



The effect of processing conditions on the mechanical properties and thermal stability of highly oriented PP tapes

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ARTICLE INFO

Article history:

Received 10 February 2009

Received in revised form 12 May 2009

Accepted 26 June 2009

Available online 3 July 2009

Keywords:

Orientation

Fibres

Composites

Drawing

Self-reinforced

ABSTRACT

It has previously been shown possible to use highly oriented polypropylene (PP) tapes to create self-reinforced (all-PP) composites. It is desirable to understand the relationship between tape processing parameters and the mechanical properties and thermal stability of the tapes, as these tape properties will govern the ultimate properties of the all-PP composite. In this paper, the effects of the tape drawing parameters such as draw ratio (λ), drawing temperature and thermal annealing on the final mechanical properties, density and dimensional thermal stability of the tapes are presented. PP tapes drawn to $\lambda = 17$ possess tensile moduli of ~ 15 GPa and tensile strengths of ~ 450 MPa. PP tapes with high draw ratios, $\lambda > 9.3$, show a decrease in density, a change from transparent to opaque appearance and increased dimensional thermal stability with increasing draw ratio. The results of an investigation into the effects of a thermal annealing step, targeted at improving the dimensional thermal stability of these highly oriented PP tapes, are also presented.

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1. Introduction

Entirely thermoplastic, “self-reinforced” polymer composites have been presented in literature as potential alternative materials to conventional polymer composites. A range of technologies have been presented in literature to develop single polymer composites from various thermoplastic polymers, such as polyethylene [1–7], polypropylene [8–20], poly(ethylene terephthalate) [21–23], poly(ethylene naphthalate) [24], polyamide [25], poly(methyl methacrylate) [26–30] and liquid crystal polymers [31,32]. The basic precursor to create a single polymer composite with good mechanical properties is a high mechanical performance polymer fibre or tape, as these will act as the reinforcement phase in the final composite. Therefore, it is key to the success of such a composite that the mechanical properties of the precursor fibre or tape should be optimised.

Previous publications by the same authors have described the development of self-reinforced (SRPP) or all-polypropylene (all-PP) composites [33–40], now commercialised by Lankhorst Pure Composites BV under the name PURE[®] and its licensee Milliken under the name Tegriss[®], comprising highly drawn PP tapes which are consolidated together to form a load bearing structure. This paper will focus specifically on the characterisation of highly oriented PP tapes for the creation of the all-PP composites described in these previous publications.

The mechanical performance of polypropylene fibres or tapes can be increased by orienting the polymer molecules in the loaded axis [41]. This can be achieved by solid state deformation below the melting temperature, but above the glass transition temperature of the polymer [42]. Solid state deformation of PP can be achieved in numerous ways, such as roll drawing sheets [43–46], die drawing [47–49], zone drawing [50], or by drawing through a hot oven [51], and the deformation parameters applied during orientation closely affect the resulting mechanical and morphological properties. As an example, roll drawn

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isotactic PP sheets have been reported with a tensile modulus of 20 GPa and a tensile strength of 500 MPa in the drawing direction [52], compared with isotropic polypropylene sheets which will typically have a tensile modulus and tensile strength of <2 GPa and <50 MPa [53].

It is well understood that highly oriented thermoplastic polymers will tend to increase entropy if given enough thermal energy to allow molecular mobility or relaxation. The practical aspect of this effect is that if sufficiently heated, highly oriented polymers will tend to shrink in the drawn direction, as the molecules seek to achieve a more random orientation. Since the high mechanical properties of these tapes are a direct consequence of molecular orientation, this shrinkage is associated with a decrease in mechanical properties in the drawn direction. As all of the processing routes to create all-PP composites involve heating the PP tapes to temperatures typically exceeding 130 °C [54] to facilitate intertape bonding, it is important to understand the possible effect of this heating on the mechanical properties of the tapes.

Therefore, the goals of this paper are to investigate the relationship between tape processing conditions and characteristics of the drawn tape, in order to understand the ways in which these properties may affect subsequent all-PP composites. The paper presents the effects of draw ratio, λ , and draw temperature on the tensile mechanical properties and density of PP tapes, and the relationship between tape draw ratio, thermal shrinkage and the associated loss of mechanical properties during exposure to elevated temperatures. It is particularly important to understand how the tapes behave when exposed to elevated temperatures, as elevated temperatures will be experienced during consolidation of the tapes into an all-PP composite structure.

2. Manufacture of PP tapes and all-PP composites

One of the simplest commercial routes for the production of PP fibres (or tapes) is by drawing an extruded fibre (or tape) through a hot oven [55], and this is the route used to create the highly oriented PP tapes presented in this paper. Tensile deformation (drawing) is achieved by pulling a tape from one set of rollers, rotating at a speed v_1 , through a hot air oven to a second set of rollers, rotating at speed v_2 , where $v_2 > v_1$. The ratio of $v_2:v_1$ defines the draw ratio, λ , applied to the tapes in each drawing stage. If necessary, this drawing stage can be repeated in numerous ovens in series, with each drawing stage adding an increase in draw ratio, until the desired total draw ratio is achieved.

This multistage drawing process has been previously reported to achieve high strength PP structures by drawing first at a lower temperature to realize the desired morphology to achieve further drawing in a subsequent drawing step at a higher temperature [56,57]. The production of the PP tapes described here was performed in a two stage drawing process as shown in Fig. 1, with applied draw ratios at oven temperatures as described in Table 1; the overall draw ratio, λ , is the product of the draw ratios λ_1 and λ_2 applied in the first and second drawing stages, respectively [58,59]. The tapes described in this paper are classified in two series; Series A describes PP tapes drawn to varying

draw ratios at the same drawing temperatures, while Series B describes PP tapes drawn to $\lambda = 13$ at a range of drawing temperatures in the second drawing stage. The temperature used in the first drawing stage is constant throughout this paper. Tapes are drawn up to $\lambda = 6$ in the first drawing stage, and are further drawn in a second drawing stage to achieve higher draw ratios. Tapes A1, A2 and A3 are drawn in a single stage process to $\lambda = 2, 4$ and 6, respectively, and experience neither a second drawing stage nor exposure to an elevated temperature in the second oven. Tapes A4, A5, A6 and A7 are drawn in a double stage drawing process, first to $\lambda_1 = 6$ in the first drawing stage and then to a total $\lambda = 9.3, 12, 14$ and 17, respectively, by further drawing in the second drawing stage. Therefore, although the drawing process is a continuous process with multiple ovens operating in series, tape A3, drawn to $\lambda = 6$, can be considered an intermediate prior to further drawing on the second drawing stage to yield tapes A4–A7.

Due to the extrusion process, it is likely that some orientation is already present in the tapes before drawing (i.e. tapes are not purely isotropic after leaving the extruder), but this is ignored in this study since the reported draw ratios are merely comparative, and so any pre-orientation effects from the extruder are similar. Thus, the effects of varying the overall draw ratio of the tapes and also the drawing temperature applied in the second drawing stage are investigated in this paper.

The PP tapes described in this paper are manufactured as a precursor to create all-PP composites, and are produced with a skin:core:skin (A:B:A) structure via a co-extrusion process [35,60]. The as-extruded PP tapes comprise a PP copolymer upper skin layer (A), a PP homopolymer core layer (B) and a PP copolymer lower skin layer (A) of approximate proportions A:B:A = 5.5%:89%:5.5%. Immediately following co-extrusion, the PP tapes are drawn as described above in a two stage drawing process through hot air ovens to increase molecular alignment and so dramatically increase longitudinal strength and stiffness. Critically, the copolymer skin layer has a melting temperature below that of the PP core. This allows the subsequent consolidation of these highly drawn PP tapes into a composite structure at a wide temperature processing range; the tapes can be consolidated into composites at a temperature high enough to melt the copolymer skin layer while reducing the risk of molecular relaxation, and so the loss of mechanical properties of the tapes. During consolidation of PP tapes into an all-PP composite, the skin layer of the co-extruded tapes is melted to bond cohesively to that of neighbouring tapes, and upon cooling, this results in a 'brick and mortar' composite morphology consisting of stacked highly oriented PP tapes bonded together by the thin copolymer skin layer. Because the skin–core morphology of the tapes is achieved when both the skin and the core are in the melt phase during co-extrusion, the bonding between skin and core is excellent [60].

The low thickness of the skin layer ($\sim 5 \mu\text{m}$) means that the final all-PP composites can contain exceptionally high reinforcement volume fractions of $\sim 90\%$. These highly drawn co-extruded tapes can be processed into composite structures by direct forming of pipes, pressure vessel and other similar structures [35,36,61] or by first weaving a

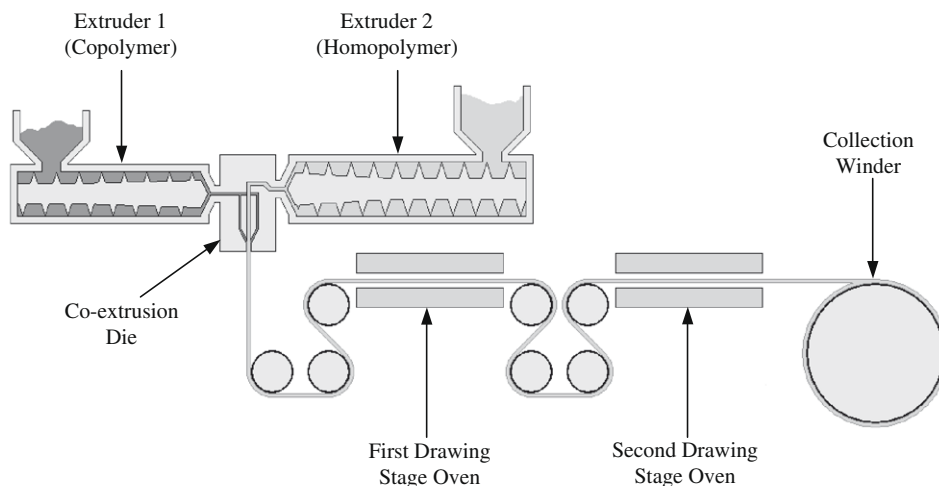


Fig. 1. Schematic of the co-extrusion and two stage drawing process used to create the highly drawn PP tapes investigated in this paper [60].

tape fabric and subsequently consolidating fabric plies into composite laminates [34]. These laminates may be further formed into all-PP products via a range of further processing steps [62,63]. Although necessary for the production of all-PP composites, the thin skin layer is not thought to contribute greatly to mechanical properties or thermal stability of the tapes, and so for the interest of this paper, the presence of this thin copolymer layer will be ignored.

3. Experimental methods

3.1. Density measurements

The density of PP tapes, ρ , was determined by measuring the apparent mass when submerged in water, and applying the Archimedes principle in accordance with ASTM D792. According to the Archimedes principle, the buoyant force of a solid that is less dense than the fluid in which it is immersed is equal to the weight of the volume of fluid it displaces when submerged, less the dry weight of the object. Because PP has a lower density than water, by measuring the buoyancy force of PP tapes

immersed in water, the density can be calculated. The density of the water was determined by using a calibrated 10 ml glass volume, and the temperature of the water was kept constant during testing to eliminate any fluctuation in water density.

3.2. Tensile testing

Tensile tests to failure of PP tapes were performed using a Hounsfield tensile testing machine equipped with a 1 kN load cell, special force reducing tape clamps and data acquisition software. A crosshead displacement of 5 mm min^{-1} and a gauge length of 200 mm were used in all cases to measure failure stress. Tensile tests to determine tensile modulus were performed using an Instron tensile testing machine equipped with a 1 kN load cell, standard grips and data acquisition software. A crosshead displacement of 64 mm min^{-1} and a gauge length of 640 mm were used. Preliminary comparisons between this method and an alternative method using a self-supported extensometer yielded equal moduli within the range of experimental scatter. Tensile modulus of each specimen is calculated between 0.1% and 0.4% strain. Five repetitions are reported for each test, and each data point reported

Table 1

Drawing parameters used to draw the tapes investigated in this paper. Note that tapes A1–A3 are drawn in single stage drawing process, while tapes A4–A7 are drawn to higher draw ratios in a second drawing stage. Tapes B1–B4 are all drawn to $\lambda = 13$, with varying temperature in the second drawing stage.

Series	Tape number	Total applied draw ratio (λ)	Drawing stage 1		Drawing stage 2	
			Draw ratio (λ_1)	Drawing temperature ($^{\circ}\text{C}$)	Draw ratio (λ_2)	Drawing temperature (DT_2) ($^{\circ}\text{C}$)
A	A1	2	2	60	–	–
	A2	4	4	60	–	–
	A3	6	6	60	–	–
	A4	9.3	6	60	1.55	160
	A5	12	6	60	2.00	160
	A6	14	6	60	2.33	160
	A7	17	6	60	2.83	160
B	B1	13	6	60	2.17	160
	B2	13	6	60	2.17	170
	B3	13	6	60	2.17	180
	B4	13	6	60	2.17	190

in this paper is an average value. The errors bars on the graphs represent standard deviations.

3.3. Free shrinkage measurements

To assess the ‘free’ shrinkage of PP tapes, i.e. shrinkage during exposure to elevated temperatures with no physical restriction applied, sets of five 1 m lengths of tapes were hung in a preheated, circulating air oven controlled by an internal thermostat and monitored by an independent thermometer fitted with two PT100 temperature probes placed at different locations in the oven. The air temperature was constant and uniform (± 1 °C) within the oven. Preliminary tests showed that for all temperatures, and draw ratios, the percentage shrinkage in the tape length direction as a function of duration in the oven, increased logarithmically with time, and that >80% of total shrinkage had occurred within 30 min in the oven. The total shrinkage is defined as the proportional decrease in tape length compared to initial tape length after exposure to elevated temperature. Therefore, all free shrinkage measurements were performed after placing tapes in an oven for 30 min.

3.4. Shrinkage force measurements

Shrinkage force measurements were conducted by placing 30 cm lengths of tape between opposing grips of an Instron tensile testing machine (as described earlier for tensile modulus tests) fitted with a circulating hot air testing chamber. Temperature was measured, as before, at two locations within the oven to ensure thermal homogeneity. The tape specimen is placed between the grips, inside the oven and the oven temperature is raised from room temperature until failure of the tape (typically ~ 190 °C) at a rate of approximately 10 K min^{-1} . Prior to testing, testing grips were preheated to reduce the effect of thermal expansion of grips during testing and so limiting this affect on shrinkage force measurements. A preload of 1 N

(~ 7 MPa) was applied to the tapes before heating to assure a taut specimen necessary to accurately measure shrinkage force.

No displacement of the crosshead was applied; a force due to the shrinkage of the tape was recorded with increasing temperature. The maximum shrinkage stress is defined as the maximum force recorded during the increase in temperature, divided by the original cross sectional area of the tape. Five repetitions of each tape were tested to provide an average value for the maximum shrinkage stress of each tape. The error bars on the graphs represent standard deviations.

4. Results and discussion

4.1. Influence of draw ratio on the mechanical properties of PP tapes

To produce all-PP composites with competitive mechanical properties, it is essential to maximise the mechanical properties of the constituent PP tapes. Tapes from Series A (see Table 1) were produced with a range of draw ratios, λ , to determine the effect of draw ratio on the mechanical properties of the tapes. With increasing draw ratio there is a noticeable change in appearance of tapes as illustrated in Fig. 2. Below a draw ratio of $\lambda = 9.3$, the tapes appear transparent, but above this draw ratio they are opaque. The opacity is first seen in the centre of the tape, but with increasing draw ratio, eventually covers the entire tape width. This phenomenon may be due to a transition from a homogenous to a highly micro-fibrous void-rich structure, established during drawing, as well described for polypropylene and polyethylene [64]. Such voiding has been reported in numerous drawn polymer systems including die-drawn PP rods [65], drawn PP fibres [57] and has been witnessed in other polymers such as polyethylene [66], poly(ethylene terephthalate)–polyethylene films [67] and poly(oxyethylene) [68].

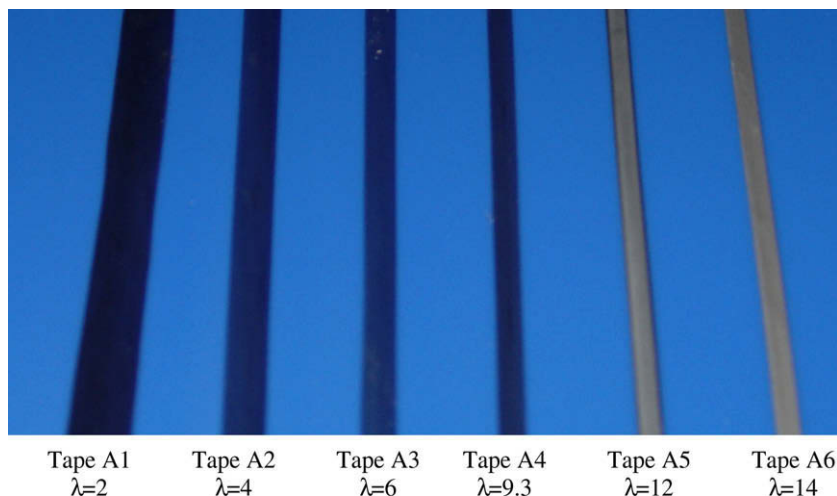


Fig. 2. Photograph of tapes drawn at increasing draw ratios, showing a change from transparent tapes at low draw ratio (λ) (shown as darker in the photograph) to opaque at higher draw ratios (shown as lighter in the photograph).

Fig. 3 shows a graph of the measured tape density of tapes from Series A, with increasing draw ratio. It is clear that density is approximately constant with increasing draw ratio until $\lambda = 9.3$, above which density sharply drops. The decrease in density is associated with the change in transparency of the tape, and may be due to microvoiding within the tape [69–71]. At $\lambda = 17$, density has reached 0.73 g cm^{-3} , and so density has been reduced by almost 20% compared to the undrawn tape. Since the density of crystalline PP is only $\sim 10\%$ higher than the density of amorphous PP ($\rho_{\text{CrystallinePP}} \sim 0.94 \text{ g cm}^{-3}$ and $\rho_{\text{AmorphousPP}} \sim 0.85 \text{ g cm}^{-3}$), a 20% decrease in density cannot be solely attributed to a decrease in the density of the polymer due to morphological changes. Therefore such a large decrease in density can only be attributed to the creation of voids within the tape, in accordance with the environmental scanning electron microscopy studies published previously [72].

The effect of draw ratio on the tensile strength and strain to failure of these tapes is shown in Fig. 4. Like density, the variation in strength and strain to failure as a function of draw ratio is non-linear. Increasing draw ratio leads to a large decrease in strain to failure from $>300\%$ for undrawn PP tapes to around 7% for tape A7, $\lambda = 17$. It is not clear if this large change in strain to failure with increasing draw ratio observed between $\lambda = 6$ (tape A3) and $\lambda = 9.3$ (tape A4) is solely a consequence of the increasing draw ratio, or is also influenced by the exposure to elevated temperatures in the second drawing stage, since tapes A4–A7, drawn to $\lambda > 6$, are also drawn in a two stage drawing process (see Table 1). As would be expected, tensile strength also increases with increasing draw ratio, but is clearly less directly linked to draw ratio than tensile modulus is. At

$\lambda < 9.3$, tensile strength increases with increasing draw ratio, but at $\lambda > 9.3$, strength reaches a plateau, only showing a slight increase at $\lambda > 14$. A similar behaviour has been reported for acetyl fibres [73]. This has been explained by Yamada et al., who described that initial drawing of semi-crystalline polymers is due to orientation of crystalline regions and amorphous regions, while drawing above $\lambda = 9$ is mainly due to increasing orientation of the amorphous phase between crystal blocks [74]. Since tensile strength is reported to be mainly governed by crystal orientation [75], it is reasonable to assume little further increase in tensile strength with increasing draw ratio above $\lambda = 9$. Fig. 3 indicated a decrease in density at $\lambda > 9.3$, implying the creation of voids at such draw ratios, and Fig. 4 shows that this is the draw ratio in which the increase in strength with draw ratio decreases, supporting this concept.

Also shown in Fig. 4 is the specific tensile strength, normalised for tape density. Since density decreases with increasing draw ratio, measuring the cross sectional area of the tape is no longer a valid method to determine stress within the tape. The specific strength takes into account the reduction in cross sectional area, but does not account for any stress concentrations that a higher degree of microvoiding may cause.

Fig. 5 shows the tensile modulus of the same group of tapes. Since the modulus is measured at low strains, the presence of microvoids is not expected to alter the modulus except by reducing the average cross sectional area of the tape. As would be expected, as λ increases, modulus increases, reaching a modulus of $\sim 15 \text{ GPa}$ at $\lambda = 17$. Again, the specific modulus shows a greater increase since the

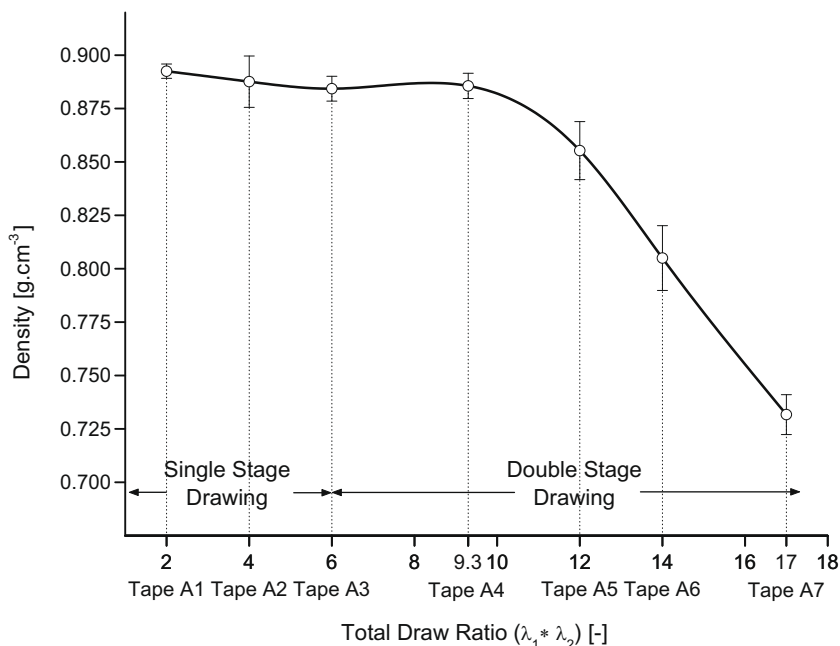


Fig. 3. The effect of draw ratio on tape density. The density of the tapes decreases with increasing draw ratio, with the greatest decrease in density occurring at $\lambda > 9.3$. As described in Table 1, tapes drawn to $\lambda < 6$ (tapes A1–A3) are produced in a single drawing stage, and these $\lambda = 6$ tapes are further drawn in a second drawing stage to achieve higher draw ratios (tapes A4–A7).

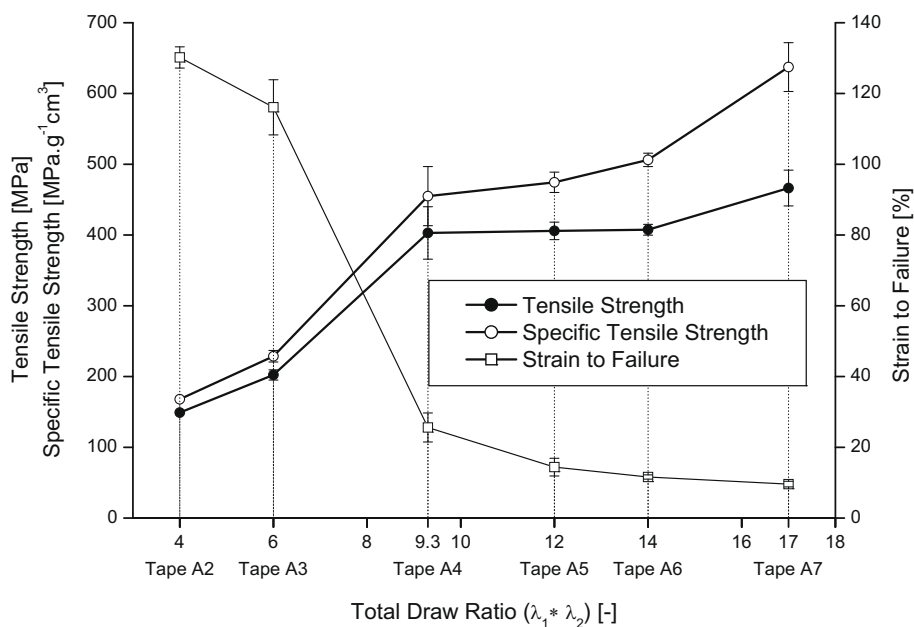


Fig. 4. The effect of increasing draw ratio on the tensile strength, specific tensile strength and strain to failure of PP tapes from Series A. Note that tapes drawn to $\lambda \leq 6$ are drawn in a single drawing stage, whereas tapes drawn to $\lambda \geq 9.3$ are further drawn in a second drawing stage (see Table 1).

density decreases with increasing draw ratio accounting for the presence of microvoids. The specific modulus of the tape exceeds $20 \text{ GPa g}^{-1} \text{ cm}^3$ which compares very well to the reported modulus (19 GPa) of a solid state oriented PP sheet [52]. Since this solid state drawn sheet is roller drawn, the formation of microvoids may be prevented by the transverse pressure applied by the rollers, and so the density of

the sheet equals that of bulk PP ($\sim 0.91 \text{ g cm}^{-3}$). Thus the specific modulus obtained in roller drawn PP sheets by Burke et al., approaches $21 \text{ GPa g}^{-1} \text{ cm}^3$, very close to the specific modulus seen in the PP tapes presented here. Based on these results, to achieve the highest mechanical properties in subsequent all-PP composites, it appears advantageous to use a tape with the highest draw ratio.

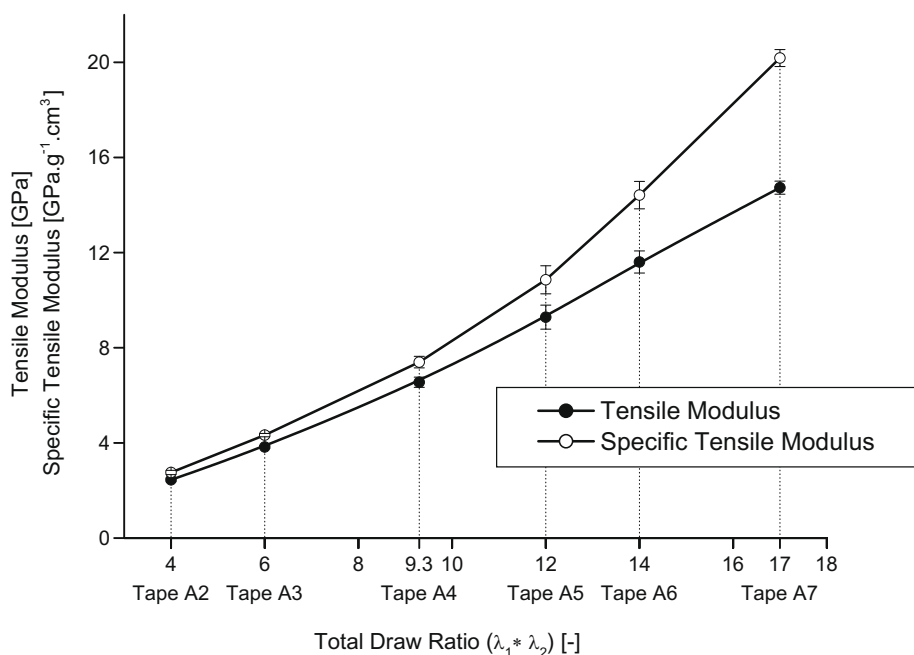


Fig. 5. The effect of increasing draw ratio on the tensile modulus and specific tensile modulus of PP tapes from Series A.

4.2. Influence of draw temperature on the mechanical properties of PP tapes

The previous section described the density and mechanical properties of highly oriented tapes which were drawn with a constant second oven drawing temperature, to various total draw ratios. The effect of the drawing temperature applied in the second oven on the density and mechanical properties of tapes drawn to $\lambda = 13$ will now be investigated. Co-extruded tapes from Series B (see Table 1) were all drawn in a multiple stage drawing process; the first drawing stage used to create tapes in Series B is the same as that used to create tapes in Series A, and provides some initial orientation. Further drawing is performed in a second drawing stage. The initial orientation imparted by the first drawing oven is necessary to allow drawing at higher temperatures in subsequent drawing stages [72]. Drawing at temperatures up to 190 °C in the second oven was possible because although 190 °C is above the melting temperature of polypropylene, the physical constraining due to the axial tension in the drawing processes artificially raises the melting temperature [76,77] and so allows tapes in tension to exist in an overheated solid state.

The first observation made from increasing drawing temperature is a return from an opaque to a transparent tape appearance. Fig. 6 shows a photograph of tapes B1–B4, all with $\lambda = 13$, with increasing drawing temperature from 160 to 190 °C in 10 °C increments. This leads to the direct assumption that since this opacity is caused by microvoiding in the highly oriented homopolymer, these must have either closed or been prevented from forming during second stage drawing at higher temperatures. Fig. 7 shows the variation in density of the tapes as a function of the drawing temperature. It is clear that density increases with drawing temperature, reaching the density of bulk PP at 190 °C. The increase in density seems to be approximately

linear, and appears to be due entirely to the decreasing proportion of voids in the tape, since the density of bulk PP is reached in tapes B4 drawn at higher drawing temperatures in the second drawing stage.

Fig. 8 shows the effect of increasing the drawing temperature on the strength and strain to failure of the tapes. There is very little change in the mechanical properties recorded despite the change in density and the apparent removal of the microvoids indicated by the optically transparent nature of the tapes drawn at higher temperatures. A gradual decrease in tensile modulus with increasing drawing temperature is observed, as shown in Fig. 9. The effect is even more obvious when specific properties are considered. An increase in the drawing temperature from 160 to 190 °C results in a decrease in specific tensile modulus of approximately 15%.

When drawing at a higher temperature it is likely that higher levels of molecular mobility allow some relaxation (hence the reduction in modulus) while drawing, and as temperature is increased, eventually this reaches a threshold where relaxation is great enough to allow tape failure. Thus tape breakage during drawing will occur above 190 °C and so a maximum drawing temperature is obtained. This molecular mobility may also explain the reduced degree of voiding observed following drawing at higher temperatures. The high degree of orientation achieved by drawing these tapes means that transverse tape properties are relatively poor [60] and so elongated voids may open due to local transverse stresses and necking within the tape. An increase in drawing temperature is likely to increase molecular mobility and so may reduce local stresses associated with lateral contractions within the tape during longitudinal stretching and so promoting a more uniform deformation [78,79]. It is clear that increasing the drawing temperature in the second drawing stage may be a way to produce optically transparent tapes if

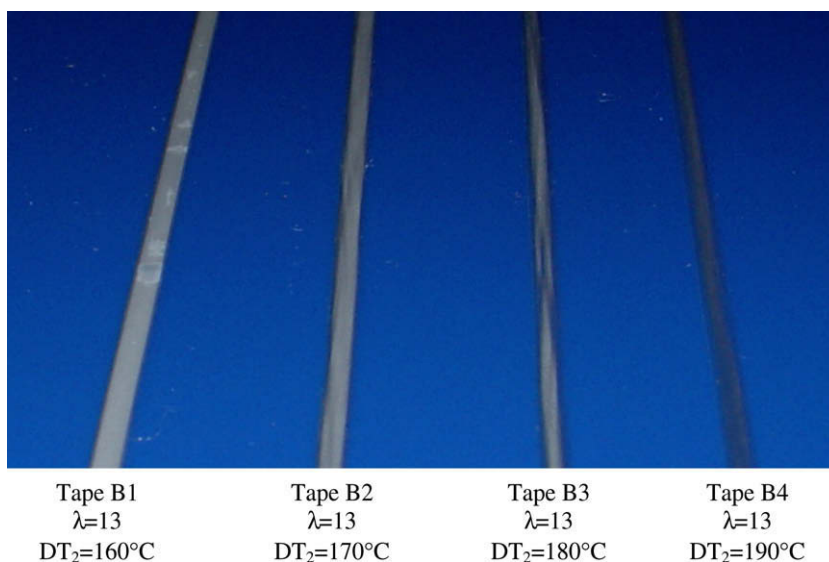


Fig. 6. Photograph of tapes B1–B4 drawn at $\lambda = 13$ at increasing drawing temperatures in the second drawing stage (DT₂). This photograph shows a change from opaque tapes drawn at lower drawing temperature (shown as lighter in the photograph) to transparent at higher drawing temperatures (shown as darker in the photograph).

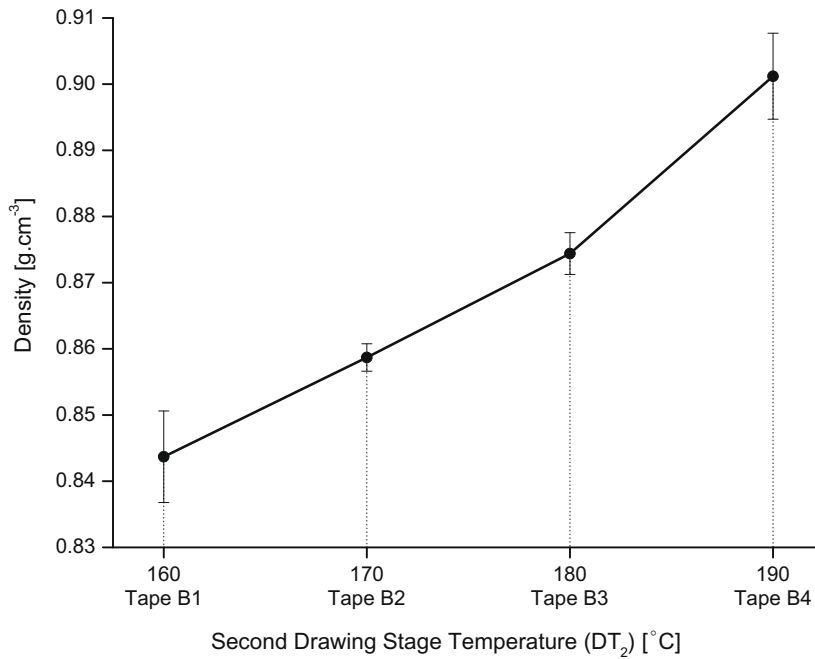


Fig. 7. The effect of increasing the drawing temperature in the second drawing stage on the density of tapes B1–B4, drawn to $\lambda = 13$.

required, Figs. 8 and 9 show that such tapes may undergo a small reduction in tensile modulus, but no significant loss of tensile strength.

4.3. Free shrinkage of PP tapes

Ultimately, the tapes described in this paper are being produced as a structural reinforcement element for all-PP

composites. A wide range of processing routes to produce all-PP composites has been investigated [33,61–63], but all of these routes feature heating of PP tapes or PP tape fabrics to facilitate consolidation. In addition to easing composite fabrication, thermal stability of the tapes is also desirable for elevated temperature exposure of the final composite part in use to prevent loss of mechanical properties and dimensional warpage.

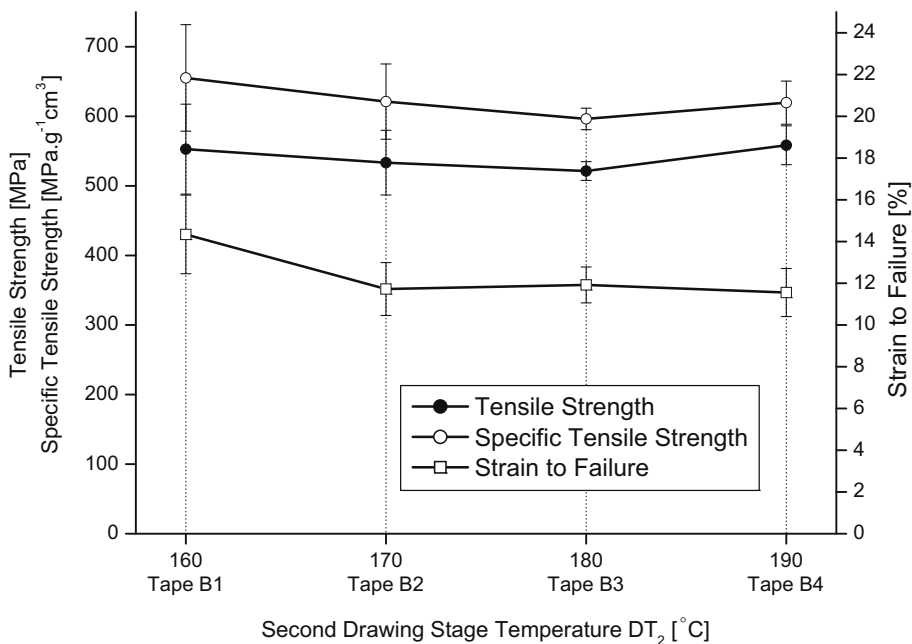


Fig. 8. The effect of increasing the drawing temperature in the second drawing stage on the tensile strength, specific tensile strength and strain to failure of tapes B1–B4, drawn to $\lambda = 13$.

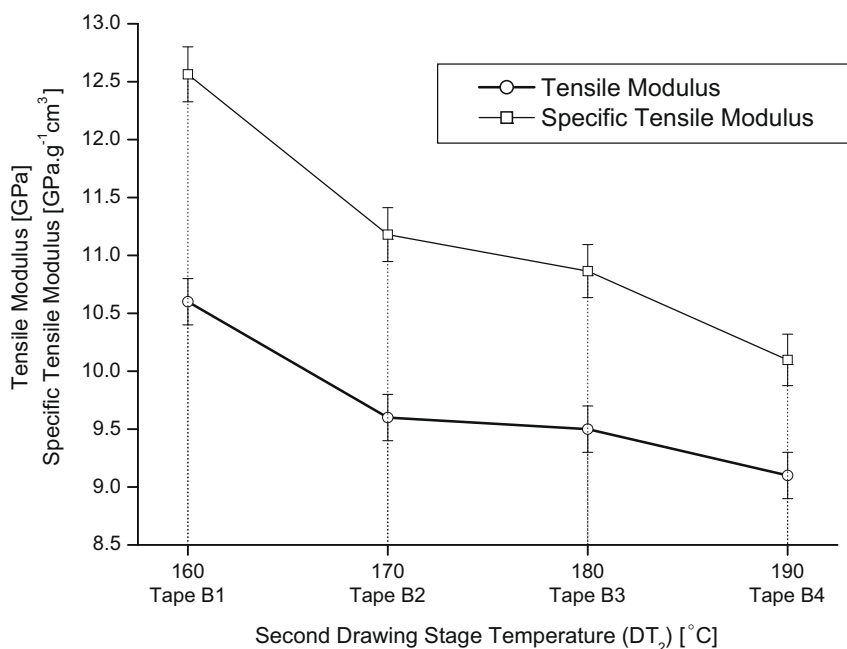


Fig. 9. The effect of increasing the drawing temperature in the second drawing stage on the tensile modulus and specific tensile modulus of tapes B1–B4, drawn to $\lambda = 13$.

The most direct measurement of shrinkage is the measurement of 'free shrinkage', which is defined here as longitudinal shrinkage of the tapes in the drawing direction. For the clarity of this paper, heating applied to cause shrinkage of the tapes will be quantified as "shrinkage temperature", while temperature used in drawing the tapes will be referred to as "drawing temperature". Fig. 10 shows the degree of shrinkage after exposure to various shrinkage temperatures of tapes with increasing draw ratio from Series A (see Table 1). Free shrinkage is clearly non-linear, increasing with increasing oven temperature, but from Fig. 10, the relationship between free shrinkage and draw ratio is ambiguous. Fig. 11 represents the same series of data, but with the free shrinkage shown as a function of draw ratio, for various discrete oven temperatures. From this graph, it is clear that the greatest free shrinkage occurs in tape A4, at $\lambda \approx 9.3$. The increase in free shrinkage with increasing shrinkage temperature is predictable since the applied shrinkage temperature encourages relaxation and molecular reorganisation.

Peterlin describes the morphology of drawn polypropylene as having a microfibrillar structure in the drawing direction. These microfibrils are comprised of crystalline blocks separated by amorphous regions, connected by tie molecules [64]. If the structure is sufficiently drawn, these tie molecules become taut, and are described to be subsequently responsible for load transfer (and hence high modulus) in the drawing direction of the structure. Upon subsequent heating, the retraction of these taut tie molecules is also responsible for the large shrinkage forces seen when polymer fibres or tapes are exposed to elevated temperatures [78]. Because the volume fraction of these inter-crystalline taut tie molecules increases with draw ratio

[80], it seems reasonable to associate the increase in fraction of taut tie molecules with the increase in free shrinkage with draw ratio in the PP tapes presented here.

However, as $\lambda > 9.3$, there is a decrease in free shrinkage of the tape, with tape A6, drawn to $\lambda = 14$, exhibiting equivalent free shrinkage behaviour to tape drawn to $\lambda \approx 5$. This observed increase in thermal shrinkage resistance with increasing draw ratio agrees with results previously reported for polyethylene [81], and may be explained by considering the increasing alignment of tie molecules with increasing draw ratio. Yamada et al. reported that when drawing PP to $\lambda \leq 9$, orientation occurred by alignment of the crystalline lamellae and amorphous regions into microfibrils [74]. When drawing to greater draw ratios, orientation mainly occurs by deformation of the amorphous regions, and an increase in the number of taut tie molecules with increasing draw ratio [81]. Although these taut tie molecules are responsible for shrinkage, they can also become more thermally stable due to their increased alignment. Groups of parallel taut tie molecules in drawn polyolefins become highly ordered and tightly packed and thus require more thermal energy to become mobile, and hence exhibit increased thermal stability compared to unoriented amorphous molecules [81,82]. This has been modelled by Pakula and Trznadel, who describe highly oriented taut tie molecules as being frozen in position and require greater heat to initiate shrinkage than less ordered molecules [83,84].

The relationship between second oven drawing temperature and free shrinkage appears to be less complex than the relationship between draw ratio and free shrinkage. The effect of second oven drawing temperature on shrinkage is shown in Fig. 12 using tapes from Series B (see Table 1).

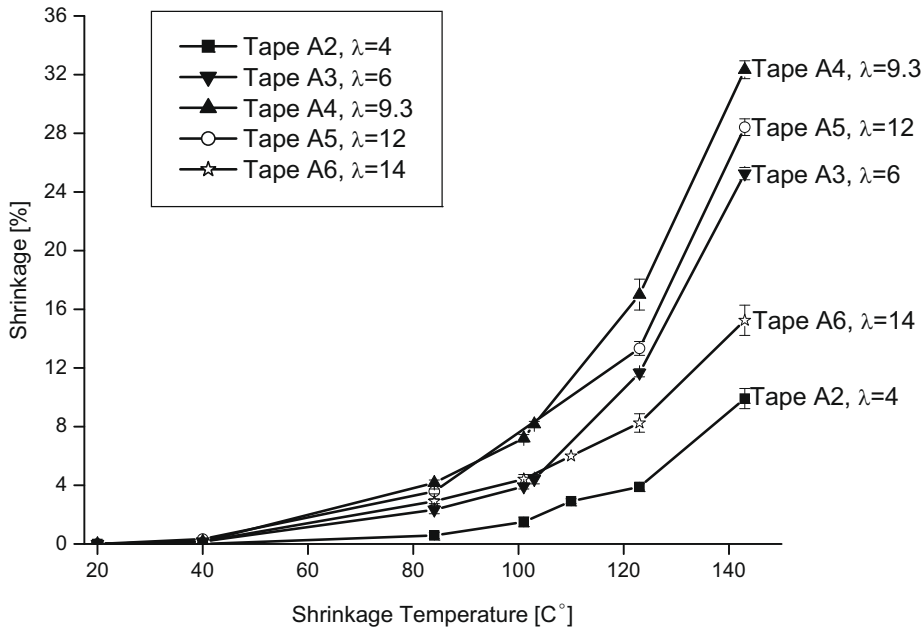


Fig. 10. The effect of shrinkage temperature on the free shrinkage of tapes from Series A with varying draw ratio, indicating that maximum free shrinkage occurs at greatest shrinkage temperature and in tapes drawn to $\lambda \approx 9$.

The general trend is similar to that seen in Fig. 10; free shrinkage increases with shrinkage temperature. Fig. 13 represents the same data as Fig. 12, with shrinkage plotted as a function of drawing temperature for a range of discrete shrinkage temperatures. There is an increase in thermal

stability with increasing drawing temperature. At higher drawing temperatures, it is possible that taut tie molecules can form more perfectly oriented quasi-amorphous bridges [78] increasing the thermal stability of the structure, making the tapes more resistant to free shrinkage.

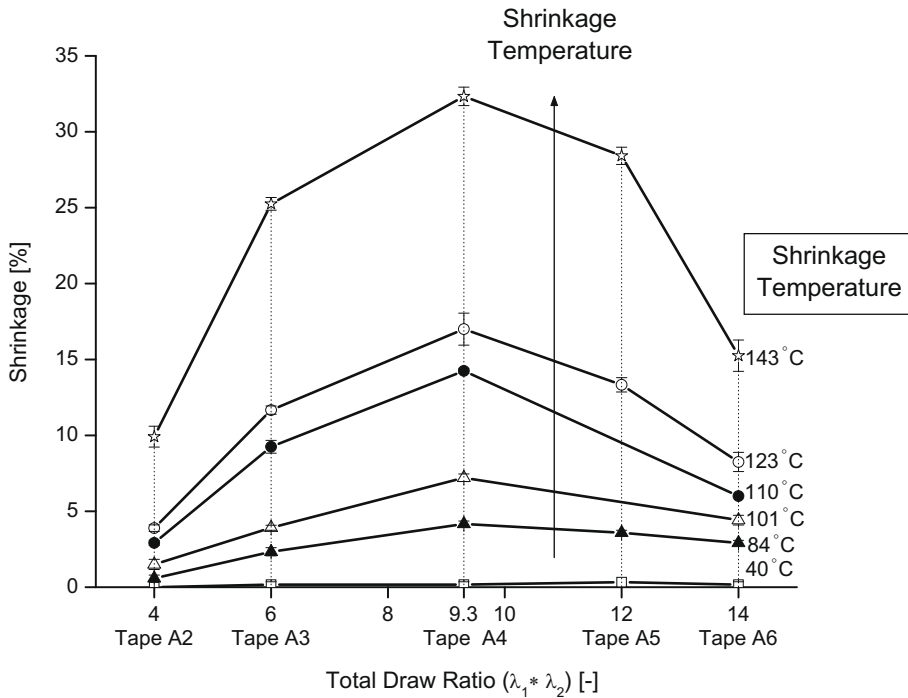


Fig. 11. The effect of draw ratio on the free shrinkage of tapes from Series A with varying draw ratio, indicating that tape A6 with $\lambda = 14$ shows a similar degree of shrinkage when exposed for 30 min to 143 °C as tape A4 with $\lambda = 9.3$ when exposed to 123 °C.

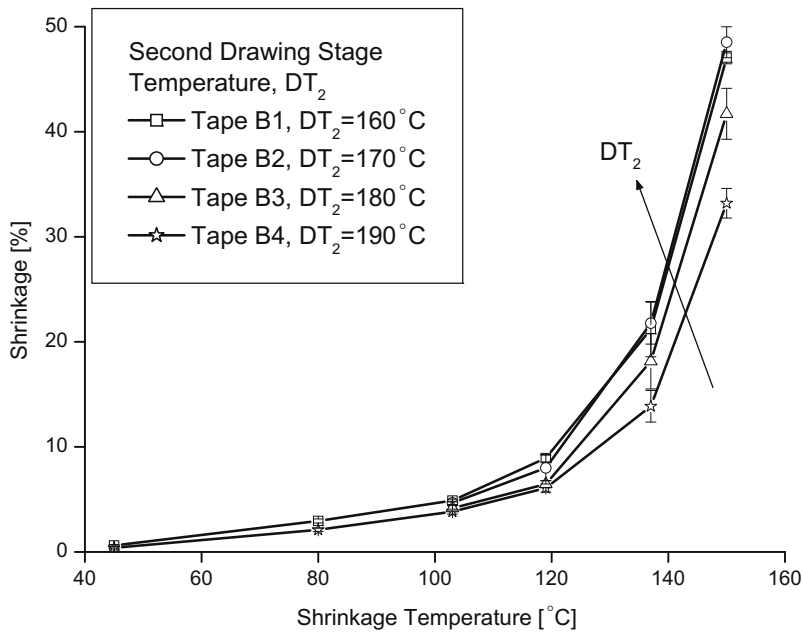


Fig. 12. The effect of shrinkage temperature on the free shrinkage of tapes from Series B with varying second drawing stage temperature, indicating that tapes drawn at higher temperatures in the second drawing oven exhibit lower free shrinkage.

One of the challenges of creating all-PP composites is the retention of the mechanical properties of the PP tape in the final composite part. Highly oriented polymer fibres that were prevented from shrinking during heating, by physically constraining the fibre ends, have been previously shown to have higher melting temperatures than equivalent unconstrained fibres [77]. To take advantage of the greater thermal stability caused by this constraining,

PP tapes or PP tape fabrics are physically constrained during consolidation into all-PP composites, to help prevent relaxation of the tapes [35]. Since the temperatures being used to test free shrinkage here are similar to those which would be used during all-PP composites consolidation [34], it is of great interest to know if there is a relationship between an observed free shrinkage and a decrease in residual properties of the PP tape. In this way, such a

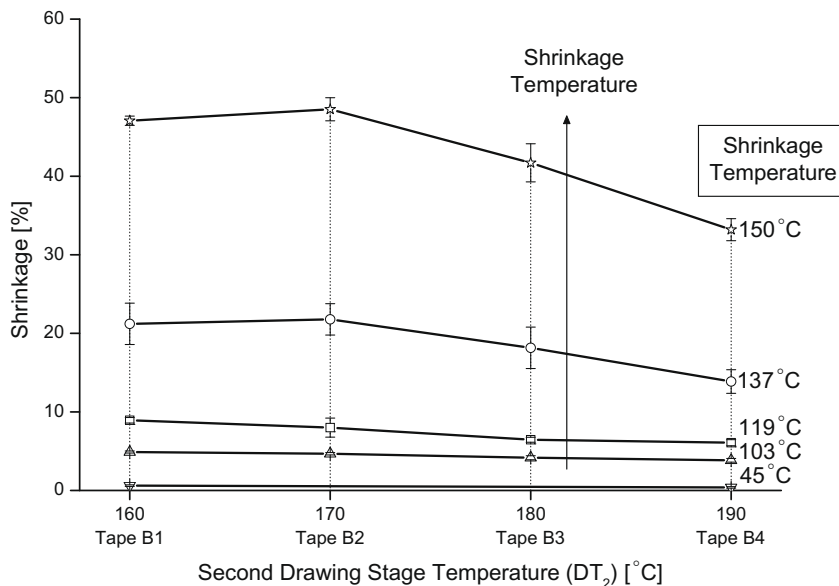


Fig. 13. The effect of drawing temperature in the second drawing stage on the free shrinkage of tapes from Series B, indicating that tapes drawn at higher temperatures in the second drawing stage (e.g. tape B4, $DT_2 = 190^\circ\text{C}$) are more resistant to free shrinkage than tapes drawn at lower temperatures in the second drawing stage (e.g. tape B1, $DT_2 = 160^\circ\text{C}$).

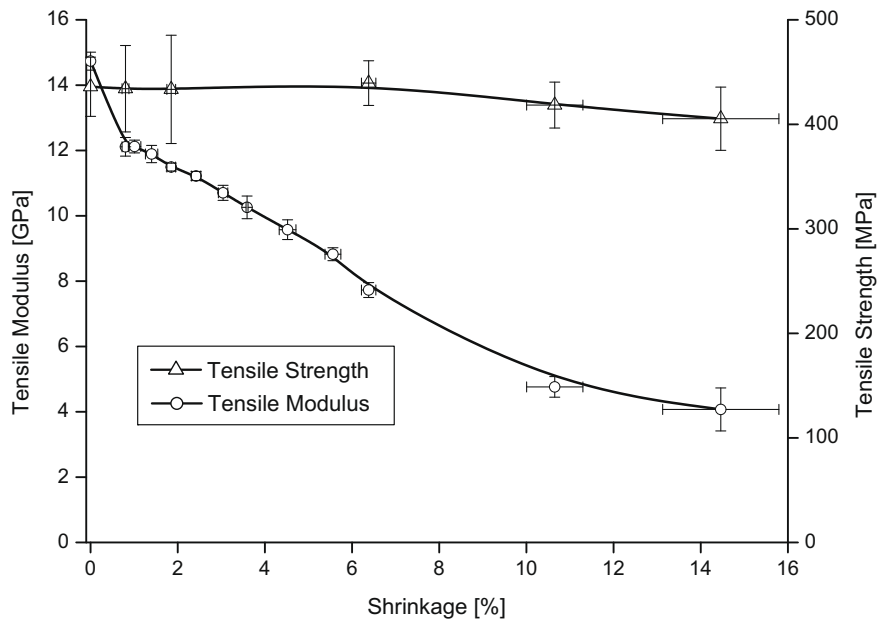


Fig. 14. The residual tensile modulus and tensile strength of tape A7 following various degrees of free shrinkage, indicating that relatively low shrinkage in the longitudinal axis of a tape can result in large decreases in mechanical properties.

relationship would enable a prediction of the loss of mechanical properties due to poorly constrained consolidation, from a dimensional measurement without the need for mechanical testing of the final part. Since both the tensile modulus and the free shrinkage of highly oriented PP tapes seem to be controlled by tie molecules highly oriented in the amorphous phase, the mechanical properties

following shrinkage were investigated. Samples of tape A7, with a total draw ratio of $\lambda = 17$ were exposed to varying shrinkage temperatures and allowed to shrink freely. Different degrees of free shrinkage were achieved by exposing the samples of the same tapes to different shrinkage temperatures. As shown in Fig. 10, the degree of shrinkage increases with shrinkage temperature, and so

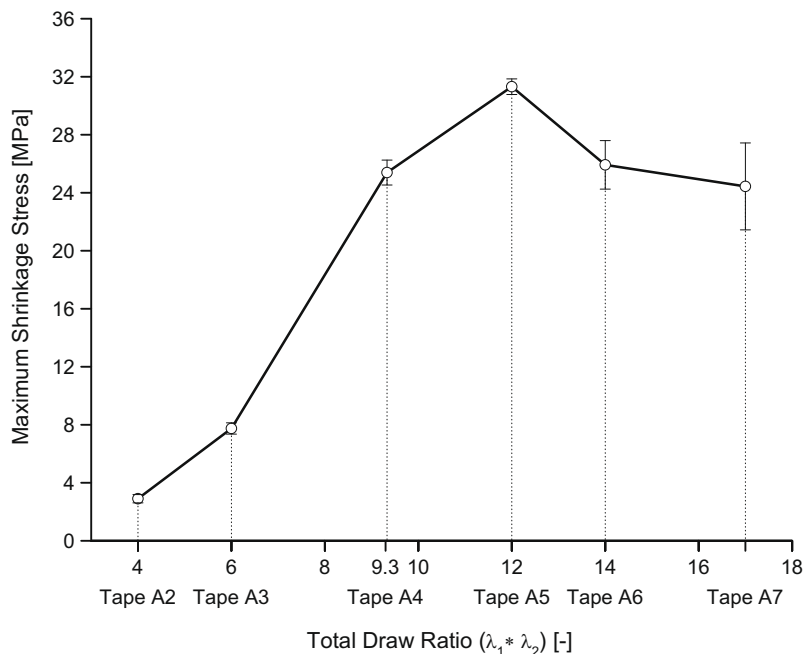


Fig. 15. The effect of draw ratio on the maximum shrinkage stress of tapes from Series A, indicating that shrinkage stress increases with draw ratio, but as seen for free shrinkage in Fig. 11, more highly drawn tapes seem to exert lower shrinkage stresses. As described in Table 1, tapes drawn to $\lambda < 6$ (tapes A2 and A3) are produced in a single drawing stage, and these $\lambda = 6$ tapes are further drawn in a second drawing stage to achieve higher draw ratios (tapes A4–A7).

exposure of the samples of the same tape to different shrinkage temperatures yielded tape samples which had undergone varying amounts of shrinkage. The tensile mechanical properties of these tapes were then measured and plotted as a function of the degree of free shrinkage. Fig. 14 shows the residual tensile modulus and residual tensile strength of tapes A7 drawn to $\lambda = 17$, following various amounts of free shrinkage. The standard deviation of free shrinkage is represented by error bars in the x-axis direction and the standard deviation of mechanical properties is represented by error bars in the y-axis direction. The decrease in tensile modulus with free shrinkage is quite dramatic; a free shrinkage of just 14.5% length results in a 73% loss of tensile modulus of tape A7.

This amount of longitudinal shrinkage may be considered equivalent in length in returning from a draw ratio, $\lambda = 17$ to $\lambda \approx 14$, but equivalent in tensile modulus to a tape drawn to $\lambda \approx 6$. Thus thermal shrinkage is not the direct reversal of solid state drawing, and apparent draw ratio and tensile modulus are not directly linked, as could be assumed from Fig. 5. The sudden loss in tensile modulus seen at very low shrinkage ($\sim 1\%$ length) in Fig. 14 may be due to the relaxation of taut tie molecules. It is conceivable that although these taut tie molecules are relatively thermally stable due their high degree of alignment, as soon as these tie molecules are able to relax, direct load transfer between crystalline regions is reduced, thus reducing macroscopic stiffness. During the heating of the tape to allow free shrinkage, it is also possible that small translational slippages in crystalline regions may further encourage taut tie mole-

cules to relax [85]. The drop in tensile modulus while tensile strength remains constant supports the theory that modulus is controlled by alignment of tie molecules, where as the strength is controlled by crystal orientation and structural effects such as microvoiding [75].

This theory would support the observation that relaxation and a decrease in tensile modulus without an obvious macroscopic shrinkage is possible. These free shrinkage experiments illustrate the effect of microstructural changes on the macrostructure of the tape, and give good indications of the molecular processes involved. This observation means that extra care must be used when processing these highly oriented tapes into all-PP composites, since morphological changes can occur which will affect the mechanical properties of the final composite without necessarily giving strong visible indications that this change in morphology has occurred.

4.4. Shrinkage force of PP tapes at elevated temperatures

The amount of longitudinal shrinkage of drawn PP tapes has been described in the previous section, and now an investigation into the magnitude of the shrinkage force will be presented to further clarify the effect of heating a PP tape. During heating of a PP tape constrained by fixed ends, physical shrinkage can be prevented, but the same mechanisms that cause shrinkage cause a retractive stress to be experienced by the tape constraints. Fig. 15 shows the magnitude of this maximum shrinkage stresses measured as a function of draw ratio.

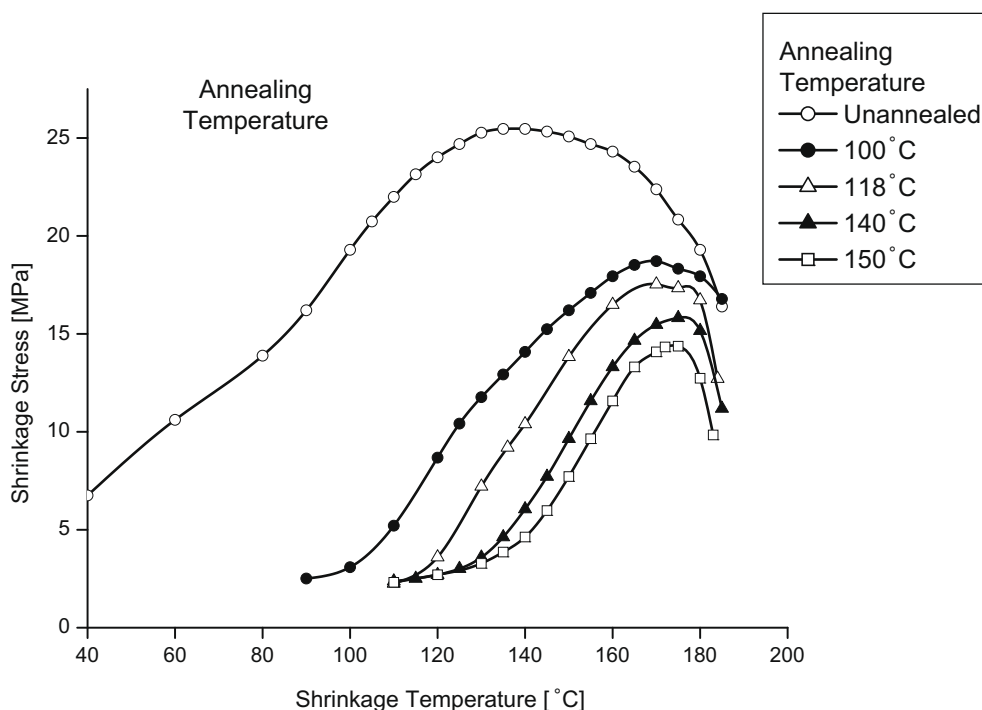


Fig. 16. The effect of shrinkage temperature on shrinkage stress for samples of tape A7, drawn to $\lambda = 17$, following free annealing to various annealing temperatures. The graph indicates that free annealing at greater temperatures results in lower shrinkage forces being exerted by the tapes during subsequent exposure to elevated shrinkage temperatures.

Maximum shrinkage force increases with draw ratio until $\lambda \approx 12$, but then decreases with increasing draw ratio at $\lambda > 12$. Since the volume fraction of taut tie molecules is reported to increase with increasing draw ratio [49], so the trend of the maximum shrinkage force cannot be solely due to changing volume fractions of taut tie molecules. As maximum shrinkage forces would be expected to increase with increasing draw ratio, these results reinforce the idea that as draw ratio increases, these taut tie molecules become arranged in a highly ordered amorphous morphology and so possess greater thermal stability. The magnitude of these shrinkage stresses is similar to those reported previously [86] although since the maximum draw ratio considered by De Candia et al. was $\lambda = 11$, a further reduction in shrinkage stress at even higher draw ratios was not reported.

One aim of this investigation is gain a greater understanding of the dimensional thermal stability of drawn PP tapes during exposure to elevated temperatures, since the results of free shrinkage experiments (shown in Fig. 14) show that a very small free shrinkage can result in a large reduction in tensile modulus. Therefore, the effect of free annealing on the tapes was investigated.

Fig. 16 shows the effect of free annealing on the shrinkage stress behaviour of PP tapes A7, drawn to $\lambda = 17$, after being annealed in an oven at various temperatures for 20 min. Fig. 16 also indicates the shape of representative curves of shrinkage stress as a function of increasing temperature, during heating. The shrinkage stresses pass through a maximum with increasing temperature and then as the temperature increases further and the tape begins to melt, stress transfer along the tape length is lost and the perceived shrinkage stress decreases. Tape failure ultimately follows when the tape yields and breaks.

Fig. 16 shows that the unannealed tape exerts a detectable shrinkage stress as temperature reaches 40 °C and shows the greatest shrinkage stress throughout. For the tapes that had been thermally annealed, two important changes in behaviour can be observed. Firstly, with increasing annealing temperature, the maximum shrinkage stress observed during subsequent heating decreases, dropping to almost half the maximum shrinkage stress of the unannealed tape, and this maximum shrinkage stress is shown in Fig. 17. Secondly, the onset temperature of shrinkage is seen to increase with increasing annealing temperature. Tapes annealed at 140 °C do not show a substantial shrinkage force until they are heated to 120 °C, compared to unannealed tapes which exert a shrinkage stress when heated to just 40 °C. Therefore, it can be seen that by free annealing highly oriented PP tapes, the thermal stability may be improved through both a reduction in maximum shrinkage stress, and an increase in the onset temperature for shrinkage. This is supported by data reported previously [75], and so a free annealing stage may be considered as an additional processing step in the creation of future tapes for all-PP composites.

During a free annealing process such as that performed here, the molecular structure is likely to relax and so a loss of modulus can be expected. This loss in modulus has to be balanced against the greater thermal stability of tape A7, following free annealing. Fig. 18 illustrates this point by comparing the onset of shrinkage stress (defined as the temperature at which shrinkage stress first exceeds 2 MPa) with the tensile modulus of the free annealed tapes. This indicates that, as suggested, free annealing can result in a decrease in tensile stiffness. This graph shows that highly drawn PP tapes can be made to be dimensionally stable to 130 °C, by free annealing, if this dimensional sta-

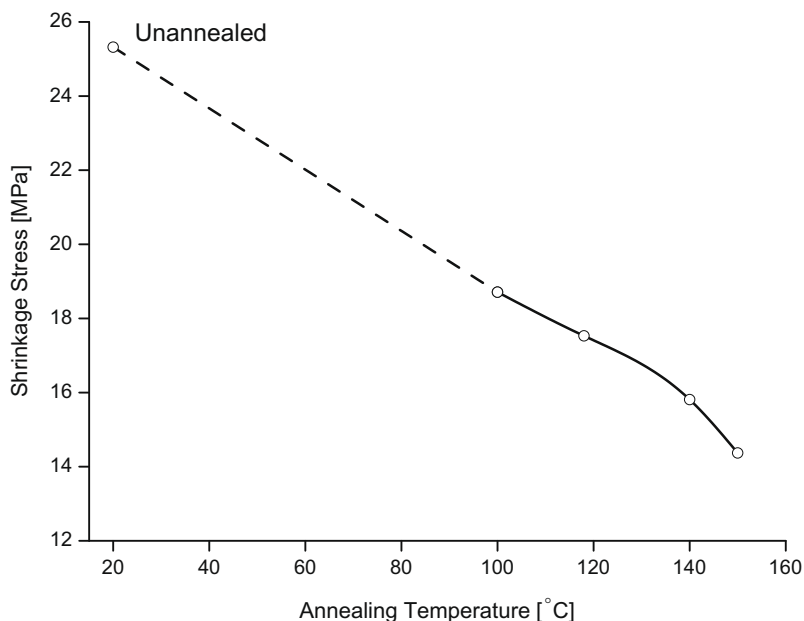


Fig. 17. The effect of free annealing temperature on the maximum shrinkage stress for samples of tape A7, drawn to $\lambda = 17$, following free annealing to various annealing temperatures. It is clear that free annealing may be used to reduce the maximum shrinkage stress of the drawn PP tapes.

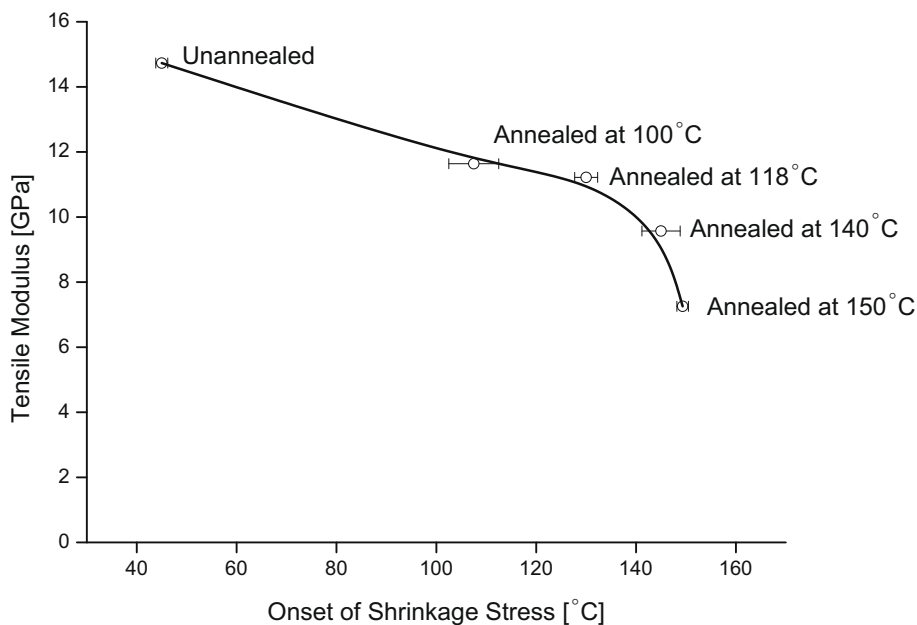


Fig. 18. The effect of free annealing to various annealing temperatures on the residual tensile modulus of samples of tape A7, drawn to $\lambda = 17$, indicating that while free annealing may be used to reduce the shrinkage stress, it is also associated with a potential larger decrease in modulus.

bility is considered valuable enough in a final product to warrant sacrificing 25% of the tensile modulus of the tapes. As seen before in the development of all-PP composites, the final mechanical and thermal properties of the composite product can be tailored to suit the specific application.

5. Conclusions

The highly oriented PP tapes described here have been developed to become the reinforcement phase of self-reinforced PP or all-PP composites, such as PURE[®]. It has been demonstrated that the drawing conditions of the PP tapes determine the microstructure and mechanical properties of the tapes. Generally, increasing the draw ratio leads to increasing mechanical properties, while it was also seen to result in a decrease in density of the tapes. This can be beneficial as it will lead to a reduction in the density of the final all-PP composite product, and high specific mechanical properties.

The thermal stability of the PP tapes was investigated using the resistance to longitudinal shrinkage as a parameter to quantify thermal stability, although the degree of shrinkage was not proportional to the loss of mechanical properties of the tapes. Free annealing was proposed as an option to reduce the longitudinal shrinkage of the tapes, although this was seen to be associated with a small reduction in mechanical properties.

An increase in thermal stability of the PP tapes would be advantageous, both in the final application and to make the tapes less sensitive to molecular relaxation during the composite consolidation process. Because thermal stability and mechanical properties are both valuable in the final all-PP composite, any increase in thermal stability due to

a thermal annealing process must be balanced against any associated decrease in mechanical properties.

Acknowledgements

The co-extruded PP tapes used in this study were prepared using facilities at Lankhorst Pure Composites BV, The Netherlands. This work was sponsored by the Dutch Government's Economy, Ecology and Technology (EET) programme for sustainable development, under Grant No. EETK97104, under the project name PURE.

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