Nanoclay assisted ultra-drawing of polypropylene tapes

Tim B. van Erpa, Christopher T. Reynoldsb, Emiliano Bilottib and Ton Peijsc

aDepartment of Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; bSchool of Engineering and Materials Science, Queen Mary University of London, London, UK; cMaterials Engineering Centre, WMG, University of Warwick, Coventry, UK

ABSTRACT
Isotactic polypropylene (i-PP) – montmorillonite (MMT) nanocomposite films were prepared by melt-compounding and hot-pressing. The influence of organoclay on the mechanical properties and drawability of these isotropic composite films was investigated. Ultimate properties of solid-state drawn PP tapes incorporating 2.5 wt% MMT outperformed those of pure PP tapes. Interestingly, these improvements were found not to be the result of a mechanical reinforcement effect of the nanoclay platelets but merely the result of a more efficient ultra-drawing mechanism with MMT acting as a processing additive that altered initial polymer morphology and drawing behaviour. Hence, the introduction of MMT resulted in higher ultimate draw ratios and subsequently higher ultimate mechanical properties of the oriented nanocomposite tapes.

1. Introduction
The mechanical properties of a semi-crystalline polymer can be significantly improved in a given direction by orienting the polymer molecules in the same direction. Different routes have been described in literature to achieve fibres or tapes with high molecular orientation including melt-extrusion or melt-spinning, gel-spinning and solid-state drawing [1–3]. In particular, solid-state drawing below the melting point has been found to be effective in developing high degrees of molecular orientation and chain extension in a wide range of semi-crystalline polymers, including polyethylene (PE) [4, 5], polypropylene (PP) [6, 7] and poly(ethylene terephthalate) (PET) [8]. By a suitable combination of initial morphology prior to drawing followed by a solid-phase stretching step, highly oriented fibres or tapes can be produced with stiffness and strength values of at least an order of magnitude higher than the original isotropic polymer. These high modulus polymer fibres or films can be used in a variety of applications ranging from ropes, strapping, protective textiles to reinforcements for composites. Moreover, when combined with a polymer matrix...
of the same chemical structure, such fibres or tapes can form the basis for a whole range of self-reinforced or all-polymer composites [9, 10].

Over the last few decades polymer nanocomposites have attracted great interest, mainly because they often exhibit remarkable improvements in materials performance and functionality at low filler loadings. The addition of nanofillers such as layered silicates or organoclays, cellulose nanocrystals, carbon nanotubes (CNT) or graphene nanoplatelets (GNP) have all been explored to boost the performance of oriented polymer fibres or films. Property improvements included not only functional properties such as electrical or thermal conductivities when using nanocarbons like CNTs or graphene but also focused on mechanical performance enhancements [5, 14, 15]. However, the question remains in many of these studies if the improvements in mechanical performance came from true nanofiller reinforcement or from some kind of modification of the polymer matrix. For example, it is well known that the addition of nanoparticles can lead to confinement effects and changes in glass transition temperature [16–18] or nucleating effects and changes in crystallinity [19, 20]. Wang et al. for example studied in detail the influence of polymer morphology on the mechanical reinforcement of an oriented poly(vinyl alcohol) (PVA)/single-wall nanotube (SWNT) composites and could show that for their system the enhanced mechanical properties were a true reinforcement effect of the nanotubes [21]. Deng et al. also showed effective nanotube reinforcement for a PP/multi-walled nanotube (MWNT) system, albeit only at very low filler loadings (≤ 0.5 wt%) [22]. Bilotti et al. showed that small amounts (~2.5 wt%) of needle-like sepiolite nanoclays resulted in a reinforcing effect in oriented PP tapes at intermediate draw ratios (10 < λ < 20). However, thermal analyses suggested that this behaviour was related to differences in degree of crystallinity and morphology of the tapes induced by the nanofiller upon drawing [23]. It is well known that Isotactic polypropylene (i-PP) can crystallise in different crystal modifications. The structure of the thermodynamically more stable α-crystal phase in i-PP does not allow for perfect chain alignment during solid-state drawing. Luijsterburg et al. showed that by adding specific nucleating agents, β-phase i-PP can be obtained which allows for higher draw ratios [24]. It was also shown that when added in the right amount, sepiolite nanoclays lead to a reinforcing effect in the PP tapes.

Recently more research activities have been devoted to the modification of polymer fibre properties using nano-additives as processing aids to improve drawability and ultimate mechanical properties of the oriented fibres or films. Steinmann et al. for example showed that the drawability of polyamide 6 (PA6) filaments could be drastically improved with the addition on nanosilicates [25]. The authors proposed a gliding mechanism between silicate layers to be responsible for the extended drawability of the fibres. Coppola et al. demonstrated that nanoclays could significantly increase the drawability and elastic modulus of polyethylene fibres [26]. D’Amato et al. reported that the introduction of nanosilica in high density polyethylene (HDPE) improved the drawability of fibres, allowing the achievement of higher draw ratios and mechanical properties with respect to the neat polymer matrix [27]. Song et al. reported a large increase in modulus and strength for poly(vinyl alcohol) (PVA)/carbon nano-chip tapes with 0.5 wt % filler loading [28]. They concluded that the nano-chips exfoliated during processing, lubricating polymer chain alignment, leading to higher draw ratios and improved molecular orientation. Yeh and co-workers reported for a range of nanoparticles, including cellulose nanofibres, activated nanocarbons, nano-alumina, nanosilica and CNTs, significant improvements in spinning and ultra-drawing behaviour of ultra-high molecular weight polyethylene (UHMWPE) fibres prepared by gel-spinning [29–32]. It has also been shown that the uniaxial or biaxial drawing characteristics of polymers like HDPE can be improved by the addition of MWCNT or GNP nanofillers, mainly as a result of enhanced strain hardening behaviour and improved deformation stability [33, 34]. All these studies reported improved fibre spinning or drawing characteristics, which potentially can result in improved mechanical properties.

The present study explores the potential of layered silicates such as montmorillonite (MMT) nanoclays as an additive to oriented i-PP tapes. It reports on the effect of MMT on drawing behaviour, potential mechanical reinforcement effects and ultimate mechanical properties of these melt-processed and drawn PP/MMT tapes.

2. Experimental
2.1. Materials and preparation
The materials used for the preparation of the polypropylene nanocomposites are natural montmorillonite (MMT) with a quaternary ammonium salt (Cloisite® 20 A) from Southern Clay Products (now part of BYK Additives & Instruments GmbH, Germany) and an isotactic polypropylene (i-PP) homopolymer resin (Dow H507-03Z) from Dow Plastics (USA). The i-PP homopolymer has a melt flow index (MFI) of 3.2 g/10 min at 230 °C/2.16 kg
and a density of 0.905 g/cm³. The specific density of Cloisite® 20 A is 1.77 g/cm³.

Polypropylene (PP) and different loadings of Cloisite® (0 wt%, 1 wt%, 2.5 wt%, 5 wt% and 10 wt%) were melt-compounded together with 0.25 wt% of Irganox® 1010, a sterically hindered phenolic antioxidant which protects against thermo-oxidative degradation, in a co-rotating micro-extruder (Xplore® MC 15 Micro Compounder, Netherlands) at 200°C for 10 min at 200 rpm. The obtained strands were pelletised in a Collin CSG 171 strand pelletizer and subsequently compression moulded into 1 mm thick isotropic sheets using a Collin E300 hot-press (Germany).

2.2. Mechanical behaviour of isotropic films

Initial mechanical properties and deformation behaviour of PP/MMT nanocomposites with different organoclay loadings were determined on tensile bars (ASTM D638 Type V), cut from the compression moulded isotropic sheets. Tensile bars were tested in a universal tensile tester (Instron 5566, UK) equipped with an advanced video extensometer at room temperature (RT). Clamping length, initial deformation rate and pre-load were 30 mm, 10 mm/min and 0.5 N, respectively.

2.3. Solid-state drawing of oriented tapes

Solid-state drawing was performed on rectangular film specimens (40 mm long and 4 mm wide), which were cut from compression moulded isotropic sheets. Oriented nanocomposite tapes were drawn using an Instron 5584 equipped with an SFL environmental chamber at 120°C, i.e. in the solid-state close to but below the melting temperature. The peak melting point for PP homopolymer and PP nanocomposites as measured by DSC was 164 ± 1°C. Clamping length and deformation rate were 20 mm and 50 mm/min, respectively. In this way, oriented tapes could be prepared that were drawn to different draw ratios. Draw ratios were determined from the separation of ink marks placed 2 mm apart on the film sample prior to drawing. The mechanical properties of the tapes were determined on the same Instron 5566 using a deformation rate and pre-load of 10 mm/min and 0.5 N, respectively. Five specimens of each composition were tested and average values are reported.

2.4. Nanocomposite characterization

The dispersion and orientation of MMT in drawn PP was evaluated using transmission electron microscopy (TEM, Jeol JEM 2010, UK) on ultra-thin samples obtained by microtoming. Wide angle X-ray diffraction (WAXD) images were taken using the Cu Kz radiation, generated with a RINT-2000 (Rigaku Co., Japan), at 40 kV and 20 mA. The distance between sample and detector was 37.5 mm. Non-isothermal thermal analysis experiments were performed using differential scanning calorimetry (DSC, Mettler-Toledo 822e, USA). Temperature was ramped from −30°C to 200°C and back to −30°C with a heating/cooling rate of 10°C/min and isothermal holding periods of 5 min at the minimum and maximum temperatures. During the first temperature ramp the samples were initially melted and re-crystallised in order to erase any previous thermal history. All measurements were carried out under nitrogen. Three samples of each composite were tested.

3. Results and discussion

3.1. Effect of clay content on deformation behaviour of isotropic films

Tensile tests were performed at RT to get some insight in the effect of filler content on the mechanical deformation behaviour of the PP/MMT nanocomposites with 0 wt%, 1 wt%, 2.5 wt%, 5 wt% and 10 wt% Cloisite®.

Table 1 gives an overview of the basic mechanical properties of the PP/MMT nanocomposites. Young’s modulus increased with filler content up to a filler loading of 5 wt% after which the Young’s modulus decreased, most probably as a result of reduced dispersion and the formation of agglomerates as typically observed in nanocomposites of high filler loadings [22]. Yield stress and elongation-at-break was maximum for composites with 1 wt% MMT and decreased gradually with increasing filler content. The elongation-at-break was dramatically reduced at higher filler loadings (Figure 1). The nanocomposites showed a transition from ductile behaviour...
similar to pure PP with yielding, necking and drawing (1 wt%, 2.5 wt%) to brittle fracture (10 wt%), with 5 wt% being the transition from ductile to brittle failure.

Based on composite theory one would expect to see a gradual increase in composite modulus with filler content. Based on a simple calculation using the generalized rule of mixture (RoM) for composites [35] the reinforcing efficiency ($\eta$) of the filler can be estimated using Equation 1.

$$E_{nc} = \eta \, E_f \, V_f + E_m (1-V_f)$$

(1)

Using experimental values for the modulus of the nanocomposite ($E_{nc}$) and assuming a matrix modulus ($E_m$) similar to neat PP (1.23 GPa) and a filler modulus ($E_f$) for MMT of 170 GPa [36], the reinforcing efficiency ($\eta$) of nanocomposites based on 1 wt% (≈0.5 vol%) clay can be estimated at 0.28. This is an indication that the reinforcing efficiency of the clay platelets even for the best performing nanocomposite is rather low at around 28%. In other words, the effective modulus contribution of the organoclays to the composites is only 28% of its theoretical value of 170 GPa. This fairly low reinforcing efficiency is not unusual for nanocomposites and can be the result of platelet misalignment or poor interfacial stress transfer, while at higher filler loadings agglomeration can also play a significant role. The latter is most likely the reason for the even further reduced reinforcing efficiency of the nanoclays at higher filler loadings. For example, for composites based on 10 wt% (≈ 5 vol%) MMT the reinforcing efficiency is only 4%.

In the above analysis we assumed that the modulus of the composite matrix is equal to that of the neat polymer. However, as the elastic modulus of semi-crystalline polymers depends on the degree of crystallinity this may not always be a valid assumption. A higher degree of crystallinity results in an increase in modulus and vice versa. Since nanofillers can act as nucleating agents in semi-crystalline polymers and increase the rate of crystallisation, the amount of crystallinity and modulus of the composite matrix may vary accordingly [19–24]. In order to demonstrate a possible matrix effect to the composite modulus the amount of crystallinity was determined using DSC experiments. Results showed however only minor differences in crystallinity for all samples investigated, with crystallinity levels of around 47% for neat i-PP and 46% for low filler content nanocomposites. Only for PP + 10 wt% MMT the crystallinity was slightly reduced to 43%. This suggests that Cloisite® 20 A did not produce a significant matrix effect and that the MMT platelets did induce some reinforcing effect into the isotropic PP matrix, albeit rather limited.

3.2. Effect of clay content on drawing behaviour of oriented tapes

Oriented tapes were produced by solid-state drawing at elevated temperature with a wide range of draw ratios ($\lambda$) to determine the effect nanoclay addition
on the drawing behaviour and mechanical properties of the resulting oriented tapes. Based on the previous tensile test results, only composites with 1 wt%, 2.5 wt% and 5 wt% were considered for these drawing experiments. Isotropic tensile testing of PP + 10 wt% MMT nanocomposites showed a marked reduction in elongation-at-break compared to pure PP and therefore no solid-state drawing was performed on this composite system.

A common problem of solid-state drawing in a hot-air oven is multiple necking of the sample, which leads to localised orientation instead of homogeneous stretching of the sample. Consequently, here tapes are produced with a minimum draw ratio $\lambda = 5$. Figure 2 gives the stress-strain curves of oriented tapes drawn at 120°C to different draw ratios, displaying an impressive tensile strength of around 860 MPa for nanocomposite tapes of the highest draw ratio ($\lambda = 27$).

Figure 3 shows a TEM micrograph of PP + 2.5 wt% MMT nanocomposite tapes drawn to a draw ratio of 17. The layered silicates are clearly well aligned in the polymer drawing direction. At the same time they also seem to suggest some solid-state drawing induced exfoliation with a sliding mechanism between the clay nanoplatelets.

2D Wide-angle X-ray diffraction (WAXD) patterns have also been obtained in the (out-of-plane) through thickness direction of PP + 2.5 wt% MMT nanocomposite films and tapes (Figure 4). Figure 4a shows the concentric diffraction pattern characteristic of undrawn isotropic films. Upon drawing, the crystallites will align along the drawing direction. This is associated with a change in X-ray diffraction pattern, which transforms into a pattern with distinct arc-shaped reflections indicating significant orientation of the sample (Figure 4b). Oriented tapes of draw ratio 17 exhibit a pattern composed of
sharp diffraction spots of the (110), (040), (130) and (111) planes of the α-crystal modification of i-PP, indicating a high degree of orientation of the c-axis in the stretching direction [6].

To describe the correlation between the axial Young’s modulus of the nanocomposites to the draw ratio, the model of Irvine and Smith [37] is used in this study. This model predicts the stiffness of oriented systems; starting from an isotropic system, where crystallites are organised randomly. The dependence of the axial Young’s modulus ($E$) on the draw ratio ($\lambda$) in an affine deformation process is given by Equation 2:

$$E = \left( E_h^{-1} - \frac{1}{2} \frac{2 + \lambda^{-3} \cos^{-1}\lambda^{-1/2}}{1 - \lambda^{-3}} \left( E_c^{-1} - E_h^{-1} \right) \right)^{-1}$$

Here, $E_h$ and $E_c$ refer to, respectively, the theoretical axial helical chain stiffness (60 GPa) and the stiffness of the non-oriented isotropic i-PP coil (0.6 GPa) [6].

The development of the tensile modulus and ultimate tensile strength with draw ratio for tapes of PP + 2.5 wt% MMT is shown in Figure 5. Figure 5a shows the outstanding agreement of the measured moduli with theoretical predictions using the Irvine and Smith model as also previously reported by other authors for oriented PP fibres and tapes [6, 38, 39, 42].

The development of the tensile modulus and tensile strength with draw ratio for pure PP and all nanocomposite tapes investigated are shown in Figure 6a and 6b, respectively. To improve clarity only the best fit lines are plotted up to the maximum attainable draw ratio ($\lambda_{max}$) for each polymer system.

Both graphs show for all investigated systems a steady increase in mechanical properties with draw ratio. However, the key thing to note in these
graphs is that the highest maximum draw ratio and ultimate mechanical properties are achieved for the PP + 2.5 wt% MMT system. In fact, the maximum draw ratio obtained for this nanocomposite system is significantly higher than that of pure PP ($\lambda = 27$ versus $\lambda = 20$). Another interesting observation is that especially in the case of modulus, all curves show a similar dependence on draw ratio. This indicates that the highest modulus obtained for the 2.5 wt.% MMT system is not the result of some direct mechanical nanoclay reinforcement effect but merely the result of a more efficient ultra-drawing mechanism induced by these clay platelets, basically extending the linear modulus - draw ratio relationship. This aspect becomes even clearer when we plot the tensile strength of the drawn tapes versus the modulus of the tapes (Figure 7). A plot of tensile strength versus tensile modulus (for the same molar mass polymers) results in a kind of master curve, which demonstrates the fundamental material behaviour upon drawing and eliminates parameters such as draw ratio or filler reinforcement. Clearly all investigated systems, PP as well as nanocomposites incorporating 1 wt%, 2.5 wt% or 5 wt% MMT, reveal the same unique relationship between tensile strength and modulus, indicating that property increase is primarily related to the oriented polymer matrix rather than an additional reinforcing effect of the nanofillers.

As mentioned above, the main effect of the addition of clay nanoplatelets is the enhanced drawability of the PP matrix. This enhanced maximum attainable draw ratio ($\lambda_{\text{max}}$) results in a higher molecular orientation and chain extension, which in turn is responsible for the subsequent increase in tensile modulus and tensile strength. It is well known that the maximum draw ratio of melt-crystallised polymers scales with the entanglement density according to the following relationship [5]:

$$\lambda_{\text{max}} \approx M_e^{0.5}$$  

(3)

For example, higher molecular weight polymers exhibiting higher levels of entanglement densities, have shown to display a reduction in maximum draw ratio. Conversely, processing of polymers from a disentangled state as in the case of gel-spinning of polyethylene or polypropylene has shown to lead to
very high draw ratios [5]. By adding 2D nanoplatelets such as montmorillonite clays, an enormous amount of surface area is created in the nanocomposite. This can potentially lead to local disentanglements in the polymer network and a subsequent increase in maximum draw ratio. Besides these type of local disentanglement effects, plasticizing effects due to the presence of organic modifiers on the surface of the organoclay needs to be considered as well. Cloisite® 20 A, for example, contains as much as 38 wt% organic modifier (dimethyl dihydrogenated tallow ammonium, 2M2HT). The addition of nanofillers could potentially also alter the initial polymer morphology and/or crystal structure. DSC results already indicated no significant changes in overall crystallinity for the investigated PP/MMT systems. However, similar to Luijsterburg et al. [24], the addition of nanoclay could lead to a change in crystal phase in i-PP from α to β, which in turn can lead to higher draw ratios.

Interestingly, DSC studies on isotropic nanocomposite films did reveal a minimum peak crystallisation temperature for the system based on 2.5 wt% MMT (Figure 8), indicating that for this particular nanocomposite the presence of the nanoclays somewhat delays the i-PP crystallisation process. This might be an indication that increased drawability for this nanocomposite system is related to a more disentangled state.

While the origin of this intriguing nanoclay assisted ultra-drawing phenomenon still needs further study, the significance of the effect becomes even clearer when we compare the highest obtained moduli and tensile strength of the current nanocomposite tapes with other highly drawn PP fibres and tapes. Earlier reported mechanical properties of PP fibres and tapes in literature are shown in Table 2. The highest mechanical properties achieved in this study were for the PP + 2.5 wt% MMT nanocomposite system. This nanocomposite exhibited a maximum draw ratio \( \lambda_{\text{max}} \) of 27, which produced a tensile modulus of 24 GPa and maximum tensile strength of 860 MPa. The maximum draw ratio for the pure PP tapes in this study was \( \lambda_{\text{max}} = 20 \) with a tensile modulus of 17 GPa and a maximum tensile strength of 650 MPa. Hence, by adding 2.5 wt% nanoclay an increase in draw ratio and tensile modulus of 35% and tensile strength of 30% was obtained compared to pure PP tapes. More importantly, the mechanical properties for the 2.5 wt% nanoclay system are among the highest ever reported for melt-crystallized PP systems. Only higher values have been reported by Kristiansen et al. [44] and Matsuo et al. [45] for gel-spun PP fibres. However, these gel-spun PP fibres or films were drawn from a highly disentangled state, which is known to lead to much greater maximum draw ratios than (highly entangled) melt-processed systems.

4. Conclusions

This paper showed that a small amount of montmorillonite (MMT) nanoclays can act as processing aid to improve the drawability and ultimate mechanical properties of polypropylene (PP) fibres and tapes. It is shown that the addition of small amounts (\( \leq 5 \text{ wt\%} \)) of MMT can improve the tensile modulus and yield stress of an isotropic PP matrix by some 26% and 5%, respectively. However, it was also found that the addition of nanoclays to PP was particularly interesting in the case of highly oriented nanocomposite tapes and improvements in tensile modulus and tensile strengths of 35% and 30% were obtained with the addition of 2.5 wt% MMT. Interestingly the enhancement in ultimate mechanical properties of these highly oriented systems was not the results of some reinforcement effect of these nanoclays but merely the result of a higher maximum achievable draw ratio for systems containing a relatively small amount of layered nanoclays. The exact origin of this nanoclay induced ultra-drawing effect still needs some further research but is most likely the result of some plasticizing effect of the MMT organic modifier or a change in entanglement density either as a result of some local disentangling due to the introduction of a large amount of polymer-filler surface interfaces or retardation of crystallisation. The achieved maximum draw ratio \( \lambda_{\text{max}} = 27 \) and subsequent tensile modulus (24 GPa) and tensile strength (860 MPa) were among the highest ever reported for melt-processed PP fibres or tapes.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on contributors

Tim van Erp obtained his PhD from Eindhoven University of Technology in the area of polymer mechanics. He is currently an R&D team leader at Sabic focusing on application technologies from initiation to commercialization.

Christopher Reynolds holds a BEng in Materials Science and Engineering from Queen Mary University of London and was a Research Manager at Nanoforce Technology Ltd. He is currently a Production Team Leader at AFC Energy plc.

Emiliano Bilotti graduated in Materials Engineering from “Federico II”, University of Naples and obtained his PhD from Queen Mary University of London in the area of nanocomposites. He is currently a Reader at Queen Mary
University of London working in the area of nanocomposites and energy.

**Ton Peijs** is a professor of Polymer Engineering at WMG at the University of Warwick. His research is in the area of structure-processing-property relationships in polymers, composites and nanocomposites. Other areas of research include multifunctional and sustainable polymeric materials.

**ORCID**

Ton Peijs  [http://orcid.org/0000-0002-6686-6005](http://orcid.org/0000-0002-6686-6005)

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