponding standard deviation is
relatively large; this is due the fact that the value is the average of the strain at break values determined at all testing-angles from 0–90°. For comparison, the as-extruded precursor tubes exhibit isotropic mechanical properties with a Young’s modulus of 0.5 GPa and tensile strength of 35 MPa only, and a strain at break of ~800%.

Figure 13. Testing-angle dependence of the tensile strength of biaxially oriented i-PP (●). Solid line indicates the tensile strength of the isotropic, unoriented precursor tube.

3.4 Optical Properties

Haze and clarity measurements are appropriate for quantifying the optical characteristics of a material in terms of transparency. Haze, the extent of turbidity, is the fraction of the total amount of transmitted light which is scattered at angles higher than 2.5°, normalized by the incoming flux.[22] High values of haze result in loss of contrast and “milky” appearance of an object viewed through the material. Clarity, the degree of sharpness, is a measure of the direct transmission in relation to scattering at low angles (≤ 2.5°), reflecting the ability of a material to transmit fine details without the distortion of contours.[23]
Haze and clarity measurements of a ~10 μm thick film exhibit values of 6% and 94%, respectively (0.5 mm thick precursor tube; haze: 86% and clarity: 10%).

Figure 14 provides a qualitative demonstration of the optical properties of precursor and biaxially deformed tubes (more precisely the yielding film).

Figure 14. Optical properties of a) unstretched i-PP precursor tube (thickness of ~0.5 mm) and b) i-PP after biaxial stretching, yielding films of ~10 μm thickness.

3.5 Wide-Angle X-Ray Diffraction

Wide-angle X-ray diffraction (WAXD) patterns, recorded in three orthogonal directions, of an as-extruded precursor i-PP tube before and after biaxial deformation are presented in Figure 15. The three identical patterns shown in Figure 15a reveal that the as-extruded tube features an isotropic orientation of the constituent polymer crystals. After biaxial deformation, the WAXD patterns are indicative of identical orientation in both the drawing and transverse directions (0° and 90°, respectively). Furthermore, the isotropic scattering pattern recorded perpendicular to the film surface (Figure 15b) suggests an isotropic in-plane orientation of the macromolecular crystals, which is consistent with the isotropic in-plane mechanical properties presented and discussed in Section 3.3.
Figure 15. WAXD patterns recorded in three directions: at an angle of 0°, corresponding to the direction of extrusion and drawing; at 90°, corresponding to the transverse direction and perpendicular to the plane. a) As-extruded i-PP precursor tube. b) Biaxially oriented i-PP, deformed in the solid-state at 160 °C and a rate of 2 m min⁻¹.
### 3.6 Platelet Filled Polymer Systems

The biaxial tube deformation process was also used for dispersing and ordering micron-sized alumina platelets in an i-PP matrix (Figures 16 and 17). For optimal performance of filled polymer systems, three aspects are important:
i) an effective dispersion of the added phase; ii) a controlled orientation of the anisotropic additive in the continuous polymer matrix; and iii) especially in the case of seeking enhanced mechanical performance, an adequate level of adhesion between the added matter and the matrix.

![SEM images of i-PP containing alumina platelets](image)

**Figure 16.** SEM images of i-PP containing alumina platelets. a) As-extruded i-PP precursor tube with 20% w/w alumina platelets. b) Biaxially oriented film containing 20% w/w platelets. c) As-extruded i-PP precursor tube with 40% w/w alumina platelets. d) Tube after biaxial deformation. e)–f) Films were stacked and consolidated at 180 °C into laminates (with 40% w/w alumina platelets). (Precursor tubes were stretched at 160 °C and 1 m min⁻¹.)
Figure 17. a) Biaxially oriented film of i-PP containing 40% w/w alumina platelets. Arrows indicate the essentially undeformed film parts at both sides of the mandrel (“leashes”) that were formed during the biaxial stretching using the wedge geometries. b) Same sample, placed on a light box showing that the alumina platelets are well dispersed in the i-PP matrix. c) As a control experiment, films were produced via film-blowing. These specimen exhibit a poor platelet dispersion.

Figure 16 illustrates that an in-plane alignment of alumina platelets in the i-PP matrix can be obtained with the presented biaxial deformation process. Figure 17 convincingly shows that biaxial solid-state deformation is superior to melt-processing in dispersing the platelets in the matrix. Therefore the first two of the main requirements for the creation of proper composite materials are reached: excellent dispersion and ordering. Unfortunately, however, the mechanical properties of the platelet-filled systems did not approach those expected from the Halpin-Tsai “rule-of-mixtures”. Clearly the third requirement, i.e. good adhesion between filler and matrix, is not fulfilled in the presented system and should be further investigated.

4 Conclusions

The laboratory-scale stretching method presented in this study involves semi-continuous biaxial solid-state deformation of i-PP precursor tubes over a heated V-shaped metal mandrel under optimal conditions, yielding balanced biaxially drawn films of ~10 μm thickness at a take-off winding speed of 2 m min⁻¹ (corresponding to initial biaxial strain rates of ~0.2 s⁻¹). The i-PP films are reproducibly manufactured and exhibit a biaxial draw ratio of approximately 7×7 that approaches that of commercially available BOPP materials and feature virtually identical properties. The method presented in this study could provide
a valuable tool for efficiently exploring new polymers and systems based on them, here illustrated with i-PP containing alumina platelets, in a laboratory-scale process of the creation and analysis of biaxially oriented polymer films.

It should be noted, though, that unfortunately, the method developed is still highly dependent on wedge shape and friction between mandrel and precursor tube. Too high as well as too low levels of friction leads to strain localization in longitudinal and/or transvers directions, and finally result in early film tearing. The remaining challenge is creating the right mandrel design for producing balanced simultaneously drawn biaxial films under fully controlled conditions. Ideally this would involve a further reduction in friction, combined with full control of feed and take-off speed. As latter determines the longitudinal stretch, the orthogonal stretch is controlled by the ratio widths at the onset and the end of the wedge. Evidently, the precise wedge shape determines the local transverse strain rates.

References


Part C

Triaxially Arranged Polymers
Chapter 5

Multi-Layered Structures
1 Introduction

In this chapter the production of multi-layered polymer based films employing (modified) static mixers, as well as their structure and selected properties, is presented. The working principle of static mixers is based on the application of the baker’s transformation: a repetitive action of stretching and folding or stretching, cutting and stacking.[1–3] If an initial two-layer system is fed into such a mixer, a stratified, alternating multiple layer structure results. Essentially any initial structure can be multiplied, and no restrictions exist regarding the number of polymers fed, flux ratio and initial configuration.

With respect to the ability to deal with materials set of different viscosity ratios, we can distinguish static mixers that rely on shear flow, such as the Kenics,[4] Ross,[5] Multiflux[6,7] and Dentinxc[8–11] mixers, and those that use more elongational flows, like the Sulzer SMX[12,13] and Peelincx[8,14] mixers. Mixers in the first group require almost equal viscosities, while those in the second are principally able to deal with viscosity ratios differing from one. Here we improve on the design of the recently-developed compact Peelincx mixer where every element increases the incoming number of layers with, nota bene, a factor 12.

The Peelincx mixer[8,14] is named after its inventors and comprises a number of vertically stacked circular plates, each having two halves where the melt flowing outwards is cut and rotated, and subsequently recombined to flow inwards again. The first design is shown in Figure 1 (a, b). It demonstrates how the incoming flow is split into a left (not shown) and a right flow, directly turning the interfaces of the two inflowing polymers into (as an illustration) colored white on top and black underneath. The horizontal flow is split into six parallel turning elements of the circumventor which rotate the flow, turning the interfaces vertical and recombine during inwards flowing towards the central exit. The second design is shown in Figure 1 (c, d). It makes maximum use of the available space, minimizes all flow paths, thereby reducing the pressure, and, most importantly, *equalizes* all flow paths, such that the outward-inward flow history of every fluid element finally is virtually identical. This allows the layering of different polymer combinations, essentially independent of their viscosity ratio. In each half of the first element, 2 layers enter, while \(6 \times 2 = 12\) layers exit. Each element, therefore, multiplies the
number of incoming layers by a factor twelve, and the total number of layers, $L$, formed equals $L = 2 \times 12^n$, where $n$ is the number of elements coupled in sequence.

**Figure 1.** Peelinx mixer (cf. ref. [8,14]): parallel flow splitting and rotation in a circular setup of the Dentinx mixer. First a) and b), and second design c) and d).

### 2 Improving the Design of the Peelinx Mixer

Exploiting computer-controlled laser welding of metal powder, the Peelinx mixer has been further optimized for use in this study.

First, the parallel channels that run closest to the radially directed walls of each half of a mixer element are given more space. This measure compensates for the (slight) channel width reduction, and, therefore, for the increase in resistance, caused by the stationary wall layers. Second, instead of a circular arrangement, all splitting operators were positioned on a (slight) ellipse. In this way, not only the
flow paths of the first and last streams are identical, but also those of the middle streams. Finally, to reduce the presence of dead corners and unequal residence time distributions, all corners are rounded, as shown in Figure 2.

**Figure 2.** Peelincx mixer as designed and made for the experiments conducted for this study. It is manufactured based on computer-aided design and manufacturing techniques (CAD-CAM), using layer-by-layer moldless laser powder sintering. Not only corners are rounded and edges are sharp, but also compensation is provided for unequal flow rates of the different parallel streams caused by stationary wall layers and slight differences in path lengths. **a)** Top and bottom view of the parts that constitute one element of the optimized Peelincx mixer. Scale bar: 3 cm. **b)** Details of the actual materialized structures. Scale bars: 5 mm.
In preliminary experiments with Multiflux and splitting serpentine mixers,\cite{15-17} it was demonstrated that for material of viscosity ratios differing from one, the homogeneity of the layer distribution was not optimal. The main deviations originated from the flow within the first few elements. Once a critical number of layers was surpassed, the quality of further layering significantly improved. Our interpretation of this is the effect of viscosity being averaged over the cross-section of the channel, by the stratifying process itself. This led us to the conclusion that for polymer systems with unequal viscosities, starting with only two layers is not optimal. Therefore we designed a forced feed element with separated intermingled flows. It creates 10 alternating layers which are fed into the static mixer (Figures 3 and 4).

**Figure 3.** Design of the 10-layer feed-die; the main component is shown in cross-section and from the top (left) and in 3D (right). See also Figure 4, middle column.
Figure 4. Photographs of the 10-layer feed element consisting of three stacked components (left, middle and right columns, respectively), as seen from the top (first two rows) and bottom (last two rows). Scale bars: 2 cm.
3 Experimental Section

Materials. Polyamide (PA), Grivory® G16, neat as delivered, and blue, colored with 0.2% w/w copper dye (EMS-Chemie AG, Switzerland), as well as polystyrene (PS) 124N (Styrolution, Germany) and polyurethane (PUR) Elastollan LP 9291 (BASF, Germany) were used for creating multi-layer structures.

Multi-Layer Extrusion. Prior to processing, the polymers were dried under vacuum (for PA: at 120 °C and for PS and PUR: at 60 °C) for at least 24 hrs. Two single-screw extruders (Teach-Line® E20T SCD15, Collin, Germany) with a barrel diameter of 20 mm were used. The extrusion of PA was performed at 270 °C whereas PS and PUR were processed at 200 °C. The pressure of both extruders was carefully maintained at 100 bar. In order to control and vary both melt streams, melt pumps (Zenith® BB PEP, Colfax® fluid handling, USA) were arranged between extruders and the die. The extrudate was collected and quenched in a cylinder filled with sunflower oil, providing less uplift compared to water and thereby resulting in more straight samples. The static mixer used for this study started with a 10-splitter element followed by a different number of Peelincx mixing elements. A nominal total number of layers of $10 \times 12^1$, $10 \times 12^2$, $10 \times 12^3$, and $10 \times 12^4$ results, thus: 120, 1'440, 17'280, and 207'360 layers, respectively. Extrudates were of a cross-section of ~$7 \times 10$ mm².

Injection Molding. PS:PUR extrudates, flux ratio 10:1, comprising 1’440 layers were granulated and dried in a vacuum oven at 60 °C for at least 24 hrs prior to further processing. An all-electric injection molding machine (Allrounder 370 Arburg, Germany) with a closing force of 600 kN was used for manufacturing dog-bone shaped samples (cross-section for testing: 4×10 mm²; total length: 170 mm). Processing and mold temperatures were 200 °C and 30 °C, respectively. Injection was performed at a speed of 50 mm s⁻¹ and a pressure of 700 bar with dwell pressure and time of 400 bar and 10 s, respectively. A cooling time of 12 s was applied.

Sample Preparation for 3-Point Bending Tests. The extruded multi-layer rods were cut into pieces of at least 40 mm in length. A diamond wire saw was used to cut out bars with a length of 35 mm and a cross-section of approximately
3.5×5.0 mm² which were polished to 3.0×4.5 mm² (see Figure 5). For the finishing, a silicon carbide grinding paper with a grit of 4'000 was used. After machining, the specimens were annealed for 8–10 hrs at 80 °C.

Figure 5. Geometry and dimensions (in mm) of samples for mechanical testing. 

a) 3-point bending; b) single-edge notched bend specimen (according to ASTM E 1820-08a; cf. ref. [18]); c) notched tensile specimen.

3-Point Bending. 3-point bending tests were performed with a tensile-tester (Instron 4111, USA) equipped with a 500 N load cell. All specimens were tested at a cross-head speed of 5 mm min⁻¹ and span length of 30 mm. Testing was carried out at ambient temperature, ~20 °C. The deflection of the specimen was derived from the cross-head movement.

Sample Preparation for Notched 3-Point Bending Test. The extruded multi-layer rods were cut into pieces of at least 80 mm in length. A diamond wire saw was used to cut out bars which were subsequently polished to specimens with cross-sections of 2.5×5.0 mm² (Figure 5). A silicon carbide grinding paper with a grit of 1’200 was used to achieve the final surface finish. Following machining, the specimens were annealed for 8–10 hrs at 80 °C, after which they were notched with a diamond wire (300 μm in diameter). The distance between the notches was 15 mm with depths of 2.3–2.5 mm (Figure 6). Each notch was created with a new razor blade (200 μm). After finishing, the notches were filled with white-out (Tipp-Ex®) to mark the initial notch length. This procedure adheres to the ASTM
E1820-08a, resulting in single-edge notched bend specimens for fracture toughness measurements.

**Figure 6.** Schematic drawing of the single-edge notched bend specimen employed for slow notched 3-point bending and crack resistance measurements. Specimen were prepared according to ASTM E 1820-08a (cf. ref. [18]). Cross-section: 2.5×5.0 mm².

**Slow Notched 3-Point Bending.** The tensile-tester (Instron 6582, USA) was equipped with a 1 kN load cell. Specimens with a span of 20 mm were tested at a cross-head speed of 0.01 mm min⁻¹, at ambient temperature. The extension or load line displacement of the specimen was measured with a linear variable differential transformer gauging transducer (GT1000, RDP Electronics Ltd., UK) for a range of ±1 mm, positioned directly below the notch.

**Crack Resistance Curves.** For crack resistance curves, cyclic loading was conducted with the same setup as for notched 3-point bending, using single-edge notched bend specimens. The measurement was controlled over load-line displacement recorded by a gauging transducer. Loading and unloading rates were 0.1 mm min⁻¹. Cyclic loading was performed as follows:

- three initial loading and unloading cycles to a load of 6, 9, and 12 N
- first loading up to a load-line displacement of 70 μm
- unloading using 20% of the previous peak load
- each subsequent loading increases the load-line displacement by 2.5 μm
- 12 s pause after each cycle

The crack resistance curves were calculated with the load-displacement lines obtained from the cyclic measurements. A nonlinear elastic fracture mechanics approach was used for calculating the resistance, referred to as the $J$-integral (strain energy release rate or work, respectively, in units of energy per unit fracture surface area). [N.B. Not only the energy consumed by the linear elastic
fracture, but also the energy for the inelastic deformation needs to be accounted for.\textsuperscript{[19]} The calculation of the $J$-integral was performed according to ASTM E 1820-08a\textsuperscript{[18]} and Launey \textit{et al.}\textsuperscript{[20,21]} (as described in the Appendix).

**Sample Preparation for Tensile Testing.** Extruded multi-layers were hot-pressed in a mold at 200 °C for 15 minutes to 4 mm thick bars, which were machined to a width of 7 mm and a length of 60 mm (Figure 5). In a final step, the tensile specimens obtained were notched on both sides with a razor blade to a depth of 200 μm (controlled by a mechanical extensometer).

**Tensile Testing.** Tensile testing was performed at ~20 °C with a tensile-tester (Instron 5864, USA) equipped with a 2 kN load cell. The cross-head speed was 2 mm min\(^{-1}\) and the gauge length was 30 mm.

**Optical Microscopy.** For ease of preparation and handling, samples for optical microscopy were embedded using a two-component epoxy resin (resin type HT2, R&G Faserverbundwerkstoffe GmbH, Germany). After curing for 24 hrs at room temperature, the embedded samples were machined and polished to plates of 0.5 mm thickness. Images were taken using a Leica DMRX polarizing microscope equipped with a Leica DFC 480 camera (Leica, Switzerland). Immersion oil was used to minimize light-scattering from any scratches resulting from machining and polishing.

**Scanning Electron Microscopy.** Samples for scanning electron microscopy (SEM) were prepared by cooling in liquid nitrogen and subsequent fracturing. Those samples were sputtered with a thin conductive layer of platinum and imaged using a LEO 1530 Gemini scanning electron microscope (Zeiss Elektronenmikroskopie GmbH, Germany) using secondary electron detection.

**Atomic Force Microscopy.** Samples for atomic force microscopy (AFM) were prepared with a cryo-microtome at a cutting temperature of −70 °C and at a glass blade temperature of −60 °C. Those samples were scanned in the tapping mode (imaging: adhesion, modulus and phase) using a Dimension Icon AFM (Bruker, USA).
4 Results and Discussion

4.1 One Polymer: Alternating Transparent and Blue-Dyed

First results obtained with a transparent and blue-dyed amorphous PA, which almost behaves like a Newtonian fluid, are shown in Figures 7 and 8.

**Figure 7.** Cross-sections of PA:PA samples comprising 17’280 alternating blue and transparent layers. The blue-transparent polymer film ratio decreases from the left to the right (from 60:1, 10:1, 2:1, 1:1, 1:2, 1:10 to 1:60).

Figure 8 presents photographs of cross-sections of continuous tapes/extrudates exiting the mixer for five sets of samples with different blue-to-transparent polymer film ratios (10:1, 2:1, 1:1, 1:2, 1:10). In each case, the photographs are taken at two different magnifications.

**Figure 8.** Photographs of cross-sections of the extrudates with blue and transparent amorphous PA exiting a) the feed section (creating 10 layers), b) the first element (creating 120 layers) and c) the second element (creating 1'440 layers). The blue-transparent polymer film ratio decreases from left to right as 10:1, 2:1, 1:1, 2:1 and 1:10.
Figure 8a shows the cross-sections of the samples exiting the 10-layer feed block only, while Figures 8b and 8c shows results for one and two elements respectively. As can be seen, the homogeneity of the layer distribution is excellent. The black spheres, seen most clearly in Figure 8b, are bubbles caused by insufficient drying of the PA.

![Figure 9](image)

**Figure 9.** Optical micrographs of blue and transparent amorphous PA (flux ratio of 10:1), exiting the second a) and third b) element, with alternating continuous layers (1'440 and 17'280, respectively) observed in each case. Scanning electron micrographs for a different system, namely PS:PUR 10:1, are shown at low c)–d) and high e)–f) magnifications. The thickness of the PUR layer is 2 μm after the second element (see c) and e)) and ~200 nm after the third (see d) and f)).
Figure 9 shows the results obtained by adding two (left column, 1'440 layers) and three (right column, 17'280 layers) mixing elements, flux ratio of 10:1, for the PA:PA (blue:transparent) and PS:PUR systems; importantly, all layers remain continuous. The PS:PUR system was further investigated since it allows “staining” followed by inspection using SEM. The PUR layer thickness after two elements equals 2 μm, and reduces to ~200 nm after employing three elements.

4.2 Two Polymers: Alternating Hard and Soft

Producing and investigating PS:PUR structures is inspired by attempts to mimic Nature and arrive at materials that combine high modulus with high toughness and/or resistance to crack growth. Deep ocean glass sponges (layer-by-layer), sea-shells of oysters and mussels (brick-and-mortar), teeth and bone (hierarchical-order) all combine such hard and soft, thin layers;[22, 23] see Figure 10 for schematic depiction of microstructures.

![Figure 10. Schematic structures of a) layer-by-layer, b) brick-and-mortar and c) hierarchical-order microstructures, which can be found in natural composites.](image)

They all serve the same purpose, namely preventing a crack from continuing to grow in one direction, causing fracture in one plane.[22, 24] Even for the strongest (covalent) bonds known, creating two new surfaces requires an intuitively-surprising low energy of ~1 J m⁻² only. The thin weak layer’s purpose is to guide away a crack in perpendicular, out-of-plane directions. A substantial increase in energy-to-break should then originate from introducing a large number of small (van der Waals) contributions, rather than a limited number of strong (covalent) elements. Deformation occurring in a volume, rather than in a plane, results in a,
sometimes, spectacular increase in energy and macroscopic strain to break.[22,25] Importantly, thin, rather than thick, layers of the soft material are required in order to avoid an accompanying substantial reduction in the modulus of the system.

Figure 11 shows images obtained with scanning electron microscopy of fracture surfaces of PS:PUR samples with 17’280 layers.

**Figure 11.** Surfaces of cross-sections obtained via cryo-fracturing of the stratified PS:PUR system comprising 17’280 layers (using three mixing elements). a) and b) composition 10:1. c) and d) composition 40:1. e) and f) composition 60:1. The right column shows SEM micrographs at a 10-times higher magnification.

From the extruded strands, samples were prepared for 3-point bending tests, as well as for notched 3-point bending and notched tensile tests. Fatigue loading was applied using the notched bending test setup and used to measure crack resistance curves which yield the $J$-integral and stress intensity factor $K_J$ as a
function of crack length, $\Delta a$. For experimental details see Section 3. The main results are summarized in Figure 12. In all cases, introducing thin rubbery PUR layers results in only a slight, on the order of 10%, decrease in the modulus of the neat PS. More importantly, however, both energy-to-break (area under the stress-strain curve), as well as strain-to-break increase by ~40% in notched 3-point bending (Figure 12b). Furthermore, in notched tensile testing the energy-to-break also increases by almost 100% (Figure 12c). Dramatic are the results of fatigue loading and testing, showing in Figure 12d and Figure 13.

Figure 12. Mechanical tests of neat PS versus PS:PUR, flux ratios 40:1 and 60:1, 17'280 layers. Results of a) pristine and b) notched 3-point bending and c) notched tensile tests, and d) results of dynamic fatigue loading/unloading (according to ASTM E 1820-08a). Dynamic fatigue testing data were used for calculating crack resistance curves, showing the J-integral and stress intensity factor $K_J$ as a function of crack extension, $\Delta a$, in Figure 13. Neat PS (black), PS:PUR 40:1 (blue) and PS:PUR 60:1 (red).
While pure PS fractures quickly already at small crack extensions, the layered structures maintain their structural integrity and only fail after many cycles when the growing crack becomes very large. This is also reflected in both the $J$-integral, as well as in the value of the stress intensity factor $K_J$ (see Figure 13).

Figure 13. Crack resistance analyses from testing single-edge notched bending specimens, yielding **a)** $J$-integral and **b)** stress intensity factor $K_J$ as a function of crack length, $\Delta a$, for PS (black symbols) and for PS:PUR 60:1 (red symbols). Three specimens were tested in each case.
4.3 Stratification *versus* Emulsification

If one further (i.e. fourth) element is added to the static mixer, one arrives at more than 200'000 layers, which, combined with the PS:PUR 10:1 ratio, causes the PUR layers to become so thin that they begin disintegrating into rows of fine droplets (Figure 14). Such structures could be useful for impact-modified polymer systems. Of significant interest is the fact that the obtained morphology is realized in one simple processing route without the presence of large stresses (and, thus, large energy input), as is the standard in classical compounding (co-rotating twin screw extruders) operations.

**Figure 14.** *SEM images of the PS:PUR, ratio 10:1, system, nominally comprising a)–b) 17'280 continuous layers, c)–d) 207'360 layers, (higher magnification on the right). The thin PUR layers in the latter system disintegrated into lines of droplets.*

Next, the feed ratio was further reduced to PS:PUR 60:1 and, unsurprisingly, very small droplets on the order of 100 nm result after complete layer break-up (Figure 15). Different AFM imaging techniques (adhesion, modulus and phase) reveal the same, as can be seen in Figure 16.
Figure 15. PS:PUR, with (originally) 207’360 layers, flux ratio 60:1; after disintegration of the ultra-thin PUR layers into very small droplets (diameter ~100 nm): a) SEM, b) and c) AFM tapping mode, phase imaging. The continuous, near-horizontal “grooves” from left to right in b) and c) originate from cryo-microtoming.

Figure 16. Disintegrated layers of PS:PUR, 60:1, of Figure 15. Different AFM imaging techniques, a) adhesion, b) modulus and c) phase, confirm the disintegration of continuous ultra-thin PUR layers into aligned nanoscale droplets.
Finally, the PS:PUR 10:1 system with 1'440 layers was processed into continuous solid strands that were subsequently granulated. The granules were reprocessed via injection molding into tensile bars.

**Figure 17.** PS:PUR, flux ratio 10:1, with 1'440 layers, solidified, granulated and reprocessed via injection molding. **a)** Image of a tensile bar cross-section. Further images were taken at three different areas: **b)** Expanded view of the selected area (red rectangle in a). With the 1'440 layer system, the stratification survives the second processing step, forming a shell of layers around the core. **SEM images d)** and **f)** were taken from the shell region (indicated by S in a)). The core C in a) is shown at different magnifications in c) and e), revealing PUR droplets, as before.

The cross-section of such a tensile bar, Figure 17a, clearly shows two different areas. The core of the injection molded specimen exhibits, again, tiny PUR droplets, see Figure 17c and Figure 17e, but in a broad range, forming a “shell” of layers around the core; unexpectedly the stratification survives the second
processing step, see Figures 17 (b, d and f). The differences between the core and
the outer shell could be attributed to the differences in process history, specifically
both shear and temperature history. The remarkable result that the layers stay
intact potentially opens interesting routes to simplify existing, usually complex,
multi-layered, multi-material processes developed to produce high oxygen-,
carbon-dioxide- and water-barrier products. It remains to be investigated
whether different processing conditions (slower or faster, lower or at more
elevated temperatures, and molding into thinner products) would result in
conservation of layers throughout the entire cross-section. Nevertheless, the core-
shell injection-molded tensile specimens of PS:PUR (10:1 system with nominally
1'440 layers) already have interesting mechanical properties featuring
ductile-like behavior with a yield point at a strain of 1.5%, and a macroscopic
strain to break of 2.5%, compared to only that of 1.5% of neat injection molded PS,
\textit{i.e.} an improvement of 65%.

\section*{5 Conclusions}

In this chapter we presented a continuous one-step co-extrusion method to
produce films, plates and rods with stratified cross-sectional structures. For this
purpose, the recently-developed compact Peelincx mixer design characterized by
its parallel multiple cutting, rotating and stacking actions, was employed. Aiming
at more flexibility in the choice of polymers with respect to differences in viscosity,
we optimized this design by enhanced compensation for stagnant layers along the
die walls and for different flow lengths of the central streams. Finally, we added a
feed section that beneficially forces the polymers to enter the mixers in ten
alternating parallel layers.

The new setup was explored with a compatible system of amorphous PA:PA,
where the two components differ in color only, and an incompatible PS:PUR
system. Thin continuous layers could be successfully obtained with both systems.

The PS:PUR system, combining alternating i) “hard” and “brittle” and ii) “soft”
polymer layers, was investigated in more detail. Stratified structures with
nominally 1’440, 17’280 and 207’360 layers were fabricated with feed flux ratios
PS:PUR varying from 10:1 to 40:1 and 60:1. The strands of the 10:1 PS:PUR system with 1,440 layers were cooled, cut into granules and reprocessed by injection molding. Remarkably, and potentially very usefully, the initially created layer structure survived this second processing step. Strands of the system comprising 17,280 layers were produced to ultimately be machined into testing bars for notched 3-point bending and tensile testing. As expected, based on inspection on how Nature successfully uses combinations of alternating hard and ultrathin rubbery layers, the stratified systems showed a ~40% and ~100% increase in breaking energy in notched 3-point bending and notched tensile testing, respectively, compared with neat PS. Especially the fatigue properties of the material systems produced improved dramatically, illustrating the means by which Nature attempts to prevent catastrophic failure.

Finally, the very thin PUR layers of the systems comprising nominally 207,360 layers broke up to disintegrate into lines of very tiny drops in the PS matrix. This potentially offers a new energy-efficient route to advanced polymer systems of enhanced impact resistance.

In conclusion, the improved Peelincx static mixer, with a multi-layered feed entrance added, is not only the device with the lowest pressure drop of all existing static mixers, but also provides a reliable, simple and versatile method for obtaining multi-layer structures of two different polymers with controllable composition and layer thicknesses. Such structures are shown to exhibit properties superior to those of a single material, especially in fatigue loading.
Appendix

Definitions and Calculations of $a$, $J$ and $K_I$

The crack length $a$ was calculated from the compliance, with following expression:

$$\frac{a}{W} = 0.998 - 3.58U - 1.51U^2 + 110U^3 + 1231U^4 - 4400U^5$$  \hspace{1cm} (1)

where $W$ is the specimen width and $U$ is a fitting function, written as:

$$U = \frac{1}{\sqrt{FC + 1}}$$  \hspace{1cm} (2)

Here $C$ is the compliance of the specimen and $F$ is a calibration factor. $F$ is calculated from the three initial loading and unloading cycles.

The value of $J$ was derived from the applied load and instantaneous crack length according to ASTM E1820-08a and was split into its elastic and plastic contributions:[18,20,21]

$$J = J_{el} + J_{pl}$$  \hspace{1cm} (3)

with

$$J_{el} = \frac{K^2(1 - \nu^2)}{E}$$  \hspace{1cm} (4)

where $K$ is the mode I stress-intensity factor, $\nu$ the Poisson ratio with a value of 0.35 and $E$ is the Young's modulus. The plastic component of $J$ is:

$$J_{pl} = \frac{1.9A_{pl}}{Bb}$$  \hspace{1cm} (5)

$A_{pl}$ is the plastic area under force-displacement curve, $b$ is the uncracked ligament length ($= W-a$).

From the obtained $J$ values a $K_I$ value are calculated containing both elastic and inelastic contributions.

$$K_I = \sqrt{JE}$$  \hspace{1cm} (6)

Values of $E$ were taken from the 3-point bending measurements.
Chapter 5  Multi-Layered Structures

References


Chapter 6

Continuous Creation of Films with Complex Cross-Sections


1 Introduction

In Chapter 5 it was investigated how to create multi-layered structures containing thousands of continuous parallel layers using compatible and incompatible polymer pairs. In this chapter, those stratified structures are used as a starting point only, and the goal is to steadily increase structure complexity as expressed by the structure’s hierarchy. In this nomenclature, stratified structures, i.e. alternating layers of polymer A and B, have hierarchy level 0. Hierarchy level 1 is a structure with layers vertically oriented between two horizontal films, like bare tree trunks standing on a horizontal ground pointing towards the sky. Hierarchy level 2 adds to the tree trunks a multitude of horizontal branches. Hierarchy level 3 adds vertical side-branches to the horizontal branches, and so on and so forth.

For this purpose, modified static mixers are employed. Static mixers frequently used in the food- and process-technology industry are those of Kenics and Sulzer;\textsuperscript{[1−3]} interesting alternatives are the Ross\textsuperscript{[4]} and the Multiflux\textsuperscript{[5,6]} mixers, while downscaling to microfluidics has recently resulted in new geometries that can also be realized on small scales.\textsuperscript{[7−10]} One of the other most interesting designs is the so-called splitting serpentine mixer.\textsuperscript{[11−13]} All static mixers are based on the baker’s transformation of a repetitive stretching and folding operation (see Figure 1a) or a stretching, cutting and stacking operation (see Figure 1b).\textsuperscript{[14]}

![Figure 1. Fundamental working principle of static mixers, applying the baker’s transformation. Repetitive a) stretching and folding or b) stretching, cutting and stacking.](image)

The splitting serpentine is realized on the parting surfaces of a device, and the basic unit operator of an element reorients the interface from vertical to horizontal (or vice-versa) during an out-of-plane 90° left or right turn going from
the lower to the upper layer (or vice-versa), see Figure 2 (a, b). If, after flow splitting, the feed channel is half the height of the exit channel, interface rotation is accompanied by interface stretching by a factor of two, Figure 2 (c–e).

Figure 2. Rotating the interface when performing the 90° out-of-plane a) left or b) right turn. c) Magnification of the feed channels showing different vertical dimensions in the case of a)–b) (top) and d)–e) (bottom). Changing the dimensions of one of the channels (in this case, feed) combines left d) or right e) interface rotation with (factor of two) interface stretching.

Combining the two operators shown in Figure 2 (d, e), yields a single element of the splitting serpentine mixer in the original Chen geometry,[11] see Figure 3a. It is appreciated that splitting occurs directly after entering the element; hence, in this case the baker’s transformation of Figure 1a reads: cutting, rotating-stretching, stacking by folding.

Figure 3. Construction of the Chen (cf. ref. [11]) mixer, Figure 3c: Two stacked operators of Figure 2d and 2e, yield a left-right rotation and thus a mirroring Chen element \(M_v\): a) 3D illustration and top and side view. b) Adding a second element \(M_v\) gives c) the repeatable unit.

It is, moreover, recognized that reorientation and stretching of the interface only occurs in an out-of-plane turn, like in the top flow that turns 90° left upwards directly after splitting. An in-plane turn only redirects the interface, as shown in Figure 3b where the top flow makes a right turn after stretching,
maintaining the horizontal position of the interface, and by the bottom flow that first goes left around the corner, keeping the interface vertical, to be followed by a 90° right upwards turn where interface reorientation and stretching takes place simultaneously with the stacking operation. By the left interface rotation of the upper flow, combined with the right interface rotation of the bottom flow, the first element of the Chen mixer mirrors the incoming structure. Furthermore, it cuts the inflowing, original vertical, interface in a horizontal plane. Therefore this element is indicated with the symbol $M_h$. Accordingly, the second element of the Chen mixer is indicated as $M_v$, since it cuts the incoming, horizontal, interface in a vertical plane, and combines after splitting a right-left interface rotation such that again mirroring of the incoming structure results (see the Appendix for mirroring operations).

Mirroring causes two incoming layers to increase to three layers, while three increase to five. With a middle layer that folds onto itself and therefore becomes thicker than the other layers, the Chen mixer results in an unequal layer thickness distribution with 2, 5, 17, 65 and 257 layers, and so on (see Figure 5a). Therefore alternative geometries were investigated. The key proved to be a change in rotation direction of the interface to result in either left-left or right-right turns,[15] see Figure 4. These elements perform the cutting-stacking operation of Figure 1b, rather than the folding operation of Figure 1a, making increasingly uniform layers. Depending on the plane of cutting of the interfaces, the elements are indicated with the symbol $L_h$ or $L_v$, where $L$ stands for layering (see the Appendix for layering operations).

Figure 4. Construction of the Dentincx (cf. ref. [15]) mixer, Figure 4c: Two operators are stacked to make the interfaces turn left-left to arrive at the layering Dentincx element $L_h$: a) 3D illustration, top and side view. b) Adding a second element $L_v$ that turns the interfaces again left-left gives c) the repeatable unit.
Numerical computations using the mapping method\cite{16,17} were applied to explore these ideas and to evaluate mixer performance in terms of homogeneity of the layer distribution. Figure 5a illustrates that the mirroring stretching-folding operation (Figure 1a) of the original Chen geometry not only gives a factor of two less layers but, more importantly, yields layers of principally unequal thickness. This problem is solved by applying the layering stretching-cutting-stacking operation, see Figure 1b, of the improved Dentincx geometry, yielding homogeneous layers that increase in number as 2, 8, 32, 128, 512, etcetera, see Figure 5b.

![Figure 5](image.png)

**Figure 5.** Mapping method (cf. ref. \cite{16,17}) results of computing the number and thickness of layers after 1-4 repeating mixing units in a) the original Chen mixer geometry and b) the Dentincx mixer geometry.

Splitting serpentine mixers have been used with Chen and Dentincx geometries in a number of applications in microfluidics, as well as in macroscopic processes like discontinuous injection molding. Here we will investigate their use in a continuous extrusion process, gradually increasing the complexity of the structures aimed at. The Dentincx elements are applied to make the layers, the Chen elements to mirror structures. Both elements are realized on the parting surfaces of two die-halves. They are easy to manufacture, and can be scaled up or down in a straightforward manner, eventually to sub-micron size. In our application, simple rectangular plates were prepared perforated with laser-cut – also rectangular – holes. Two plates make up the
Chapter 6  
Complex Cross-Sections

geometry of an element, one – the upper part, the other – the bottom part. Staggered and mounted in a U-shaped housing (covered with a bolted top plate) they can be combined to almost any 3D internal geometry, provided that there are not too many concerns about rounding corners. After start-up, the flow becomes stationary and the corners get filled with stagnant layers that create a smooth natural flow channel for the incoming fluid. As long as the experiments do not last for extended periods of time, degradation of a polymer remaining in the corners is not an issue.

In the present design the first die element consists of two parallel rows that each contain three Dentincx elements, where each element comprises two layering actions $L_h$ and $L_v$, see Figure 4; therefore layering in each row is indicated with $6L$. A valve at the end of the rows controls the flow direction such that experiments can be performed using either one row of elements, $6L$, or both, $12L$. For flexibility in the choice of polymers, a multi-layer forced feed of, in this case, eight parallel layers is added, indicated with $F_8$. Consequently, the number of layers exiting the layering section is either about 500 or 30'000 (to be nominally precise: $8 \times 2^6 = 512$ or $8 \times 2^{12} = 32'768$, respectively).

In all experiments in this chapter, only 512 layers are produced: $F_8 \cdot 6L$. The die section that follows this $F_8 \cdot 6L$ feed was varied. Different number of mirroring elements are combined with different numbers of addition and, if required, rotation elements, to arrive at structures of different hierarchy.

2 Experimental Section

Materials. Polystyrene (PS) 124N (Styrolution, Germany), neat as delivered and filled with 0.1% w/w carbon black, as well as an amorphous polyamide (PA) Grivory® G16 (EMS-Chemie AG, Switzerland), neat as delivered and colored with 0.2% w/w copper dye, were used. Polymers were dried in a vacuum oven at temperatures prescribed by the producers (PS: 60 °C and PA: 120 °C) for at least 24 hrs prior to processing.
Extrusion. Two single-screw extruders (Teach-Line® E20T SCD15, Collin, Germany) with a barrel diameter of 20 mm were employed. Extrusion of PS was performed at 200 °C whereas PA was processed at 270 °C. The pressure of both extruders was carefully maintained at 20–30 bar and, in order to control and vary both melt streams, melt pumps (Zenith® BB PEP, Colfax® fluid handling, USA) were arranged between the extruders and the die. Extrudates were collected without external calibration and quenched in a cylinder filled with water. As a consequence some inhomogeneous swelling inevitably occurred, distorting the cross-section.

Optical Microscopy. For ease of preparation and handling, samples for optical microscopy were embedded using a two-component epoxy resin (resin type HT2, R&G Faserverbundwerkstoffe GmbH, Germany). After curing for 24 hrs at room temperature, the embedded samples were machined and polished to plates of 0.5 mm thickness. Images were taken using a Leica DMRX polarizing microscope equipped with a Leica DFC 480 camera (Leica, Switzerland).

3 Results and Discussion

3.1 Hierarchy Level 1: Layers Perpendicular to the Surface

First a structure with a stack of layers of clear and dyed amorphous PA oriented perpendicular-to-the-surface is realized. The horizontally oriented stratified layer stack exiting $F_8$-$6L$, comprising 512 layers (Figure 6), is subsequently stretched in width, cut into four streams that are each individually rotated using the elements shown in Figure 2a, and subsequently recombined. Extra channels run from the two polymer feeds on the left, via sub-structure channels, to four individual control valves, see Figure 7. By opening the valves, addition of layers on strategic positions can be realized. The first two valves add onto the two sides of the multi-layered structure just after its completion. [N.B. These are not used in the experiments described in this section.] The last two valves open channels that flow above and below the rotated, recombined structure to add layers from the top and bottom. It should be noted that in our flexible laboratory setup all different melt channels, and thus melt flows, act in
parallel and, since the route of the least resistance is, of course, preferred, some careful, iterative control of valve positions is required while conducting the experiments.

Figure 6. Structured amorphous PA, transparent and blue-dyed, exiting the $F_{8-6L}$ configuration of the static mixer, comprising 512 near-horizontal layers.

Figure 8 illustrates the working principle of the die that, in the end, produces a structure with either around 2'000 or 120'000 layers perpendicular to the surface, supported by a bottom layer and protected by a top layer (“ground” and “sky”, respectively). The simplest co-continuous structure with an enormous interface is the result. If required, more supporting layers can be added at the bottom, and protection layers can be added onto the top. The structure can be subsequently stretched in the machine direction, without destroying the perpendicular layer orientation, virtually to any thinness desired.
Figure 7. The layering, flow-widening, -cutting and -rotating die elements: a) 3D overview; b) 3D, c) side and d) top view of the internal channel structure. In all cases at the left hand side of the die, the forced multi-layer eight parallel channel feed $F_8$, followed by two rows each containing three Dentinx elements and a control valve to allow producing either 512 or 32'768 layers. Here, only one row was used 6L. On its right hand side the flow is spread in the width direction, cut into four parallel channels, rotated over 90° and recombined. Additional polymer A and B layers can be applied onto each side after the layering section, and on top and/or bottom after the flow splitting, rotating and recombining section. Individual valves, as indicated, control these “addition” flows. Arrows indicate the flow directions.

Figure 8. Schematic of the working principle of the perpendicular-to-the-surface layering die. a) Black and white “colored” polymers are fed into the eight parallel forced feed to enter the layering section and produce ~500 or ~30'000 horizontal layers. b) Next, the layers are horizontally stretched, prior to be cut in four, rotated, recombined, and fitted with a white top and black bottom layer c).

A first example is shown in Figure 9, where simple manual melt-stretching of these structures already yield ultra-thin tapes. No haul-off equipment was used and, consequently, the width of the samples also reduces during stretching.
Figure 9. Samples of structured PS extrudates without and with application of manual melt-stretching. a) Cross-section of an unstretched sample and b) melt-stretched samples.

Figure 10 shows a cross-section of a non-calibrated rectangular extrudate after it vertically exited the mixer directly into a cooling water bath. The discontinuity seen in Figure 10c originates from a flaw in the process of cutting into four parallel channels that are recombined after rotation (dashed lines).

Figure 10. a) Images of an actual cross-section of structured transparent and blue-dyed amorphous PA, hierarchy level 1. The extrudate features small top and bottom layers and ~2'000 vertical layers. Details of layers b) and transition between layers and sky c).
3.2 Hierarchy Level 2: Multiple Tree Structures

The next goal is to create structures with stacked horizontal layers, vertically connected in a discrete number of positions to the bottom and top layers in order to create co-continuity. In essence, these structures consist of a row of parallel trees with their “trunks on the ground” and their leaflets directly connected to the trunks. This is a structure of hierarchy level 2. Increasing hierarchy requires the multiplication of structures rather than layers. Multiplication follows the cutting-rotating-recombination protocol. Symmetry is used, and the mirroring Chen elements are applied. The main question in structure-, rather than layer-, multiplication is: where is the line of symmetry in the structure, and where can the flow be cut in the middle?

The answer is that for every increase in the level of hierarchy, side layers need to be added. These layers have a vertical orientation (since they are added from the sides only) and they can be cut in the middle. For addition $A$ on both sides, an addition element is required (Figure 11a) while for structure rotation $R$ with the entrance and exit located on the same plane a rotation element is designed, see Figure 11b.

![Figure 11. a) Addition A and b) structure rotation R elements.](image)

Combined with the mirroring operators of Figure 3 and the layering operators of Figure 4, all tools to create complex structures in the cross-section of extrudates are available. In parallel-tree creation, we start again with the $F_8-6L$ as used in the previous section (Figure 6) that yields 512 horizontal layers.
Figure 12. Die for parallel-tree creating geometry: a) 3D overview; b) 3D and c) top view of the internal channel structure. On the left side of the device, as before, the forced multi-layer eight parallel channel feed, $F_8$, followed by two rows each containing three Dentinx elements, $2 \times 6L$, and a control valve to allow producing either 512 or 32’768 layers. Here, only one row was used: 6L. On the right two side layers are added; thereafter the flow is repeatedly cut and mirrored using two Chen elements, each with two mirroring operators $M_h$ and $M_v$, thus in total $4M$. Finally, the flow is extended in width, and top and bottom layers are added. Arrows indicate direction of flow.

The right hand side of the die in Figure 12c, which is the tree-making part, is different from that in the previous section where the target was layering perpendicular to the surface. Four cutting and mirroring operations are performed using two Chen elements. The first cut is perpendicular to the two side layers added perpendicular to the stratified system. Figure 13 illustrates the working principle. The first cut in Figure 13b occurs in the horizontal plane, followed by mirroring via counter-rotation of the two halves and recombining, $M_h$. The second cut takes place in the vertical plane, mirroring follows, $M_v$; the third cut is horizontal $M_h$, the fourth again in the vertical plane, $M_v$. After the mirroring operation, eight parallel trees result. They can be stretched in the horizontal direction and a top and bottom layer can be added, see Figure 13c.
Figure 13. Schematic working principle of the parallel tree-making die. **a)** Black- and white-dyed polymers are fed into the eight parallel forced feed to enter the layering section and produce either 512 or 32768 horizontal layers. **b)** Two side layers are added, and the structure is four times cut into two halves that are mirrored to result in eight parallel trees with either ~30 or ~2'000 leaflets on each side. **c)** Upon exiting, top and bottom layers are applied to the structure.

First experimental results are shown in Figure 14. As before, the employed materials are blue-dyed and transparent neat amorphous PA. Obviously, the orientation of the leaflets is not horizontal, neither are the trunks perfectly vertical. This is due to structure compression perpendicular to layer directions. Once a subsequent cross-stretching in the final film production is applied, the leaflets will turn horizontal again. The trunks will, of course, not stay vertical, though this is of secondary importance since their primary function is to provide connectivity.

Figure 14. **a)** Creating layers comprising eight trees with leaflets; hierarchy level 2. The connecting ground and top layers are not shown. The materials used are neat, transparent and blue-dyed amorphous PA. Details of **b)** branches and **c)** connection between branches and trunk.
3.3 Higher Hierarchy: Fractal Structuring

Finally, we investigate how to create co-continuous fractal structures, i.e. trees of high hierarchy. The necessary die is built with five distinct sections that can be combined in (almost) any sequence. The most extended one used is shown in Figure 15. It has four places where four side additions are applied, therefore yielding a tree with hierarchy level 5. After the $F_8-6L$, as already used in the experiments described in the previous two sections of this chapter and that yields 512 horizontal layers, we mount first a $4M-R$ element. After addition $A_1$ from the two sides, this element cuts and mirrors the structure four times. Thus far, this is exactly the same die configuration as used in the previous section to produce eight parallel trees. The principal difference is that it now ends with a structure rotation element $R$, see Figure 11b, to prepare for the following addition that marks the next step in hierarchy. [N.B. Apart from the last addition that is performed from the bottom and the top of the final film, additions $A_1$ to $A_4$ always occur from the sides. Therefore, if the number of mirroring steps is even, rotation is required; if it is odd, no rotation is needed, see also Figure 15.]

![Figure 15. The die required to create a tree of hierarchy level 5: (a) 3D overview; (b) 3D and (c) side and (d) top view of the internal channel structure. Arrows indicate flow directions.](image-url)
The next element is a $3M$ that, after the addition $A_2$, cuts and mirrors the structure three times. This followed by a $2M-R$ element (cutting and mirroring twice after addition $A_3$ and before rotation $R$) and finally $M$ that mirrors once more after $A_4$. To end the process, top and bottom layers are applied. The construction thus comprises the forced feed $F_8$, the layering elements $L_h$ and $L_v$, Figure 4, the mirroring elements $M_h$ and $M_v$, Figure 3, and the addition and rotation elements $R$ and $A$, Figure 11. The total sequence of the die in Figure 15 reads in detail:

<table>
<thead>
<tr>
<th>Feed</th>
<th>Layering</th>
<th>Mirroring 1</th>
<th>Mirroring 2</th>
<th>Mirroring 3</th>
<th>Mirroring 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_8$</td>
<td>$6L-A_1$</td>
<td>$4M-R-A_2$</td>
<td>$3M-A_3$</td>
<td>$2M-R-A_4$</td>
<td>$M-A_5$</td>
</tr>
</tbody>
</table>

The developing structure is shown in Figure 16. Figures 16 a)–i) show what happens inside the first element $4M-R-A_2$; Figures 16 j)–m) illustrate the same for the second element $3M-A_3$; Figures 16 n)–q) for the third one $2M-R-A_4$, and Figures 16 r)–t) for the last element $M-A_5$. Between elements, addition takes place to enable an increase in the level of hierarchy and to introduce symmetry back into the system.
Figure 16. Visualization of the structure development during flow in the die shown in Figure 15. The polymer used is PS (transparent and filled with 0.1% w/w carbon black). a), c), e)–h), j)–l), n)–p), r) and s) schematically show the development of cross-sections along the die; b), d), i), m), q), and t) show micrographs of actual samples (cross-section dimensions are 4.6 × 4.6 mm²). The final result in t) is a tree with hierarchy level 5.

Figures 17–20 show, in selected cross-sections, the details of the structures obtained and reveal some of the points of interest discussed in the legends.
Figure 17. Experimental results of structure formation at selected positions along the die. The presented result shows the hierarchy level 1 layering process after addition of the side layers perpendicular to the stratification; compare Figures 6, 10 and 16b. Sample overview in real a) and schematic f). Enlargements at different positions are shown in b)–e). Distinct layers are present everywhere in the cross-section, c), but layer uniformity is, however, not perfect everywhere, e). Contact between stratification and added side layers is satisfactory, d), or somewhat unclear, b), probably due to the non-perfectly orthogonal sample-cut direction relative to that of the flow throughout the entire sample.
Figure 18. Experimental results of structure formation at selected positions along the die. The presented result shows the hierarchy level 2 process of the formation of eight parallel trees; compare Figures 14 and 16i. Sample overview in real a) and schematic f). Enlargements at different positions are shown in b)–e). The orientation of the leaflets looks more parallel than perpendicular, probably due to the compression of the layer stacks, but stretching of the film in the “width” direction is expected to ameliorate the problem. b), c) and e) show the presence of remaining distinct layers.
Figure 19. Experimental results of structure formation at selected positions along the die. The presented result shows the hierarchy level 3 process of the creation of four trees with trunks, branches and leaflets; compare with Figure 16m. Sample overview in real a) and schematic f). Enlargements at different positions are shown in b)–e). The structure becomes somewhat ill-defined due to deformation occurring during local structure compression. b)–e) show that layers are still present nonetheless.
Figure 20. Experimental results of structure formation at selected positions along the die. The presented result shows the hierarchy level 4 process of the creation of two trees with trunks, branches, side branches and leaflets; compare with Figure 16q. Sample overview in real a) and schematic f). Enlargements at different positions are shown in b)–e).
4 Summary and Conclusions

In this chapter we attempted to produce in a continuous one-step co-extrusion process films, plates and rods with unique, complex cross-sectional structures. We chose as tools the static mixer elements of the splitting serpentine geometry. They are easily made on the parting surfaces of two mold or die-halves on basically any scale, ranging from macro-mixers to microfluidics. The steady development of splitting serpentine mixers is presented, starting with the original Chen design that mirrors structures, to the improved Dentincx design that stacks structures.

Polymeric material structures are realized with a systematic increase in complexity, characterized by their hierarchy. Adopting the notion of a ground and a sky, i.e. the bottom and top layers generally added at the end of the extrusion process, the structures in between resemble trees. If only bare trunks are formed vertically from the ground to the sky, we have hierarchy level 1. If the vertical trunks are decorated with horizontal leaflets, hierarchy level 2 is reached. Hierarchy level 3 is the structure with vertical trunks connected to horizontal branches covered with leaflets. Side branches on the branches increases the level to 4, side-side branches on side-branches to 5, etcetera.

Hierarchy levels higher than 1 require structure-, rather than layer-, multiplication. The exponential baker’s transformation needs a main orientation direction which allows symmetrical cutting of the flow prior to interface rotation, stretching, and recombining, that is achieved by providing additional side layers. Flow cutting continues in the mid-plane perpendicular to the added layers. Every hierarchy level therefore requires a further addition.

In our experimental die, all layer additions are controlled by valves provided from the sides. Therefore, sometimes structure rotation R is required, prior to addition A. A static mixing element following an addition A is always a $M_h$ element that mirrors the vertical interface after cutting in the horizontal plane.

To realize hierarchy level 2 structures, the same die is used as for hierarchy level 1: A multi-layer feed connects to a series of Dentincx elements that yield the layers, $F_8-6L$ or $F_8-12L$. After addition A of two side layers, perpendicular to the
(horizontal) orientation of the stratified structure, two Chen elements with $4M$ operators follow that cut, mirror and recombine the structure to result in eight parallel simple trees. Once top and bottom layers are added, the trees connect to the “ground” and are directed to the “sky”. They feature either about ~30 or ~2'000 leaflets on each side of their trunks, again depending on the position of the return valve. Also this co-continuous structure can, if required, be biaxially stretched at a high rate in the machine- and perpendicular direction to virtually any thinness. The leaflets, that lost their orientation during compression of layer stacks in the production of the structure, will then turn horizontal again. The trunks will lose their largely vertical orientation, but keep their principal function in connecting leaflets to the ground and the sky.

Finally, high-hierarchy structures are investigated. Starting with the die-system used for hierarchy level 2 parallel tree structures, a series of new Chen elements is added. For the simplest hierarchy level 5 tree, with only one side-branch on each branch, we need after the $F_8$-$6L$-$4M$ tree-making section to add $3M$, $2M$, and $M$ sections with additions $A$ in between and rotations $R$ if required. The complete die thus contains a sequence of the following elements:

$$F_8 + Lh Lh Lh Lh Lh A_1 + M_h M_v M_h M_v R A_2 + M_h M_v M_h A_3 + M_h M_v R A_4 + M_h A_5.$$  

Initial experiments show that a hierarchy level 5 tree structure can indeed be created and that interesting morphologies are obtained. However, full control over the horizontal and vertical orientation of the (sub-)branches is lost, due to severe compression of the structures during the fabrication process – an issue that could and should be addressed in future studies.
Appendix

Layering Operations

Layer producing operator $L_h$ co-rotates and compresses after a horizontal cut, see Figure A1.

![Figure A1. Horizontal co-rotation: i) a square is divided horizontally into two halves; ii) both parts are co-rotated by 90°; iii) the obtained structure is compressed back to unit square.](image)

The operator $L_v$ that expresses a co-rotation and compression after a vertical cut, see Figure A2.

![Figure A2. Vertical co-rotation: i) a square is divided vertically into two halves; ii) both parts are co-rotated by 90°; iii) the obtained structure is compressed back to unit square.](image)
Mirroring Operations

Mirroring operator $M_h$ with counter-rotation and compression after a horizontal cut, see Figure A3.

**Figure A3.** Horizontal counter-rotation: i) a square is divided horizontally into two halves; ii) both parts are counter-rotated by 90°; iii) the obtained structure is compressed back to unit square.

Mirroring operator $M_v$ with counter-rotation and compression after a vertical cut, see Figure A4.

**Figure A4.** Vertical counter-rotation: i) a square is divided vertically into two halves; ii) both parts are counter-rotated by 90°; iii) the obtained structure is compressed back to unit square.
References


Chapter 7

Conclusions and Outlook
1 Conclusions

The aim of this thesis was to develop and apply new processing methods for the creation of polymer systems exhibiting favorable mechanical properties by achieving macromolecular orientation or, exhibiting potentially interesting new properties by directing the internal polymer arrangement in complex structures. The results presented are divided into three sections: A) uniaxially oriented, B) biaxially oriented and C) triaxially arranged polymeric materials; graphically summarized in Figure 1.

![Figure 1. Summary of Creating Complex Polymer Systems.](image)

Although, nowadays, some people claim that “Polymer technology is finished” the work presented in this thesis proves that there is still vast room for optimization, improvement and innovation – even for supposedly well-understood processes and techniques.
2 Outlook

Recommendations Related to Part A

1. In Chapter 2, processing uniaxially oriented polymer systems is addressed with emphasis on ultra-high molecular weight polyethylene (UHMW PE). The use of poor solvents for this polymer – using the same polymer concentration – was shown to either yield a major improvement in mechanical properties of the final, drawn product, or allows – for achieving the same properties – to enhance the processing efficiency by up to twice that of conventionally processed material from good solvents. The improvement remains not completely understood and, as such, based on our findings a systematic investigation into the role of the solvent is recommended by i) selection of fatty acid solvents of varying chain length, ii) exploring the impact of alcohol chain length in decalin-alcohol mixtures and iii) investigating the effect of degree of saturation of triglycerides from natural oils.

2. Crystallization at lower undercoolings of UHMW PE from bad solvents suggests an intimate interaction between the polymer chains and small molecular solvent molecules. The crystalline lamellae seem to be uniquely tailored by the specific solvent employed. Measurable changes in mechanical properties result when the polymer is processed – at the same solution concentration – from different solvents. We believe that a direct relation exists between solvent quality and the lamellar thickness of the crystal, and the resulting drawability that dictates the ultimate mechanical properties. This could be further studied using differential scanning calorimetry (DSC) as an indicator of solvent quality, in combination with such techniques as small-angle and wide-angle X-ray scattering, (SAXS) and (WAXD), to provide information on lamellar thickness, width, and perhaps unit cell dimensions.

3. In addition, it is possible that more advanced rheological measurements could be employed to determine the entanglement densities of the polymer chains, which is relevant considering the inverse dependence of drawability on the –0.7 power of the polymer volume fraction in solution in different solvents.

4. In Chapter 3, liquid-crystalline polymer films were investigated with the goal to develop monolithic structures. Due to weak internal coherence of the material
Chapter 7

Conclusions and Outlook

itself, these were found to be unsuitable for use as traditional composite materials, failing rapidly under compressional and shear loading; although exhibiting good high specific tensile and damping properties. In principle there are two main strategies to hamper coherent failure. The first is chemical modification of the polymeric chain, wherein the co-monomer’s chemical identity strongly influences the internal coherence. However, it should be taken into consideration that whilst it is possible to select a co-monomer such that there is increased resistance against coherent failure in the material, this is often accompanied by a significant reduction in its mechanical performance.

5. A second option involves the use of an alternative processing route that makes use of the unique capability of the LCP tape making die. When two polymers streams are fed into the feed block of the die, for instance 50% LCP and 50% of an adhesive, they will form alternating bands over the width of the tape. If the feed ratio is reduced to 95% LCP and 5% adhesive, then every twentieth fiber in the tape is a continuous glue “fiber”.

Recommendations Related to Part B

6. In Chapter 4, an alternative method employing a V-shaped heated mandrel for continuous, simultaneous biaxial drawing of polymers was introduced. The importance of friction between the mandrel and deforming polymer was underestimated at the beginning of investigation, and to produce films with balanced properties an optimum combination of friction and wedge angle of the heated mandrel was required. A desirable process would eliminate friction as a variable in the stretching history and consequently in the properties of the final product.

7. Biaxially oriented films of i-PP containing up to 40% w/w micrometer-sized alumina platelets, were produced and stretching of the composite precursor tube was still possible at these concentrations. Higher platelet concentrations may yet be possible. Further, adhesion between platelets and the polymer matrix should be addressed.
Recommendations Related to Part C

8. In Chapter 5, the creation of alternating multi-layers of two different polymers has been investigated using a recently designed static mixer that allows combining polymers with different viscosities. Using a 10-layer feed section followed by four parallel flow cutting, rotating and recombining elements, systems consisting of up to 200'000 layers could be produced. Feeding PS:PUR in a 60:1 ratio caused disintegration and break up of thin layers of the PUR in to droplets. Remarkably, they improved the fracture toughness of the PS matrix. There is still an opportunity for increasing the number of mixing elements further to investigate whether even finer droplets result, more closely spaced in the matrix. Potentially yielding even tougher PS, or other brittle polymeric materials for that matter.

9. New multi-layer experiments could be aiming at creating nanofoams. Alternating layers of two polymers, one containing a chemical blowing agent, like sodium bicarbonate, could be fabricated. Nanofoams are of considerable interest due to their combination of low mass with good mechanical bulk properties and have potential even in bulk applications such as concrete fillers.

10. Chapter 6 details the application of the static mixer technique to the formation of complex hierarchically ordered structures. Further process improvements can be envisioned:

   i) If enhanced contact between stacks of layers and added side feeds is required, with less influence of stagnant layers close to walls, side feeds could be introduced via slits from below or from above the flow channel of the stratified structure, at a slight distance from the side walls.

   ii) From the results obtained in this work it seems that for non-Newtonian fluids a series of mirroring Chen elements yields less optimal interface rotation compared to a series of layering Dentinx elements. Geometry optimization to improve upon this aspect in an efficient way could be based on non-Newtonian flow analyses using the Mapping Method, and less on trial and error. Parameters to be optimized are the distance between successive rotation elements and the angle of their turn.
iii) An interesting alternative could be to use Chen elements only if required, thus using after each addition only one such element and replacing the next ones by Dentinex elements. For the hierarchy level 5 systems the layout would be:

\[ F_8 + L_h L_v L_h L_v A_1 + M_h L_v L_v R A_2 + M_h L_v L_h A_3 + M_h L_v R A_4 + M A_5. \]

11. To realize hierarchy level 1 structures, a layering die is used with a multi-layer feed system \( F_8 \) connected to a series of Dentinex elements that result in \( 6L \) or \( 12L \) operations that first make the layers. The stratified flow is extended in width, cut, rotated, and recombined. Top and bottom layers are added. In the resulting structure about \( \sim 2'000 \) or \( \sim 120'000 \) layers (depending on the position of the return valve) connect perpendicularly the top and bottom layers. The structure is co-continuous and can, if required, be stretched at high rate in the machine direction to basically any thinness. If no top layer is applied, and if one of the vertical layers is dissolved, soft-touch surface layer structures will result. These layer structures could, if desired, be modified into rod structures: truly “hairy” surfaces therefore could principally be made – an area of research worthwhile exploring.

12. More challenging is trying to truly mimic Nature and produce structures with an infinite stack of thin platelets oriented perpendicular to the surface of an object, separated by thin soft layers, and covering a similar structure underneath with parallel to the surface orientation of the same. Since in extrusion the volume fraction of fillers remains limited, \( in-situ \) platelet making could be considered. Embedding platelets and thin soft layers in POSS (polyoctahedral silsesquioxane) or water glass (sodium silicate) that is polymerized after shaping and processing, could be an interesting new route to indeed realize nacre-, shell- and teeth-type of structures.

All these issues are challenging and potentially rewarding; however they were beyond the scope of this thesis.
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Curriculum Vitae

The author of this thesis was born on the 2nd of February 1983 in Fribourg, Switzerland. After finishing school in 1998, he began a four-year apprenticeship as a technician in synthetic materials at SIKA AG in Düdingen. Following that and serving in the Swiss army as a medic, he started to work as a group leader in the field of injection molding of high-performance polymers at Saia-Burgess AG (now Johnson Electrics) in Murten. During this period he also received the Eidgenössische Maturität. In September 2007, he began his undergraduate studies in Materials Science at the Swiss Federal Institute of Technology Zurich (Eidgenössische Technische Hochschule, ETH Zürich), graduating with a Master’s degree in September 2012 with a focus in Materials Creation and Materials Properties and Analysis. During his studies he also worked as prototype designer at Mammut Sports Group in Seon. His Master’s thesis was carried out in the research group of Prof. Ton Peijs at Queen Mary University, London, in the field of self-reinforced polymers. In October 2012, he commenced his doctoral studies, described in this thesis, in the Department of Materials of ETH Zürich under the supervision of Prof. Paul Smith and Prof. Theo A. Tervoort, and additionally advised by Prof. Han E. H. Meijer of the Technical University Eindhoven, The Netherlands.