Interfacial Properties of Highly Oriented Coextruded Polypropylene Tapes for the Creation of Recyclable All-Polypropylene Composites

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ABSTRACT: The creation of highly oriented, coextruded polypropylene (PP) tapes allows the production of novel, wholly thermoplastic, recyclable ''all-polypropylene'' (all-PP) composites, which possess both a large temperature processing window (>30°C) and a high volume fraction of reinforcement phase (highly oriented PP tapes: >90%). This large processing window is achieved by using coextruded, highly drawn PP tapes. To achieve coherent all-PP composites the interfacial characteristics following consolidation must be understood. This article investigates the interfacial characteristics of these coextruded tapes by using microcomposite models to create interfaces between tapes of varying draw ratios, drawing temperatures, skin/core ratios, and skin layer thicknesses. The tape drawing parameters are seen to control the interfacial properties in subsequent microcomposite models. The failure mode of these specimens, and hence bond strength, varies with consolidation temperature, and a model is proposed describing and explaining this behavior. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 118–129, 2007

Key words: recycling; self-reinforced composites; interface; T-peel

INTRODUCTION

In a series of academic theses[1–3] and publications,[4–9] composite materials in which both the fiber and the matrix are based on polypropylene (PP) have been described. These 'all-PP' composites possess similar mechanical properties to glass fiber reinforced polypropylene (GFRPP). Highly oriented PP tapes, with high tensile strength and stiffness achieved by molecular orientation during solid state drawing,[10–20] are a prerequisite. However, to consolidate these tapes into a coherent all-PP composite, the effect of tape manufacturing and consolidation parameters on the interfacial properties of these tapes must be investigated. The interfacial properties of fibers or tapes are key to the optimization of any composite system. These interfacial properties of a composite can be investigated directly as microcomposites such as fiber pull-out, microdebonding, and fiber fragmentation tests, or indirectly as macrocomposite systems such as interlaminar shear stress (ILSS) analyses or transverse tensile tests. The use of microcomposite systems allows the isolation of failure modes and the understanding of these failure modes can then be applied to predict the failure of real composite systems. The effect of consolidation parameters on the mechanical performance of all-PP macrocomposites has been presented elsewhere,[2,7,8] while this article investigates the effect of consolidation temperature and tape structure on all-PP microcomposite systems.

The creation of single polymer composites is motivated by the desire to enhance recyclability of composite materials. Conventional composites employ very different materials for the matrix and reinforcement phase and this complicates recycling. All-PP composites overcome this problem since at the end of the life of an all-PP product, the entirely polypropylene composite can simply be melted down for reuse in a PP feedstock or even in a subsequent generation of all-PP composite.

While the concept of single polymer composites is not new,[21–32] existing technologies have inherent limitations which reduce their viability, such as a small temperature processing window or a low volume fraction of reinforcement, which limits the ultimate mechanical properties of the composites. Highly oriented, high modulus fibers or tapes can be effectively welded together by selective melting of the surface of the fibers or tapes and applying pressure to achieve a good bonding and fill any voids.[32–35] In these monoextruded tape or fiber systems, the process becomes highly sensitive to compaction temperature, since there is a risk of molecular relaxation

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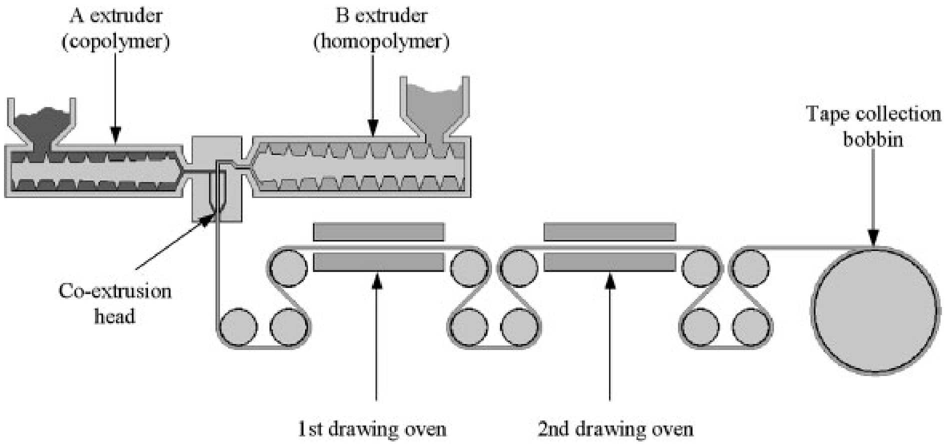

Figure 1 Schematic of continuous tape coextrusion and solid state drawing line for the production of highly drawn polyolefin tapes possessing a high degree of molecular orientation.

during the high temperature consolidation of tapes or fiber bundles into composites.

The research reported in this article focuses on the use of coextruded tape technology to create novel all-PP composites, which possess both a large processing temperature window and high volume fraction of reinforcement. These coextruded tapes possess a skin-core morphology and are composed of a core of PP homopolymer surrounded by a thin skin of a PP copolymer. The copolymer is propylene-based and contains 6% (w/w) ethylene, which results in a significantly lower melting temperature. The three layer structure of the tape is coextruded in a high viscosity melt phase and subsequently drawn in a two-stage solid-state drawing process shown in Figure 1, and described in greater detail elsewhere.[2,19,36]

This drawing process results in a high degree of molecular orientation and the drawn tapes possess a high tensile strength (>450 MPa) and stiffness (>15 GPa).[2,3] These coextruded tapes can then be consolidated into a composite material by the application of heat and pressure, either by filament winding for unidirectional specimens or by stacking plies of woven tape fabrics. The application of pressure also causes a physical constraining effect which has been shown to artificially raise the melting temperature of highly oriented polymers allowing them to be ''overheated,''[5,19,37] and this effect further protects the high degree of molecular orientation in the tapes by preventing relaxation during consolidation. Since the copolymer used possesses a lower melting temperature than the homopolymer core, it allows tapes to be effectively welded together at temperatures far below the melting temperature of the homopolymer core. The proportional thickness of the skin to the core can be altered during coextrusion, but since the skin layer is present only to facilitate intertape bonding, it is desirable for optimal composite properties, to have this skin as thin as possible while achieving a high interfacial strength. The high mechanical properties of these tapes together with the inherent low density of PP, and the high volume fraction of reinforcement present in these composites ($V_f > 90\%$) make these all-PP composites competitive with conventional PP matrix composites. Since the PP tapes used in this research are coextruded, the matrix phase (skin layer) is carried by the reinforcement phase (core layer), in one tape. The optimization of both the homopolymer reinforcement core for high mechanical properties and the copolymer (matrix) layer for good interfacial strength must be considered simultaneously. While the extrusion and solid state drawing parameters determine the mechanical properties of these tapes, the same parameters also affect the morphology of the copolymer layer and the strength of the interfaces formed when these tapes are bonded to each other in a composite system.

Thermodynamic considerations of bonding oriented polymers

In the case of highly oriented polymers, the melting behavior may differ from isotropic polymers. The

TABLE I
Ideal Tape Characteristics for All-PP Composite Production

Tape layer	Material	Desired structure	Entropy	T_m	Tensile properties
Core	Homopolymer	Highly oriented	Low	High	High
Skin	Copolymer	Isotropic	High	Low	Unimportant: low volume fraction

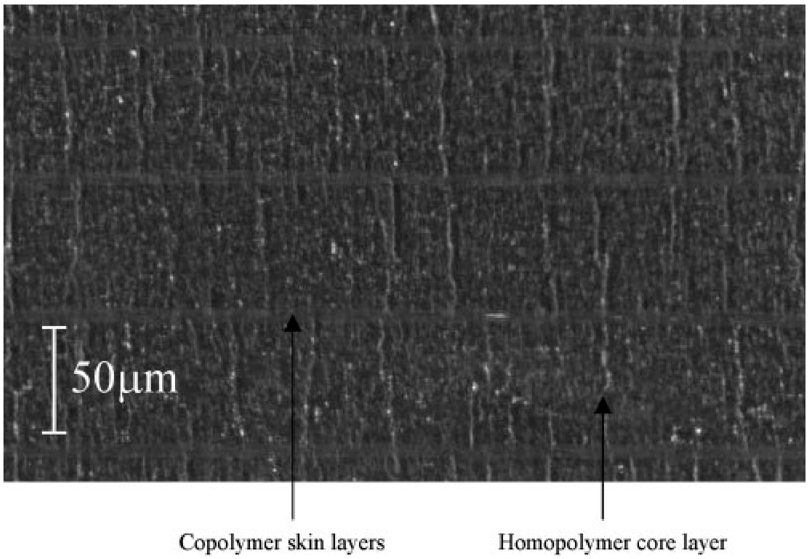

Figure 2 Optical micrograph of a cross section of unidirectional all-PP composite showing the skin-core morphology of stacked tapes in a consolidated composite laminate (the tapes are oriented horizontally, with tape thickness oriented in the vertical direction, and tape width oriented out of the plane of the paper). The copolymer layer is clearly visible in between the highly oriented homopolymer core even within the consolidated composite.

second law of thermodynamics states that at constant temperature,

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

where ΔG is the Gibbs free energy difference between crystal and liquid, ΔH is the enthalpy difference between crystal and liquid, and ΔS is the entropy difference between crystal and liquid. At the crystal melting temperature, $T = T_m$, there is thermodynamic equilibrium between crystalline polymer and the melt. Therefore, $\Delta G = 0$, so:

$$T_m = \frac{\Delta H}{\Delta S} \tag{2}$$

From eq. (2), it is clear that increasing the molecular orientation of a polymer by solid-state drawing and the resulting decrease in entropy causes an increase in the melting temperature. Until now, maximum molecular orientation has been the target for a coextruded tape to achieve ultimate mechanical properties. However, during drawing, both the copolymer and the homopolymer are subject to this molecular orientation. From eq. (2), the effect of this molecular orientation on the copolymer would be an increase in melting temperature. This will adversely affect the ability of the tapes to bond at the lower end of the temperature processing range, by hindering interdiffusion.

In a highly oriented polymer, the increased molecular alignment will also reduce molecular freedom.

TABLE II
Tape Construction Parameters and Test Specimen Nomenclature

Tape name	Tape width (mm)	Draw ratio (λ)	Relative tape configuration (A:B:A)	Copolymer layer, total (%)	Copolymer layer thickness, each side (μm)
4-8	4.2	4	4.2:91.6:4.2	8.4%	5.25
6-8	3.6	6	4.2:91.6:4.2	8.4%	4.02
9-8	3.0	9.33	4.2:91.6:4.2	8.4%	3.35
12-8	2.6	12	4.2:91.6:4.2	8.4%	3.04
14-8	2.5	14	4.2:91.6:4.2	8.4%	2.86
15-8	2.5	15	4.2:91.6:4.2	8.4%	2.83
14-15	2.5	14	7.7:84.6:7.7	15.4%	5.67
14-18	2.5	14	9.3:81.4:9.3	18.6%	7.12
14-24	2.5	14	12.1:75.8:12.1	24.2%	9.18
13-21 (160)	2.5	13	10.8:78.4:10.8	21.6%	7.61
13-21 (170)	2.5	13	10.8:78.4:10.8	21.6%	7.61
13-21 (180)	2.5	13	10.8:78.4:10.8	21.6%	7.61
13-21 (190)	2.5	13	10.8:78.4:10.8	21.6%	7.61

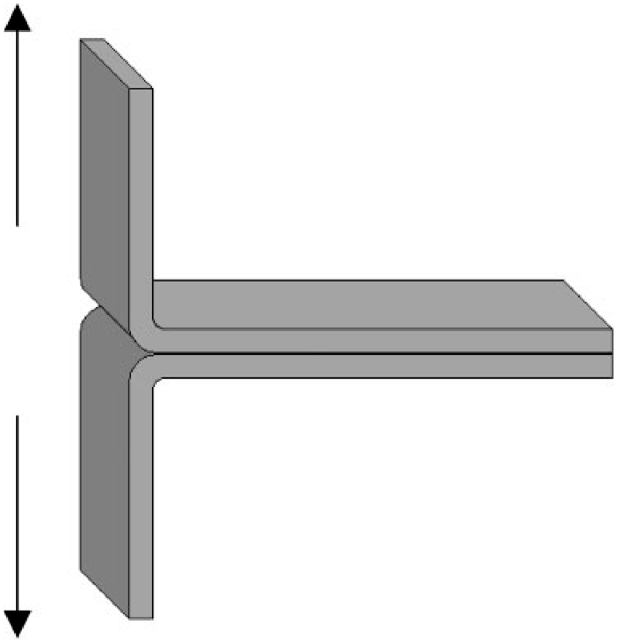

Figure 3 Schematic of micro-composite T-peel specimen consisting of two tapes bonded by selective melting of the copolymer skin layer.

Since the coextruded polymer tapes are constrained during consolidation to preserve orientation, a highly oriented copolymer (skin) layer may also experience a constraining effect and a further increase in melting temperature, as described previously. This would raise the minimum temperature required to bond adjacent tapes together, and reduce the processing temperature window for composite consolidation. Thus, it is desirable to achieve high orientation in the homopolymer layer and high mechanical properties, but also to retain isotropy in the copolymer layer to facilitate autohesion between adjacent tapes. The ideal coextruded tape for all-PP composite production is proposed in Table I. To promote rapid cycle times in composite part production, it is not feasible to achieve autohesion between tapes by using large time scales. Therefore, adhesion between coextruded tapes must be achieved by heating the tapes to temperatures close to, or exceeding, the melting temperature of the copolymer layer. There is a balance between processing all-PP composites at sufficiently high temperatures which allow complete autohesion of adjacent tapes, and processing at sufficiently low temperatures to prevent molecular relaxation of the highly oriented tapes.

The focus of this article is to investigate the effect of tape production and consolidation parameters on the interfacial properties of all-PP composites by using microcomposite model systems made from coextruded tapes. The parameters investigated here are tape draw ratio, copolymer layer thickness, compaction temperature, and tape drawing temperature. The effect of these parameters on the mechanical properties of all-PP systems has been investigated and are presented elsewhere.[7,8] The interfacial properties of coextruded tapes in a woven fabric form will be presented in a separate publication.

EXPERIMENTAL

Tape production and nomenclature

The interfacial strength of all-PP composites is determined by first creating a model microcomposite by bonding two coextruded PP tapes together. This is achieved by applying heat to facilitate molecular interdiffusion across the interface between adjacent tapes, and then, after cooling, pulling this interface apart while measuring the force required. The tapes are created using a coextrusion and solid-state drawing line, fitted with two postdrawing ovens, at Lankhorst Indutech BV, The Netherlands. The tape-drawing process is described in more detail elsewhere,[1,2,36,38] but in essence consists of a first, low temperature drawing stage, followed by a second high temperature drawing stage. The temperatures applied have been optimized for mechanical properties of the tapes, but the effect on interfacial properties will be presented in this article.

The polymers used for coextrusion were selected by virtue of their different melting temperatures, and by matching viscosities at the extrusion temperature. The tapes are coextruded to possess an A:B:A (copolymer:homopolymer:copolymer) structure as shown in Figure 2. This figure shows a transmission optical micrograph of a group of tapes consolidated into a unidirectional composite. The bonded copolymer skin layers between each tape are clearly visible between the oriented homopolymer cores. The side view of three layers of tape are shown, and each tape is 65-μm thick.

The greatest proportion of the tape is the homopolymer layer, which is the highly oriented structural component of the tape. The copolymer layer is present to facilitate bonding of the tapes to each other during composite compaction, and so a minimum continual thickness of copolymer layer is desired to

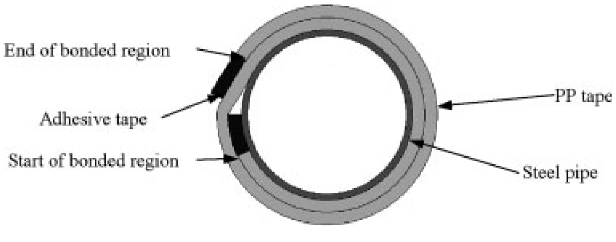

Figure 4 Schematic of tape winding process for the production of tape micro-composites for T-peel and single lap shear interface test specimens.

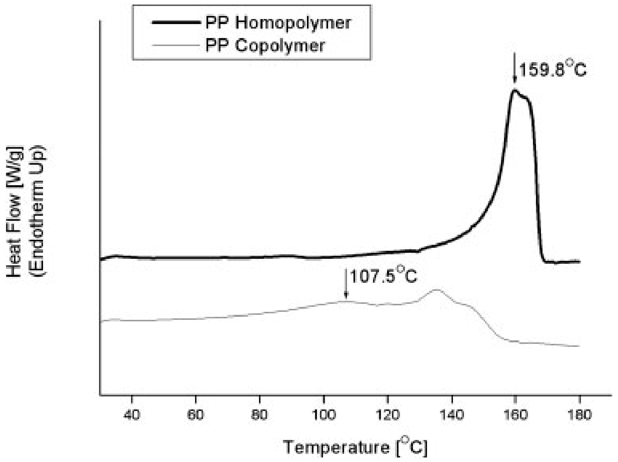

Figure 5 DSC traces of homopolymer and copolymer used in tape production showing the broad melting behavior of the copolymer used for the skin material and the sharp melting peak of the homopolymer core material.

achieve maximum volume fraction of reinforcement in the final composite. This is important as the maximum modulus achieved in PP tapes is 18–20 GPa, while glass fibers possess a tensile modulus of 70 GPa,[39] so for all-PP composites to compete with GFRPP, the volume fraction of PP tapes in the all-PP composite must be maximized. The proportion of these layers can be controlled simply by altering the relative outputs of the A and B extruders. Typically these tapes have dimensions of 2–4.5 mm width and 60–125 μm thickness, depending on the draw ratio, λ. The range of tapes produced for interfacial investigations are summarized in Table II.

The nomenclature used to identify the tapes is described below,

$$x - y - (z)$$

where x is the draw ratio, λ, y is the approximate total percentage copolymer layer, and z is the drawing temperature (where altered).

Differential scanning calorimetry measurement

To determine the melting temperatures of both the homopolymer and copolymer components of the tape, differential scanning calorimetry (DSC) was performed on 5 mg samples of polymer taken from the pellet form, using a TA Instruments DSC Q1000 differential scanning calorimeter. To remove the effect of thermal history on the DSC results, samples were heated in the DSC from ambient temperature to 180°C at 10°C min^{-1} and then cooled to 20°C, also at 10°C min^{-1}. Immediately, the samples were reheated to 180°C at 10°C min^{-1} and the endothermic data was taken from this second heating stage. The data obtained from this method describes the crystalline melting temperature, which is shown as a peak endotherm.

T-peel testing of tape micro-composites

Interfacial failure modes have been investigated by T-peel testing to determine the tapes' resistance to failure by peeling (mode I failure). These T-peel tests were performed on a variety of tapes to determine the effect of draw ratio, copolymer layer thickness, relative copolymer:homopolymer proportion, and drawing temperature on the peeling strength. The T-peel test specimens are composed of two pieces of tape welded together by heating, and then a non-welded region is used to start peeling the welded tapes apart along the weld zone at an angle of 180°. This is illustrated in Figure 3.

Creating model composite specimens via production methods used for all-PP composites are problematic due to the small size of the specimens involved. A hot press typically used for subsequent composite production[2] lacked the accuracy of pressure to provide suitably low pressure to weld the tapes without totally plastically deforming the specimens. To overcome this problem, a new method of creating T-peel test specimens was developed by the author for this research. Coextruded PP tapes were twice wound around a steel pipe, both ends secured with heat-resistant adhesive tape (Fig. 4), and placed in an oven which has been preheated to the desired temperature. The temperatures of the steel pipe and the circulating air are monitored independently by PT100 temperature probes. Once the steel pipe has reached the air temperature, the specimens are held at the required temperature for 5 min. This gave a total residence time in the oven of 15 min. As the pipe temperature increases, the PP tapes exert a cir-

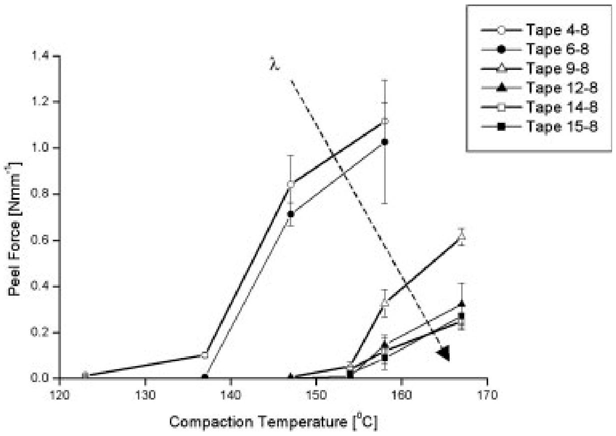

Figure 6 Peel force versus compaction temperature for tapes with increasing draw ratio and constant percentage copolymer showing an increase in peel force with compaction temperature for all specimens but a decrease in peel force with increasing draw ratio.

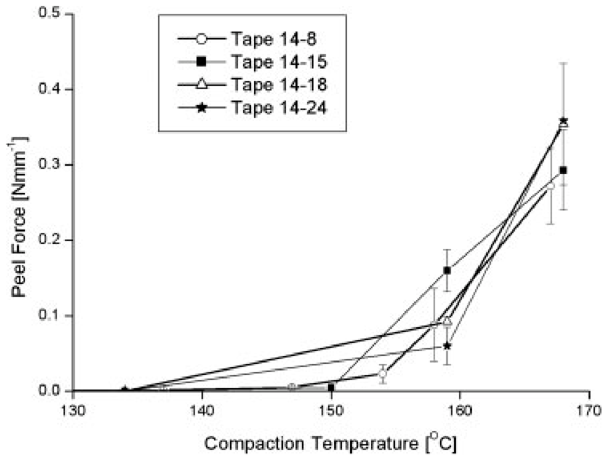

Figure 7 Peel force versus compaction temperature for tapes with increasing layer content showing a uniform increase in peel force with compaction temperature but no significant effect of skin layer thickness on peel force.

cumferential force because of longitudinal shrinkage of the oriented microstructure. This shrinkage is prevented by constraining the PP tapes at either end by the adhesive tape, and also opposed by a radial thermal expansion of the steel pipe. Thus the tape is constrained longitudinally during heating.

As the desired welding temperature is achieved, the two adjacent copolymer layers of the neighboring tapes are bonded to one another, while relaxation of the homopolymer layer is prevented by the longitudinal constraining. After heating, the pipe is removed from the oven, quenched in cold water, and the bonded tape is removed from the pipe. This 'hoop' of tape is then cut to provide two adjacent tape ends, which are used for the T-peel initiation.

T-peel tests are performed in accordance with ASTM 1876; peeling is performed in a Hounsfield HK25S tensile testing machine fitted with a 5 N load cell, appropriate grips, and QMat testing software. The crosshead displacement causes the two-bonded tapes to peel apart in a mode I failure. The tests were performed at a crosshead displacement of 5 mm min^{-1}, and each test was repeated at least five times to ensure reproducibility. Because of the variation in failure modes seen, some tests required further repetition to be sure that the test results accurately reflect the T-peel strength. The values presented for peel force are defined as the force per unit width of tape required to peel the tapes apart, since this tends to a constant value during peeling.

RESULTS AND DISCUSSION

DSC analysis

To understand the thermal properties of the polymer grades used in tape production, DSC traces were recorded as described above. Figure 5 shows the DSC traces of the homopolymer (the reinforcement phase) and the copolymer (the matrix phase). The copolymer used is a random block PP copolymer containing ∼ 6% (w/w) ethylene. The DSC traces shown in Figure 5 have been shifted vertically for clarity. The copolymer possesses a very broad melting peak, with the first maximum at 107°C.

The homopolymer shows a much narrower melting peak at 160°C, and so the melting behavior is much more closely defined. However, the thermal stability of the tape has been investigated,[2] and since molecular relaxation, and hence loss of molecular orientation and associated high mechanical properties, occurs at temperatures far below the melting temperatures of the homopolymer; the melting temperature of the homopolymer is not directly relevant to composite production.

The effect of draw ratio on T-peel strength

T-peel tests performed on tape microcomposites provide useful information about mode and location of failure, as well as peel strength. The parameters varied in this study are tape draw ratio, compaction temperature, and copolymer layer thickness, as described in Table II. Figure 6 shows the effect of compaction temperature on the T-peel force of a range of tapes created with identical composition, but varying draw ratio and compaction temperature. In these tapes, it is clear that there is an increase in peel force with increasing compaction temperature and a decrease in peel force with increasing draw ratio. There is also a noticeable shift in the onset of adhesion with increasing draw ratio, but even for lowest draw ratio tapes, the onset of adhesion is 15°C higher than the initial melt peak of the copolymer determined from DSC measurements as shown in Figure 5.

The onset adhesion temperature is the most important factor because this minimum temperature required for the onset of adhesion will define the

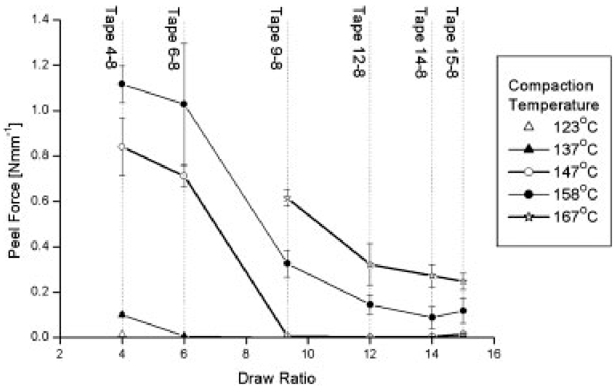

Figure 8 Peel force versus draw ratio for tapes with increasing draw ratio showing a decrease in peel force with increasing draw ratio.

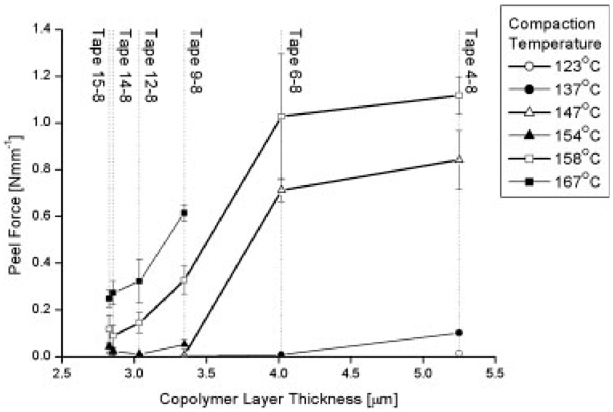

Figure 9 Peel force versus copolymer layer thickness for tapes with increasing draw ratio showing an increase in peel force with increasing layer thickness.

compaction processing window applicable to the final composite. The lowest possible temperature for the onset of adhesion defines the lower limit of the temperature processing window for the manufacture of all-PP composites; the upper limit of this processing window is governed by the temperature at which the tape will show loss of mechanical properties by molecular relaxation. Tapes 4-8 and 6-8 ($\lambda = 4$ and 6, respectively) show very similar behavior, and there is a clear transition to a much lower peel force when $\lambda > 6$. This will be explained later in this article by considering the failure modes operating during interfacial failure.

The effect of copolymer layer thickness on T-peel strength

The increase in the minimum temperature for the onset of adhesion with increasing draw ratio could be due either to an effect of the drawing process on the structure of the copolymer layer or to the reduced thickness of copolymer layer as a consequence of drawing. Figure 7 shows the effect of altering the copolymer layer thickness in tapes with the same draw ratio. Tapes 14-8, 14-15, 14-18, and 14-24, possess increasing proportions of copolymer layer with a constant thickness of homopolymer core, and it is clear that there is little difference in either the onset of adhesion or the levels of peel strengths obtained. It seems that if there is a minimum thickness of copolymer required to obtain good peel strength between two parallel tapes, this thickness is below that of the tapes investigated in this study. Figure 7 also suggests that since all these tapes show very similar peel strength, the difference in peel strength seen in Figure 6 must be related to the drawing of the tapes, rather than the dimensions of the copolymer layer.

Figure 8 shows data for the same specimens that have been presented in Figure 6, but now as a function of draw ratio. The vertical lines superimposed on the graph represent lines of equal draw ratio. Again, the aforementioned transition in peel force at $\lambda \geq 6$ is seen. The high peel strength of tapes with lower draw ratios is of less interest to this research due to the lower stiffness and strength of such tapes. The tapes with lower draw ratios exhibit higher standard deviation in recorded peel force. This is because, during specimen production, the thicker copolymer layers of low draw ratio tapes effectively lubricate adjacent tapes, allowing relaxation and encouraging melting of the tape.

The actual copolymer layer thicknesses due to increasing draw ratio are seen in Figure 9 for tapes 4-8, 6-8, 9-8, 12-8, 14-8, and 15-8, with constant compaction temperatures. Once again, it can be seen that with increasing draw ratio there is a decrease in peel strength. However, Figure 10 shows that the relative thickness of copolymer layer for tapes 14-8, 14-15, 14-18, and 14-24, causes no significant change in peel strength despite a wide range of copolymer layer thicknesses. This proves that the onset of adhesion and the maximum level of peel strength seen is not due to either the relative proportion of copolymer layer on the tapes or the absolute thicknesses of copolymer layer.

The effect of drawing temperature on the T-peel strength

The effect of increasing the temperature in the second drawing oven (Fig. 1) on the mechanical properties of the tapes has been described.[2] Figure 11 shows the effect of this increase of drawing temperature on the

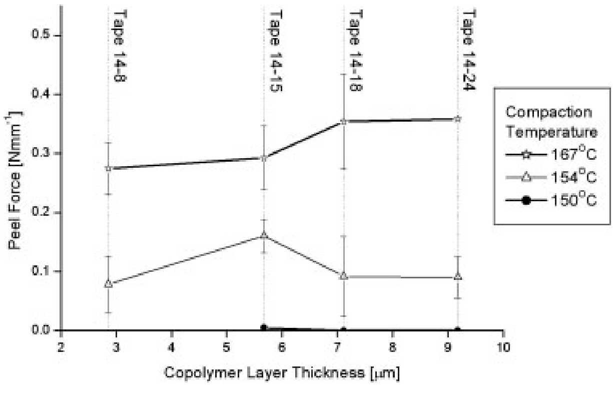

Figure 10 Peel force versus copolymer layer thickness for tapes with increasing proportion of copolymer showing no effect of increasing copolymer layer thickness on peel force. This reveals that the increase in peel force with layer thickness shown in Figure 9 is actually controlled by changes in draw ratio rather than layer thickness itself. (Even though proportions of the tape are constant, tapes with higher draw ratio have thinner skin layers).

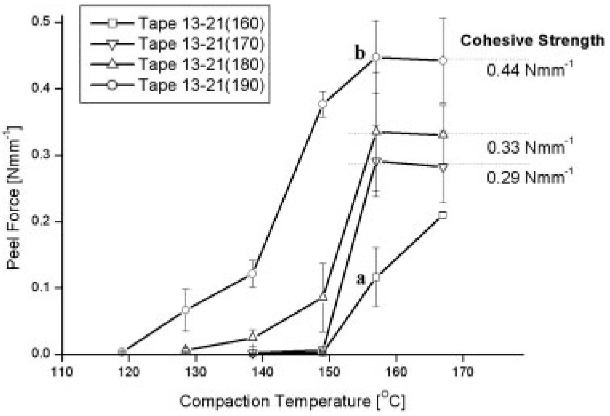

Figure 11 Peel force versus compaction temperature for tapes with increasing drawing temperature showing an increase in peel force with compaction temperature until a maximum is reached for each drawing temperature. Samples a and b are highlighted and shown in further detail in Figure 12.

peel properties of four tapes with the same composition. There is a shift in the onset of adhesion to lower bonding temperatures with increasing second oven drawing temperature. There is also an increase in the maximum peel strength for these tapes.

As the drawing temperature in the second oven is increased, increased relaxation is seen in the orientation of the tapes. This is seen as a decrease in tensile modulus, and also appears here as an increase in the maximum peel strength of the tape. Just as increasing draw ratio causes greater orientation which reduces the cohesive strength (through thickness tape strength) of the tape, increasing the drawing temperature allows relaxation, reducing the orientation, and reducing the degree of fibrillation in the tape. This can also be seen from the transition from an opaque tape appearance to a transparent tape appearance with increasing drawing temperature (Fig. 12). Therefore, with increasing tape drawing temperature, the cohesive strength, which limits maximum peel strength, increases.

The increase in onset of adhesion can also be explained by a similar mechanism. During drawing, orientation is achieved in the homopolymer because the tapes are drawn at an optimum temperature for the homopolymer, which allows enough molecular mobility to allow alignment of tie molecules between crystalline lamellae, but insufficient mobility to allow total flow which would lead to tape breakage in the drawing line. Early work[1] revealed that this optimum temperature is based on achieving the highest tensile stiffness in monoextruded homopolymer tapes. The temperature used to promote the correct degree of molecular movement is relative to the melting temperature of the homopolymer.

During composite consolidation, the melting temperature of the homopolymer is artificially raised by lateral constraining, preventing shrinkage and relaxation of the microstructure.[5,37,40–46] However, during compaction it is necessary for the copolymer to melt to provide bonding between adjacent tapes. Therefore, it is advantageous for the copolymer skin layer to be *unoriented* (Table I). Since the homopolymer and copolymer layers are drawn as one tape during tape production, and the copolymer is present as a very thin film on the surface of the homopolymer core, it is likely that the copolymer will tend to be oriented along with the homopolymer. Thus when the resulting tape is constrained, it is likely that the overheating by constraining technique will apply to increase the melting temperature of both the homopolymer and copolymer. This explains the fact that the onset of adhesion in highly drawn tapes ($\lambda > 6$) bonded so far, occurs above the melting temperature of the copolymer (Fig. 5).

This effect can be reduced by increasing the drawing temperature in the second oven. The temperature in the first oven is not a major concern here, as this needs to be far below the melting temperature of the tapes to facilitate further drawing in the second drawing stage.[1,38] However, since the melting temperature of the copolymer is less than that of the homopolymer, it should be possible to draw the entire tape at a temperature high enough to allow maximum relaxation of the copolymer, while allowing minimum relaxation, and so, loss in tensile properties, of the homopolymer.

In Figure 13, a model of the effect of increasing drawing temperature on interfacial strength of the coextruded tape is shown. It can be seen that increasing the drawing temperature increases the cohesive peel strength suggesting that molecular orientation is reduced with increasing drawing temperature. Tapes drawn at higher temperatures also show a decrease in the temperature of the onset of adhesion since the less oriented copolymer skin layer can exhibit greater molecular mobility at lower temperatures and encourage autohesion between adjacent

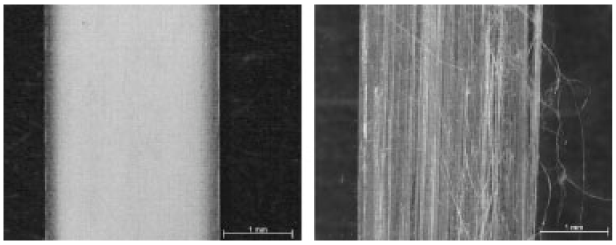

Figure 12 Optical micrographs of peel surfaces taken from samples a (left) and b (right) as shown in Figure 11, indicating the effect of drawing temperature on tapes compacted at the same temperature. Tape a has a smooth surface, indicating adhesive failure between the bonded tapes, whereas tape b has a fibrillated surface indicating cohesive failure within the highly oriented homopolymer core.

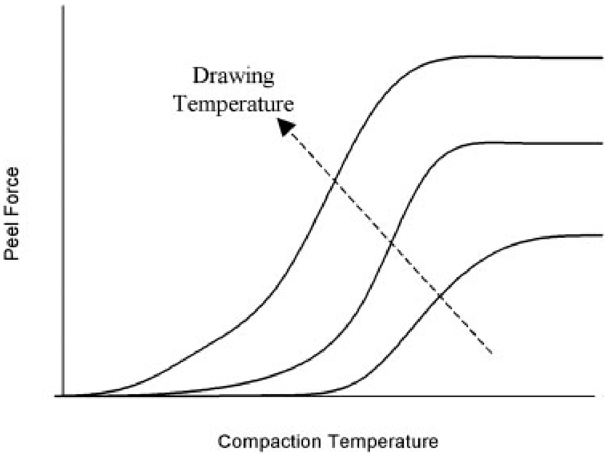

Figure 13 The general effect of drawing temperature on the cohesive strength (the maximum limit for peel force) and the onset of adhesion in all-PP micro-composites.

tapes. This seems a very positive step for the potential production of all-PP composites, as the temperature processing window is widened to facilitate compaction at lower temperature extremes. However, this superior adhesion has to be balanced against the loss in mechanical properties resulting from drawing at a higher drawing temperature, since the reduced orientation which increases cohesive strength also results in lower tensile modulus.[2] Combining tensile data for these tapes with adhesion data from Figure 11, gives Figure 14. Tape 13-21 (160) did not reach a cohesive limit in Figure 11, but the cohesive strength may be predicted from Figure 14 to be ~ 0.26 N mm^{-1}.

Since the improved peel strength is matched with decreased tensile modulus, the exact optimum tape drawing temperature depends on the final composite application. If composite processing techniques can be optimized to reduce the importance of a low onset of adhesion, the optimum tape drawing temperature will shift towards lower drawing temperatures and the subsequent higher mechanical property tape. Conversely, if composite adhesion is required at these very low temperatures, a decrease in tensile modulus is the penalty for this lower temperature adhesion. The cohesive strength seen in tape 13-21 (190) is the maximum possible for this draw ratio, since drawing tapes above this temperature (190°C) resulted in frequent tape breakage during drawing in the oven.

T-peel failure modes in micro-composites

During the experimental research it was noted from these tests that the compaction temperature controls the measured peel force and so also the location of failure of the tapes (see Fig. 12). The interfacial failure can be seen to occur in three regions of the tape, as shown in Figure 15: (a) adhesive failure between two adjacent layers of copolymer, (b) a combination of adhesive failure between adjacent copolymer layers and cohesive failure within the oriented homopolymer layer, and (c) cohesive failure within one of the oriented homopolymer layers. Generally, at lower temperatures (below the crystalline melting point of the copolymer layer) the copolymer layer begins to become 'tacky' as interdiffusion starts to occur (Fig. 5), bonding of the tapes is weak and in peeling, adhesive failure is seen between the two adjacent copolymer layers. As compaction temperature is increased, the adjacent copolymer layers fuse together and molecular interdiffusion causes a combination of failure within the copolymer layer and within the homopolymer layer. This involves an increase in recorded peel force. As the compaction temperature is increased further, the adjacent copolymer layers are allowed to melt and excellent bonding is seen between the two adjacent copolymer layers and also the surface of the homopolymer layer.

Failure in peeling now occurs through a cohesive failure mode within the highly oriented homopolymer layer. This is due to the high orientation of the homopolymer layer which develops a highly anisotropic, fibrillar structure in the drawing process.[47] As draw ratio increases, the amount of isotropic polymer molecules decreases. This means that the transverse strength of the tape also decreases since the strength of the tape in a given direction is due to the proportion of molecules oriented in that direction. Other research[2] presented the effect of molecular orientation on transverse strength by trouser tear tests. These proved inconclusive since the crack had to cross the tough, isotropic copolymer layer which increases the tear resistance and

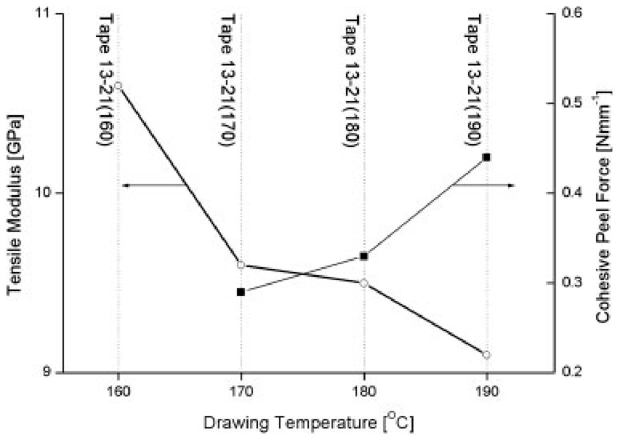

Figure 14 Cohesive peel strength and tensile modulus of tapes drawn as a function of the drawing temperature showing that an increase in cohesive peel strength achieved by increasing the drawing temperature is accompanied by a decrease in tensile modulus.

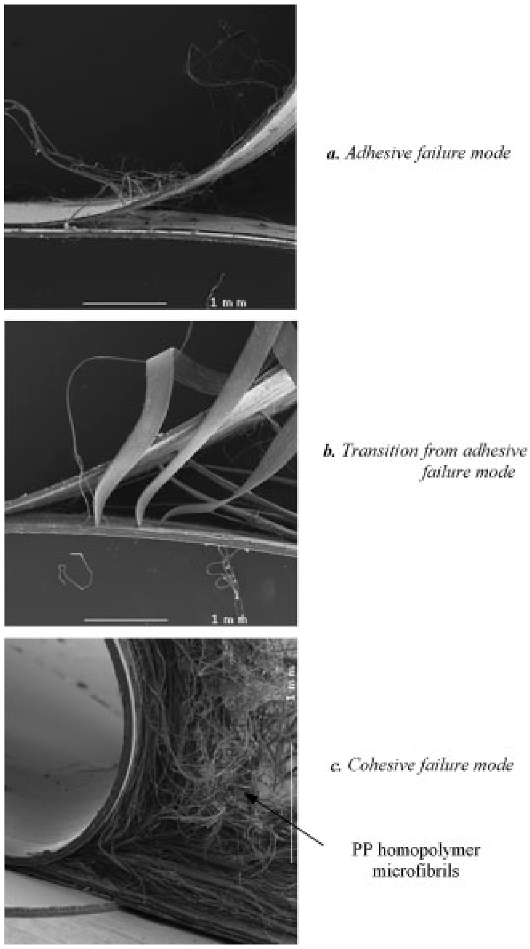

Figure 15 SEM images of different failure modes in bonded tapes showing the range of failure modes witnessed in these tests.

will obscure any possible effect of the increased orientation on the transverse strength of the homopolymer core. The decrease in cohesive strength shown in Figure 14 clearly reveals the decrease in transverse strength because of increasing molecular orientation of the homopolymer core. Hence, a highly drawn tape possesses very high tensile strength in the drawing direction but very low transverse strength, since the exploitation of strong covalent bonds in the drawing direction reduces bonds acting in the transverse direction.

In addition to this orientation factor is the presence of microvoids; a highly oriented tape can be considered to be a bundle of microfibrils held together by few interfibrillar tie molecules and weak van der Waals attraction.[47,48] As the adhesion between neighboring tapes improves, the adhesive strength of the bond exceeds the cohesive strength of the homopolymer layer and so failure moves from an adhesive failure of the interface between the bonded copolymer layers to a cohesive failure of one of the homopolymer layers. The cohesive (transverse) strength of a tape decreases with increasing draw ratio because of molecular orientation (Fig. 6), and so the maximum strength measured during peeling of a tape also decreases with increasing draw ratio since the peel strength is now limited by the cohesive strength of the homopolymer core. For tapes of constant draw ratio, increasing compaction temperature rapidly increases the adhesive strength until it exceeds the cohesive strength of the oriented tape and so the maximum achievable peel force, i.e., the cohesive peel force, is reached.

The relationship between failure location and peel strength is illustrated by test specimens which show transitional failure behavior. This transition is accompanied by a fluctuation in the recorded peel force of the tape. One such example is presented in Figure 16: a force displacement curve, Figure 16(a), a schematic showing the crack path through the thickness of the specimen, Figure 16(b), and a composite photo of one of the peel surfaces, Figure 16(c). In Figure 16(c), the microfibrils are clearly visible on the surface of the tape, and the tape thickness measurements confirm the crack path as described in Figure 16(b). The increase in peel force is clear from Figure 16(a), with the peel force increasing by almost three times during failure in a cohesive failure mode. This is due to the higher energy involved in pulling large numbers of microfibrils from the homopolymer layer.

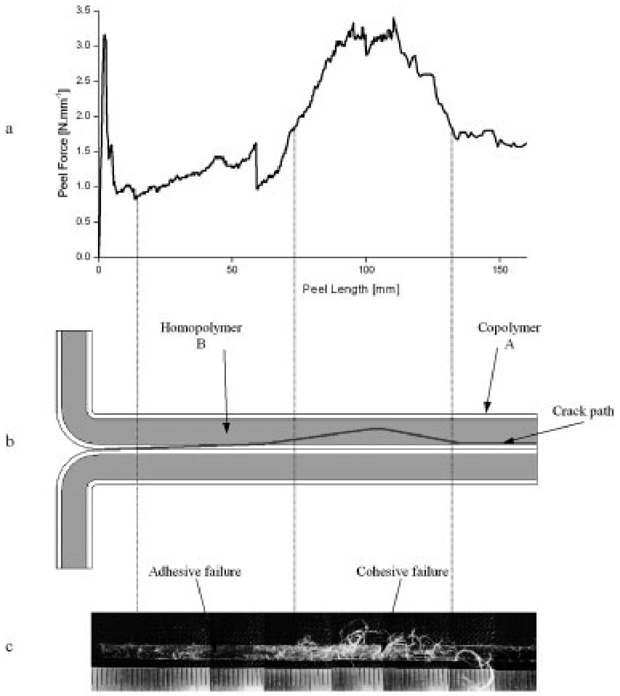

Figure 16 Failure location of a single T-Peel specimen: (a) peel force versus peel length, (b) schematic of peel path, and (c) composite photo of peel surface with mm scale increments. These diagrams illustrate the relationship between failure mode and peel strength.

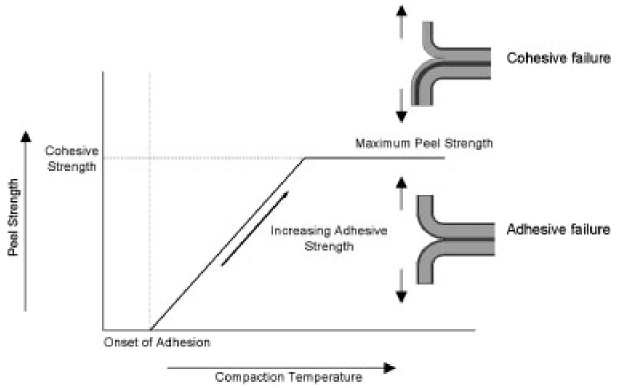

Figure 17 T-peel failure model showing the change of failure mode from adhesive to cohesive with increasing compaction temperature.

The peel strength of tapes can be simplified to a model shown in Figure 17. Bonding starts at an onset temperature dependent on the melting temperature and the degree of orientation of the copolymer used. Peel strength increases with temperature as higher temperatures allow more interdiffusion. Ultimately, the cohesive strength of the highly oriented component of the tape is reached, and this upper bound limits the peel strength. A further increase in temperature may improve adhesion, but since this has exceeded cohesive strength of the oriented homopolymer layer, it is irrelevant to further failure. As temperature increases further, eventually the melting temperature of the homopolymer core will be reached and the entire system will breakdown. These high temperatures are of little interest to all-PP composites since molecular relaxation will have reduced the tensile properties of the tape before the actual melting temperature is reached. Table III summarizes the main effects of tape and composite production parameters on the interfacial properties established in this article.

CONCLUSIONS

The interfacial properties of many composite systems will depend on the compaction conditions during composite production. This is particularly true of single polymer composites, in which compaction parameters control not only the interfacial strength, but also the residual mechanical properties of the reinforcement due to relaxation. The interfacial properties of any composite system may determine the failure mode. The failure mode in all-PP composites has been shown to be controlled by the manufacturing parameters of the tape and the compaction parameters of the composite. Here microcomposites were employed to investigate a wide range of these parameters.

The T-peel strength of all-PP composites for a given homopolymer/copolymer combination is determined by the tape draw ratio, the compaction temperature, and the drawing temperature of the tape. The thickness of the copolymer layer did not affect T-peel strength within the range examined. As adhesive strength increases, it rapidly exceeds cohesive strength, indicating optimal adhesion. The temperature at which bonding occurs is dictated by the melting temperature of the copolymer skin layer. However, it is also affected by the temperature applied during solid-state tape drawing since drawing at too low temperatures results in greater orientation of the copolymer layer and more effective physical constraining of the copolymer layer during consolidation. This decreases molecular mobility of the copolymer skin layer meaning that greater temperatures are required during composite consolidation to achieve autohesion between neighboring tapes.

The temperature processing window for all-PP composites is determined by the difference between the onset of adhesion of adjacent copolymer skin layers at lower consolidation temperatures and the loss of tape properties due to molecular relaxation at higher consolidation temperatures. In this research, the temperature processing window was seen to be >30°C allowing all-PP composites to be consolidated at a range of temperatures. Thus the interfacial properties of the composite can be tailored during production to suit the final application.

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TABLE III
Summary of the Effects of Various Co-Extruded Tape Production Parameters on the Interfacial Behavior of the Final Tapes. ▲/▼ = Property Increases/Decreases, — = No Effect on Property Seen

Production parameter	Temperature processing window	Tape cohesive strength
Increasing draw ratio	▲	▼
Increasing copolymer layer thickness	—	—
Increasing drawing temperature	▲	▲
Increasing compaction pressure	—	—

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