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Review

Fibre preparation and mechanical properties of recycled polypropylene for reinforcing concrete

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ABSTRACT

Polypropylene (PP) fibres have been widely used to reinforce concrete footpaths as an alternative to steel mesh. The reinforcing effect of the PP fibre is directly proportional to its tensile strength and Young modulus. This research explored the feasibility of using an improved melt spinning and hot drawing process to produce virgin and recycled PP fibres of high mechanical properties in an industrial scale. Commercial grade granules of virgin PP, recycled PP and HPDE were mixed in different proportions in preparing five different types of fibres. All the fibres obtained high tensile strength and Young modulus. A relationship between the structural parameters and mechanical properties was then established. It was observed that the melt spinning and hot drawing process formed both α -form and β -form crystals in the PP fibres, and significantly improved crystallinity from about 50 % to 80 %.

KEYWORDS: manufacturing, mechanical properties, differential scanning calorimetry (DSC), crystallisation

INTRODUCTION

Concrete is widely used in construction industry because all the raw materials required are widely available and are of low cost. Concrete is very strong in compression; however, it has a very low tensile strength. To improve its tensile strength, reinforcing steel is often used in concrete. Apart from traditional steel reinforcement, various fibres are used to improve the properties of concrete, such as steel fibre, glass fibre, natural fibre and synthetic fibre.¹

The fibres in concrete can bridge concrete cracks to reduce stress intensity factor at the crack tip and thus prevent the propagation of the crack tip.² In addition, the fibre bridging can decrease crack width, which prevents water and contaminants from entering the concrete matrix to corrode reinforcing steel and degrade concrete.³ The fibres can effectively control and arrest crack growth, hence preventing plastic and dry shrinkage cracks,⁴ retaining integrity of concrete,⁵ and altering the intrinsically brittle concrete matrix into a tougher material with enhanced crack resistance and ductility.⁶ The reinforcing effect of fibre is directly proportional to its tensile strength and Young modulus.⁷

Several techniques and methods have been developed to produce thermoplastic fibres with high tensile strength and Young modulus.⁷⁻¹³ The melt spinning and hot drawing technique is a common method of producing thermoplastic fibres for toughening concrete. The fibres are firstly extruded, and then slowly stretched in an oven with a temperature of 130-150 °C.¹⁰ This method can give polypropylene (PP) fibres of 250-650 MPa tensile strength and Young modulus of 5-15 GPa.¹¹ Another popular processing technique is extruding poly(ethylene terephthalate) (PET), PP or

polyethylene (PE) pellets through a rectangular die to form film sheets. The resulting film sheets are then slit longitudinally into equal width tapes.¹² Kim et al.¹³ melted PET bottles, and then pressed and rolled them into a roll-type sheet (0.2-0.5 mm in thick). The sheets were slit into 1-1.3 mm width thin strands by a slitting machine. Finally, the fibres obtained a tensile strength of 420.7 MPa, and elastic modulus of 10.2 GPa.

A common deficiency of these methods is that they are based on laboratory processes, and they have an extremely low production rate and ensuing high cost. Our research, on the other hand, is focused on development of an improved melt spinning and hot drawing process under industrially feasible conditions. In order to reduce landfill of plastic wastes and improve environmental sustainability, recycled PET fibres have been recently become a focus of research.^{7,10,12-15} However, recycled PP fibre literature is very limited. This paper investigates the possibility of producing recycled PP fibre with high mechanical properties by this process. High-density polyethylene (HDPE) and virgin PP were mixed into the fibre from recycled PP to improve mechanical properties as well. Finally, a more detailed investigation of the structure and relationship between the structural parameters and mechanical properties is presented in this study.

Similar with other polymer fibres, the tensile strength and Young modulus of PP fibres are affected by their physical structure, which is normally controlled by both the choice of starting material and the fibre formation conditions.¹⁶⁻¹⁸ The various conditions for fibre formation during melt spinning and hot drawing caused different arrangement of the supermolecular structural elements, further leading to different

fibre mechanical properties. The starting material with different molecular structure, such as different polymer molar mass and molar mass distribution, contributes to determination of the final mechanical properties of PP fibres.¹⁹ Structural changes in terms of the crystallinity and crystal size distribution, orientation of the amorphous and crystalline phases, and the deformation behaviour at the crystal lattice and lamellae scales occurring in the semicrystalline PPs due to the hot drawing process have been extensively studied.

Lupke et al.²⁰ found that the hot drawing process transformed the initially spherulitic morphology of the PP film into a stacked lamellae morphology (shish kebab) by partial melting. Tabatabaei et al.²¹ found that the deformation behaviour of the crystal structure was dependent on the draw ratio. With increase of drawing rate, the crystal lamellae were first sheared and oriented along the drawing direction and then, at high drawing rate, they were deformed and created a fibrillar structure.

Feng et al.²² reported that during the hot stretching process, the chain disentanglement process dominates, resulting in the relaxation of restrained tie chains and the formation of more folded-chain lamellae. Choi and White²³ found that the mesomorphic structure of isotactic PP (iPP) is more readily formed in lower tacticity fibres, and significant amounts of hexagonal β -form crystals are found in low tacticity iPP fibres spun at high draw-down ratios. Low tacticity iPP fibres exhibited a significant decrease in the crystalline chain-axis orientation at high draw-down ratios, resulting from increased epitaxially branched lamellae. Diana found that in the hot drawing process, the initial metastable structure of low crystallinity was disrupted and a chain-axis orientation of monoclinic crystalline modification was developed.

The hot drawing process increased the crystallite size and crystallinity, the orientation of crystalline domains, and average orientation of the macromolecular chains and resulted in extensive fibrillation and void formation.²⁴

This research has explored the industrial feasibility of using melt spinning and hot drawing process to produce PP fibre under factory conditions instead of laboratory conditions. Virgin PP fibre of high tensile strength and Young modulus has been successfully produced by this method. A relationship has been established between mechanical properties, crystallinity, crystal structure and orientation of PP in the fibre. However, the production of recycled plastics with sufficient mechanical properties is still a major challenge due to degradation during their service life and heat processing stage. The aim of this research is to improve the tensile strength and Young modulus of fibres from recycled PP produced through the melt spinning and hot drawing process. Besides 100 % recycled PP fibre, 50 % of virgin PP and 5 % of HDPE were mixed into the recycled PP fibre to produce 50:50 Virgin-Recycled PP fibre and 5:95 HDPE-Recycled PP fibre, respectively. The mechanical properties of these recycled fibres produced by the melt spinning and hot drawing process are presented and compared with the virgin PP fibre. The effect of 50 % of virgin PP and 5 % of HDPE on fibre from recycled PP are studied in terms of crystal structure and crystallinity by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS).

EXPERIMENTAL

Materials

Raw materials for producing virgin PP, recycled PP and HDPE used in this study are commercial grade granules. Their characteristics given in the manufacturer specifications are presented in Table 1.²⁵⁻²⁷ Five types of fibres were prepared: (a) 100% virgin PP fibre, (b) 5:95 HDPE-virgin PP fibre containing 5 % HDPE and 95 % virgin PP, (c) 100 % recycled PP fibre, (d) 5:95 HDPE-recycled PP fibre produced by extruding 5 % HDPE with 95 % recycled PP, and (e) 50:50 virgin-recycle fibre that was made by extruding mixed raw materials of 50 % virgin PP and 50 % recycled PP.

(Insert Table 1 here)

Preparation of the thermoplastic fibres

As shown in Figure 1, the plastic granules were fed into a single-screw extruder and melted. Temperatures of five heating zones of the extruder were set at 218, 223, 225, 233 and 235 °C. Fibres were then extruded into a water bath from the nozzle at the tip of the extruder. The extruded fiber was pulled to a chill roll and hot-drawn in the oven at 120-150 °C. The resulting fibres through the second chill roll were smooth and had a circular cross-section of around 0.9 mm². An indented roller die was used to mark indents on the fibres, in order to increase the bond strength between the fibres and concrete. After indentation, fibers were cut into a length of 47 mm as Figure 2.

(Insert Figure 1 and Figure 2 here)

Measurements

Tests for tensile strength and Young modulus were performed on the virgin and recycled PP fibres according to ASTM D3822-07.²⁸ The tensile test instrument used for the tests was United STM 'Smart' Test System (STM-50KN) from United Calibration Corporation and was equipped with a 2 kN load cell and data acquisition software. Distance between the clamps was adjusted to obtain a gauge length of 25.4 mm, and extension speed was set as 60 % of the gauge length/min (15.24 mm/min). 30 specimens were tested for each sample. Testing temperature was 20 ± 2 °C.

Fourier transform infrared (FTIR) measurements were carried out with a Perkin-Elmer spectrum 100 FTIR Spectrometer. Fibre orientation degree was obtained by measuring the FTIR spectra with radiation parallel and perpendicular to fibre direction. Contents of crystal and amorphous were calculated in terms of intensity of the absorption bands at 998 and 1153 cm^{-1} bands, respectively.²⁹

Non-isothermal crystallisation and melting behaviour of the fibres were studied using a Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC). About 3 mg of the PP was weighed accurately and encapsulated in an aluminium pan. Samples were heated from 30 °C to 220 °C at the heating rate of 10 K/min to study the melting behaviour of the fibres. The crystallinity and crystalline structure of the PP fibres can be calculated through this heating. The samples were then kept at 220 °C for 5 min to eliminate their thermal history. Subsequently, the samples were cooled to 30 °C at the rate of 10 K/min to study their crystallisation behaviour with temperature; and reheated to 220 °C at the heating rate of 10 K/min to study their

melting behaviour with temperature. All measurements were carried out under a nitrogen atmosphere to avoid thermal-oxidative degradation. In both crystallisation and melting experiments the peak temperatures were obtained for crystallisation temperature (T_c) and melting temperature (T_m), respectively. The crystallinity of the PPs was calculated using Equation (1)³⁰

$$\text{Crystallinity} = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (1)$$

where ΔH_f is the heat of fusion of PP fibres and ΔH_f^0 is the heat of fusion of a totally crystalline PP taken as 207 J/g.³¹

Wide-angle X-ray scattering (WAXS) measurements were performed in reflection mode at ambient temperature using an X-ray diffractometer (Bruker D4 Endeavor). The generator was set at 40 kV and 40 mA and the copper Cu-K α radiation was selected using a graphite crystal monochromator.

RESULTS AND DISCUSSION

Mechanical properties

As can be seen in Figure 3, all the fibres produced by the melt spinning and hot drawing process show a brittle mode of failure, with a short elastic period of steep slope and a regime of sharply rising specific stress until fracturing occurred at strains between 8 and 16 %. Table 2 presents average of the tensile strength, Young modulus and extension of these fibres and their standard deviation. Compared with the mechanical properties of virgin and recycled PP raw materials in Table 1, the

melt spinning and hot drawing process offers the PP fibres much higher mechanical properties. The virgin PP fibre obtains highest tensile strength at 457.1 MPa and very high Young modulus at 7526 MPa, while the recycled PP fibre exhibits 341.6 MPa of tensile strength.

As the raw material properties in Table 1, the MFI of raw recycled PP is 13 dg/min, which is much higher than that of raw virgin PP (only 3.5 dg/min). This means that the fibre from recycled PP has much lower molar mass and hence shorter molecular chains than the virgin PP fibre.³² During the service life of PP products, the recycled PP materials normally have natural aging from long exposure to the air, light, moisture, temperature and weathering.³³ Moreover, the multiple processes under high shear forces and temperatures, and the presence of impurities and oxygen severely damage molecular chain of PPs, including crosslinking, chain scission and formation of double bonds.³⁴ The chain scissions and degradation make the molecular chain easier to be pulled out, forming disentanglement and promoting nucleation of micro-voids and micro-cracks.³⁵ Therefore, the recycled PP fibre had much lower tensile strength and extension than the virgin PP fibre.

When 5 % HDPE was mixed with both the recycled and virgin PP fibre, the Young modulus of both fibres were decreased and the tensile elongations were increased compared with the 100 % recycled and virgin PP fibre. This indicated that the HDPE brought ductility to the PP fibres. However, when 50 % of the virgin PP was mixed with 50 % of the recycled PP, the Young modulus was considerably increased to 9016 MPa, which was even higher than that of virgin PP fibre, and the tensile strength remained as high as the virgin PP fibre at 435.5 MPa. Therefore, the

recycled PP fibre can obtain good ductility from the 5 % of HDPE and can be well modified to obtain high tensile strength and Young modulus by mixing with 50 % of virgin PP.

(Insert Figure 3 and Table 2 here)

Molecular Orientation by FTIR

Molecular orientation of the recycled PP fibre and its raw material was measured by using FTIR spectra with radiation parallel and perpendicular to the fibre and raw material. The intensity of absorption bands at 998 and 1153 cm^{-1} were used to calculate the contents of crystal and amorphous, respectively.²⁹ For quantitative estimation of orientations, the dichroic ratios of 998 and 1153 m^{-1} bands, R_{998} and R_{1153} , were calculated with dividing the intensity of absorption bands in parallel direction (A_{parallel}) by the intensity in perpendicular direction ($A_{\text{perpendicular}}$), that is, $R = A_{\text{parallel}} / A_{\text{perpendicular}}$. The degree of orientation f of crystal and amorphous was further calculated through Equation (2)³⁶

$$f = (R - 1) / (R + 2) \quad (2)$$

As shown in Equation (2), the closer to zero the absolute value of f is, the less orientation the molecules have, and vice versa. As can be seen in Figure 4(a), the recycled raw material in both parallel and perpendicular directions shows similar intensity of absorption bands at 998 and 1153 cm^{-1} . The f_{998} and f_{1153} were calculated as -0.09 and 0.05, respectively. Therefore, the raw material has not obvious molecular orientation. However, after the melt spinning and hot drawing process, the intensities of absorption bands at 998 cm^{-1} of the recycled PP fibre

exhibit significant difference on the both directions as Figure 4(b). The f_{998} was calculated as -0.5, thus the crystal phase of the recycled PP fibre exhibits considerable molecular orientation.

(Insert Figure 4 here)

Crystal structure and crystallinity by DSC

The crystal structure of the PP fibres was studied by DSC. As shown in Figure 5(a) and 6(b), the raw material of recycled PP has a broader melting endotherm than that of the virgin PP, which indicates that the raw recycled PP has more crystals of different sizes, and the raw virgin PP has more uniform crystal sizes. From the Table 3 the raw recycled PP exhibits higher heat of fusion (ΔH) than the raw virgin PP, indicating the raw recycled PP has higher crystallinity. This is why the raw recycled PP has higher mechanical properties than the raw virgin PP as Table 1. As Table 1, the raw recycled PP has much higher MFI than the raw virgin PP, indicating that the raw recycled PP has lower molar mass and shorter molecular chains. In the processing stage and service life of the recycled PP, chain scissions frequently occur, thus significantly reducing the molar mass and shortening the molecular chains. The lower molar mass and shorter molecular chains are easier to rearrange, orient and form into crystals than the longer molecular chains of the raw virgin PP.³⁷

As shown in Table 3, the ΔH and crystallinity of the raw virgin PP are very small (only 76.2 J/g and 36.8 %, respectively). However, after the melt spinning and hot drawing process, the ΔH and crystallinity of the virgin PP fibre are increased dramatically to 106.7 J/g and 51.5 %, respectively. Similar with the recycled PP, the process

improved the crystallinity of the recycled PP from 41.5 % to 50.9 %. Furthermore, as Figure 5(c) the virgin and recycled PP fibres exhibit a double melting endotherm at around 154 and 168 °C. The peak located at 154 °C is ascribed to the β -form crystals and the other is to the α -form crystals.²¹ According to Huo et al., this oriented molecular chains formed α row-nuclei and the oriented α row-nuclei can induce to form β -crystals.³⁸ Somani et al.³⁹ reported that the PP fibres which have a double melting endotherm show a specific shish-kebab structure. The shish in PP had a melting temperature of about 5-10 °C higher than that of the kebabs and about 15-20 °C higher than that for spherulites.

On the α -form crystallisation in Table 3, the virgin PP fibre exhibited higher peak melting temperature (T_m) than its raw material. As Zhao and Ye,⁴⁰ the high-temperature endotherm represents the melting of the highly chain-extended and the highly oriented crystalline blocks formed during the hot drawing process and the low-temperature endotherm is due to the melting of strained non-crystalline region and some partially oriented lamellar. According to Elias et al.,⁴¹ the hot drawing process also can result in a connectivity of molecular chains in the shish or fibrils, thus increasing the crystal thickness. Therefore, a higher melting point was obtained by the virgin PP fibre. However, the recycled PP fibre had slightly lower peak temperature of melting than its raw material probably because of molecular defects and lower purity.

As seen in Table 3, the recycled PP fibre and virgin PP have similar ΔH s (105.4 J/g and 106.7 J/g, respectively) and similar crystallinity (50.9 and 51.5, respectively).

However, as Figure 5(a) and (b) the recycled PP fibre has much higher ΔH on β -form

crystals than the virgin PP fibre. The β -form crystals are much less stable than the α -form crystals.⁴² Due to a large amount of β -form crystals, the recycled PP fibre showed lower tensile strength and Young modulus. Although the oriented α row-nuclei of the virgin PP fibre induced some β -crystals, the α -form crystals were still dominant and the ΔH of β -form crystals was very low in the virgin PP fibre. Therefore, the virgin PP fibre had a large amount of stable α -form crystals, thus showing higher tensile properties.

When 5 % of HDPE was mixed with the virgin PP fibre as Figure 5(a), the ΔH of α -form crystals was decreased and the α -form crystallisation was significantly affected by the heterogeneous structure between HDPE and virgin PP. Moreover, the HDPE offered nucleation sites for β -form crystals, thus improving rate of the β -form crystals. Therefore, the tensile strength and Young modulus of the virgin PP fibre was weakened by the HDPE. On the contrast, the 5 % of HDPE restrained the formation of β -form crystals in the recycled PP fibre, more stable α -form crystals were produced by add the HDPE as Figure 5(b). The recycled PP normally has more molecular defects and lower purity due to the degradation in its service and processing history. The HDPE can act as a compatibilizer, which changes rough phase structure of the molecular defects and some impurities, thus more stable α -form crystals were obtained.

When 50 % of virgin PP was mixed with 50 % of recycled PP as Figure 5(c), a double-melting endotherm is found on the α -form crystallisation. One peak is located on 167 °C, which is close to the T_m of α -crystals of recycled PP fibre; the other peak at 169.8 °C, which is similar with the T_m of α -crystals of virgin PP fibre. Moreover, the

ΔH of β -form crystals on 154.3 °C is much lower than that of recycled PP fibre and slightly higher than that of virgin PP fibre. Therefore, the 50 % of virgin PP not only retains high crystallinity and crystal structure, but effectively restrains the formation of β -form crystals in the recycled PP fibre. Finally, the 50:50 virgin-recycle fibre shows very high tensile strength and Young modulus as shown in Table 2.

(Insert Figure 5 and Table 3 here)

The samples were then held at 220 °C for 5 min, and cooled from 220 °C to 30 °C at a scan rate of 10 K/min. As seen in Figure 6(a), (b) and Table 4, the raw material of recycled PP has lower T_c (114.8 °C) than the raw virgin PP (119.8 °C), indicating that the raw recycled PP is easier to crystallise and can crystallise at a lower temperature. This is due to the lower molar mass and shorter molecular chains of recycled PP, which can be reflected by its lower MFI in Table 1. According to Horvath et al.,⁴³ the shorter molecular chains are easier to be released from the strained or entangled macromolecules, thus the crystallisation can be further developed by the rearrangement of these freed macromolecules segments. The heat of fusion of raw recycled PP is 87.9 J/g, which is lower than that of the raw virgin PP (88.4 J/g), indicating that the raw recycled PP released less thermal energy, formed fewer crystals and less perfect crystals than the raw virgin PP, because the raw recycled PP has more defective molecules and impurity.

As Table 4 and Figure 6, after the melt spinning and hot drawing process, both the virgin PP and recycled fibres obtained much higher T_c (124.8 °C) and more narrow crystalline peaks than their raw materials, indicating the hot drawing process highly oriented and aligned the crystal structures. When the temperature cooled down

from the 220 °C, the ordered molecular structure was more active at higher T_c and thus formed more perfect crystals than the raw materials, which leads to significantly improved mechanical properties of the fibres.

The heat of fusion of recycled PP fibre was also improved to 89.4 J/g, because its short oriented molecular chains can be crystallised easily and quickly. However, the virgin PP fibre obtained lower heat of fusion (87.6 J/g) than its raw material. The oriented molecular chains of virgin PP fibre is more likely to form perfect crystals than its raw material, but it needs more time due to the long molecular chains.

However, because of the same cooling rate in the DSC tests, the virgin PP fibres did not have enough time to form perfect crystals, thus obtained lower heat of fusion.¹⁷ Moreover, the long molecular chains were easier to entangle and entwist together, thus decreased molecular order degree and crystallinity.⁴⁴

When 5 % of HDPE was mixed with the recycled and virgin PP fibres, their ΔH s were improved to 93.8 and 97.8 J/g, respectively, indicating the HDPE had heterogeneous nucleation effect on the PP crystallisation. The crystallisation of HDPE, which can be seen on the small peaks around 118.8 °C in Figure 6(a) and (b), also contributed to the ΔH s. When 50 % of the virgin PP was mixed with 50 % of the recycled PP, the T_c and ΔH was slightly decreased probably due to compatible problems between the virgin and recycled PPs.

(Insert Figure 6 and Table 4 here)

Thermal history of all the samples was eliminated through heating and cooling process, and then the samples were reheated from 30 to 220 °C. As seen in Figure

7(a) and (b), the raw materials still have broad peaks, which are related to three-dimensional crystals known as spherulites and/or rows of lamellae.³⁹ Further, the raw material of the recycled PP has a broader peak than the raw material of the virgin PP, which indicates the crystals of recycled PP have broader size distribution. However, all the fibres show narrow peaks, because the highly chain-extended and the highly oriented crystalline blocks formed fibrils during the hot drawing process. The thermal history of highly extended and oriented molecular chain is hard to be fully eliminated in the first round of heating and cooling.⁴⁰ Small melting peaks from the HDPE can be found for the 5:95 HDPE-virgin PP fibre and 5:95 HDPE-recycled PP fibre. As Table 5 the T_{ms} of all the fibres are only about 165 °C, which are much lower than the T_m of α -form crystals from the first heating in Table 3, indicating that the hot drawing process highly extended and oriented crystalline blocks. Furthermore, the ΔH_s of all the fibres in Table 5 are much lower than those in Table 3, indicating that the hot drawing process significantly improved the crystallinity of the fibres.

(Insert Figure 7 and Table 5 here)

Crystallinity by WAXS

Crystallinity of all the fibres and their raw materials was determined using wide-angle X-ray scattering (WAXS) measurements. In the Figure 8, the raw materials of virgin and recycled PP have four distinct diffraction peaks at $2\theta = 14.2^\circ, 17^\circ, 18.8^\circ,$ and $21.4^\circ/21.9^\circ$, associated with the (110), (040), (130) and (111)/(041) planes, respectively.⁴⁵ The peaks at $2\theta=21.4^\circ$ and 21.9° are the co-diffractions of β phase and α phase. The virgin and recycled PP fibres obtain five diffraction peaks at $2\theta = 14.2^\circ,$

17°, 18.8°, 25.5° and 28.4°. The α - and β - content of the PPs was calculated via the K-value of Turner Jones et al.:⁴⁶

$$K_{\alpha} = \frac{I_{\alpha}}{I_{HDPE} + I_{\alpha} + I_{\beta}} \quad (3)$$

$$K_{\beta} = \frac{I_{\beta}}{I_{HDPE} + I_{\alpha} + I_{\beta}} \quad (4)$$

Accordingly, $K_{\alpha} = 1$ and $K_{\beta} = 1$ for the fully α - and β -crystalline PP, respectively. The overall crystallinity (X_c) was determined by:

$$X_c = \frac{A_c}{A_c + A_a} \times 100 \quad (5)$$

Where A_c and A_a are the areas under the crystalline peaks and amorphous halo, respectively.³⁰ The α -crystallinity is given by $K_{\alpha} X_c$, whereas for the β -crystallinity $K_{\beta} X_c$ holds. The crystallinity values derived from the WAXS measurements are summarized in Table 6.

As shown in Table 6 the raw material of recycled PP has slightly higher crystallinity (51.2 %) than the raw material of virgin PP (47.2 %), because the raw material of recycled PP has lower molar mass, shorter molecular chains and more impurities. The lower molar mass and shorter molecular chains were easier to align and form into crystals, and the impurities greatly decreased the free enthalpy required for the formation of a critical nucleus, which further reduced the critical size of the nucleus and then led to the formation of heterogeneous nuclei.⁴⁷ However, the hot drawing process can considerably improve the crystallinity of the virgin and recycled PP fibre

to 82.7 % and 81.7 %, respectively. The α -crystallinity (given by $K_{\alpha} X_c$) of the virgin and recycled PP fibres were significantly improved, while the β -crystallinity (given by $K_{\beta} X_c$) kept similar to their raw materials.

As shown in Figure 8, after the hot drawing process the virgin and recycled PP crystallise into the monoclinic α -form via diffractions at $2\theta = 14.2^{\circ}$, 17° and 18.8° , associated with the (110), (040) and (130) planes, respectively.⁴⁵ On these facets the diffraction peak positions have no change, but the intensities of the peaks increased drastically. The intensity of the diffraction peak reveals the crystallinity and orientation of materials. It indicates that the hot drawing process did not affect the α -form crystal type, but significantly improved the crystallisation and orientation of the PP fibres. It was interesting to note that these three peaks overlapped to some extent, indicating that both crystal and mesomorphic phases co-existed in the fibres. The (111) and (041) doublet peaks moved to the off-axis and disappeared from the equator after the hot drawing process. On contrary, new peaks at $2\theta = 25.5^{\circ}$, 28.4° are visible, indicating the generation of new β -form crystals.

When 5 % of HDPE was added into the virgin and recycled PP fibre, both their crystallinity were slightly decreased due to the heterogeneous structure. The crystallisation of HDPE restrained α - and β -crystallinity, as shown in Table 6.

Therefore, the HDPE decreased the Young modulus of PP fibres, but increased the ductility of PP fibres as shown in Figure 3. However, when 50 % of virgin PP was mixed with the recycled PP, the α -crystallinity kept as high as the virgin PP fibre, but the β -crystallinity was limited to lower rate of 6.9 % (in Table 6). Therefore, 50:50 Virgin-Recycled PP fibre obtained the highest Young modulus in all the PP fibres.

(Insert Figure 8 and Table 6 here)

CONCLUSIONS

This research explored the feasibility of using a melt spinning and hot drawing process to produce virgin and recycled PP fibres in the factory conditions, in an industrial scale. Virgin PP fibres of high tensile strength and Young modulus have been successfully produced by this method. However, the production of recycled PP fibres with sufficient mechanical properties is still a challenge due to the degradation that has taken place during its service life and heat processing stage. This study focused on improving tensile strength and Young modulus of recycled PP fibres by introducing 50% virgin PP or 5% HPDE during the manufacturing process. Finally, a relationship was established between the mechanical properties, crystallinity, crystal structure and orientation of the PP fibers. The following conclusions can be drawn:

1. The virgin PP fibre of high tensile strength (457 MPa) and high Young modulus (7526 MPa) was successfully produced by the melt spinning and hot drawing process under factory conditions. However, the recycled PP fibre produced by the same method showed significantly lower tensile strength (342 MPa), but comparable Young's modulus (7115 MPa). Fibres made of virgin or recycled PP, modified with 5% HPDE showed higher ductility than the pure PP fibres. Fibres made from 50% virgin and 50% recycled PP showed similar tensile strength and higher Young's modulus compared to the virgin PP fibres.

2. From the FTIR tests, the crystal molecular orientation was found in the recycled PP fibre. The orientated molecular structure offered the fibre high tensile strength and Young modulus.
3. After the melting spinning and hot drawing process, the melting enthalpy and crystallinity of the virgin and recycled PP fibres were increased dramatically. Both α -form and β -form crystals were found in the PP fibres. The virgin PP fibre had high rate of stable α -form crystals, thus obtaining high mechanical properties. However, the recycled PP fibre was found to have a large amount of less stable β -form crystals, so it had lower tensile properties. 5 % of HDPE was found to decrease the α -form crystallisation in the virgin PP fibre, while restrain the formation of β -form crystals in the recycled PP fibre. When 50 % of virgin PP was mixed with 50 % of recycled PP, the 50 % of virgin PP not only retained high crystallinity and crystal structure, but effectively restrained the formation of β -form crystals in the recycled PP fibre.
4. From the WAXS measurements, the crystallinity of raw materials of virgin and recycled PP was measured as 47.2 % and 51.2 %, respectively. The melt spinning and hot drawing process significantly improved the crystallinity of virgin and recycled PP fibres to 82.7 % and 81.7 %. Therefore, the high tensile strength and Young modulus were obtained due to the significantly improved crystallinity.

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Captions for Figures and Tables

FIGURE 1 Extrusion apparatus for monofilaments

FIGURE 2 Virgin (a) and recycled (b) PP fibres

FIGURE 3 Typical stress-strain curves of the PP fibres

FIGURE 4 FTIR spectra of recycled raw material (a) and recycled PP fibre (b) on parallel and perpendicular directions to the raw material and the fibre

FIGURE 5 DSC heating curves of the PP fibres and their raw materials (First round of heating from 30 to 220 °C)

FIGURE 6 DSC heating curves of the PP fibres and their raw materials (cooling from 220 to 30 °C)

FIGURE 7 DSC heating curves of the PP fibres and their raw materials (second round of heating from 30 to 220 °C)

FIGURE 8 WAXS profiles of the polypropylenes

TABLE 1 Characteristics of raw materials of plastic fibres

TABLE 2 Tensile properties of the PP fibres

TABLE 3 Peak temperatures of melting and heat of fusion for the α - and β -form crystals (first heating from 30 to 220 °C)

TABLE 4 Peak temperature of crystallisation and heat of fusion (cooling from 220 to 30 °C)

TABLE 5 Peak temperature of melting and heat of fusion (second round of heating from 30 to 220 °C)

TABLE 6 Crystallinity of the polypropylenes

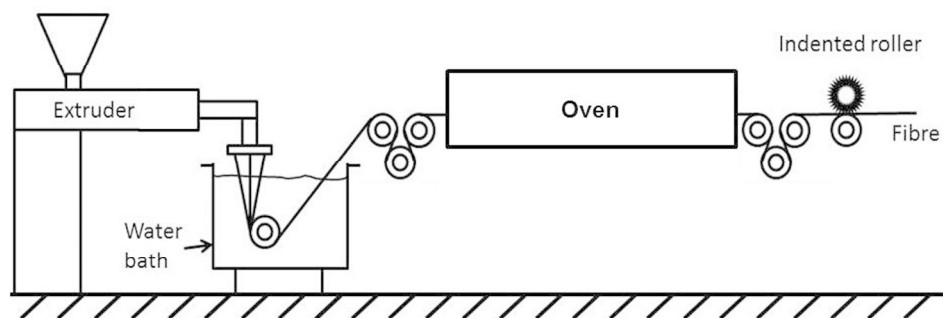


FIGURE 1 Extrusion apparatus for monofilaments
199x76mm (300 x 300 DPI)

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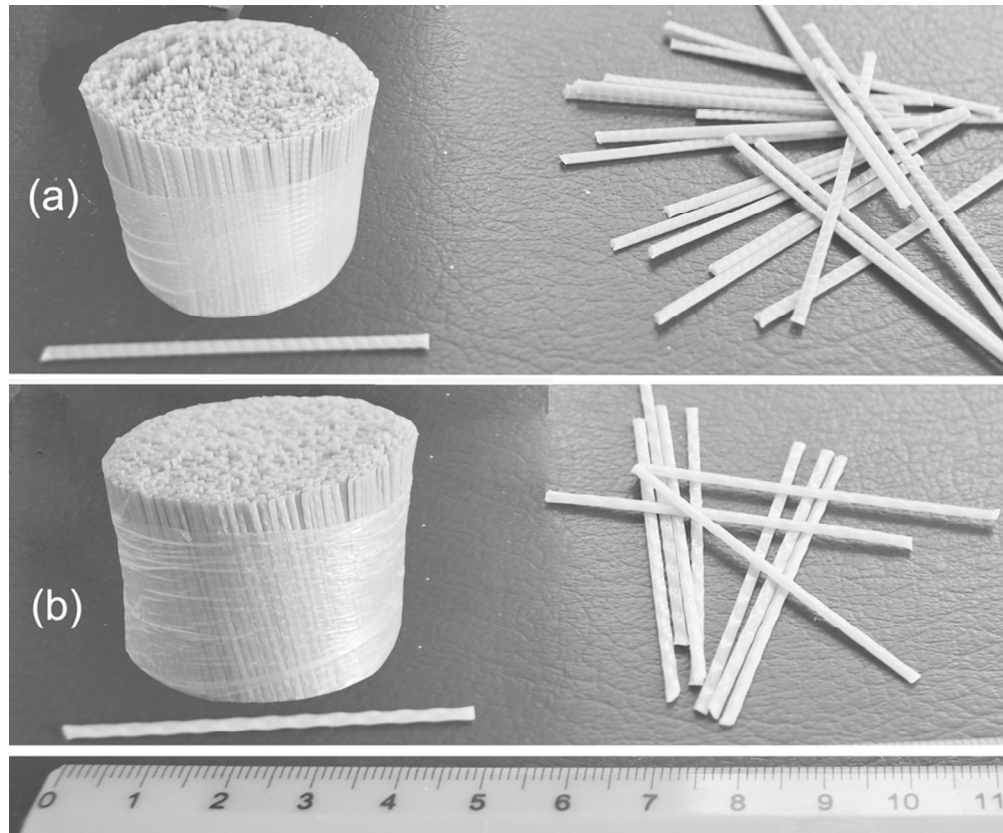


FIGURE 2 Virgin (a) and recycled (b) PP fibres
41x34mm (600 x 600 DPI)

view

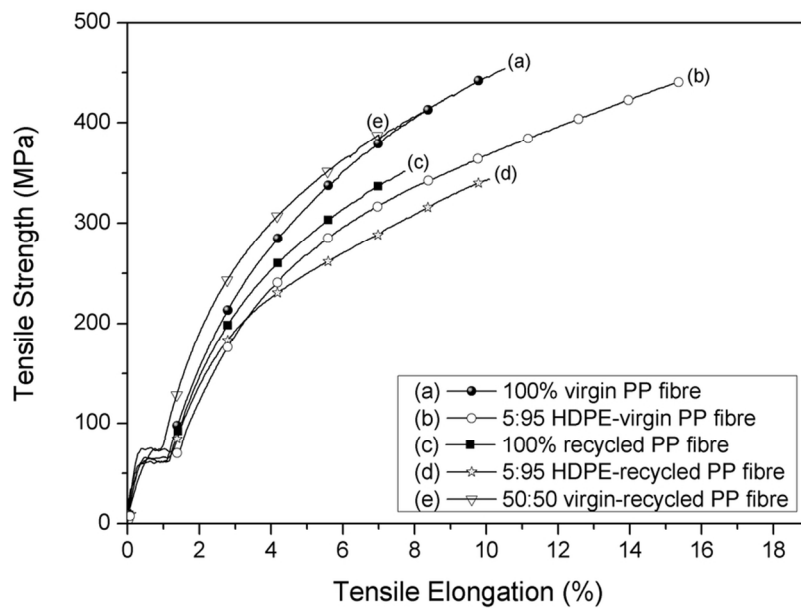


FIGURE 3 Typical stress-strain curves of the PP fibres
48x34mm (600 x 600 DPI)

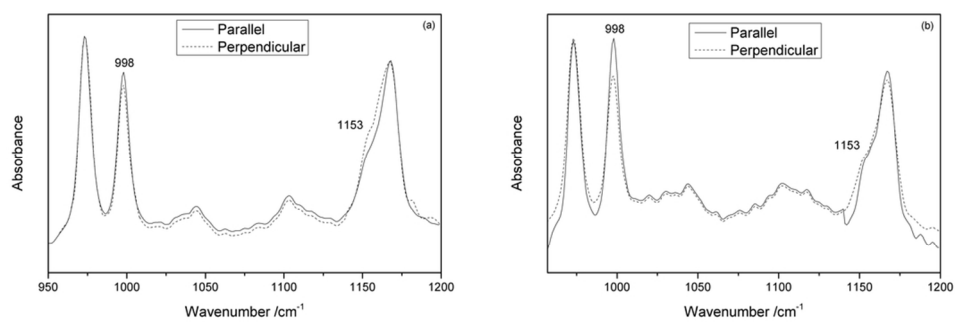


FIGURE 4 FTIR spectra of recycled raw material (a) and recycled PP fibre (b) on parallel and perpendicular directions to the raw material and the fibre
47x16mm (600 x 600 DPI)

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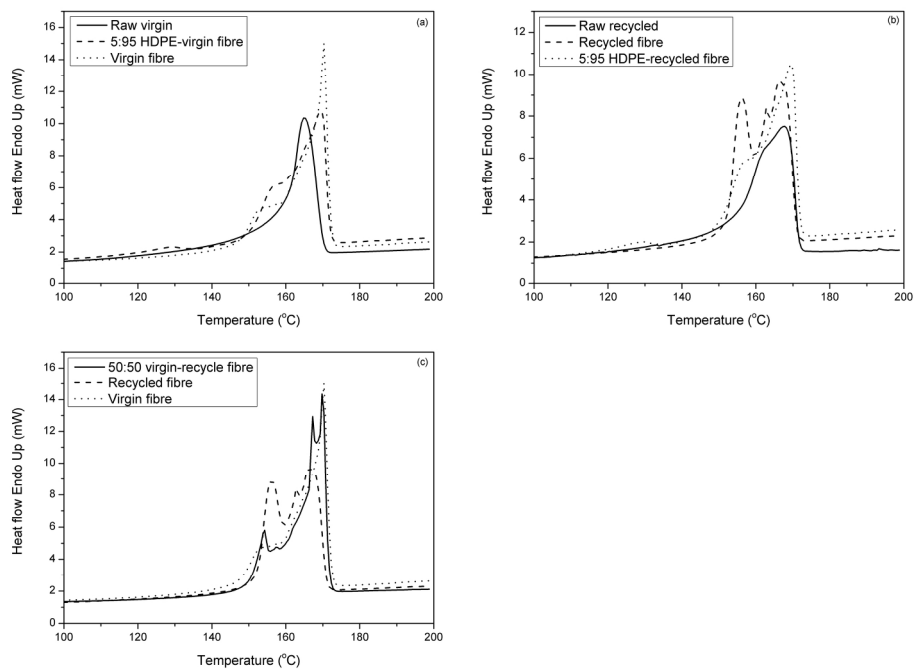


FIGURE 5 DSC heating curves of the PP fibres and their raw materials (First round of heating from 30 to 220 °C)
99x69mm (600 x 600 DPI)

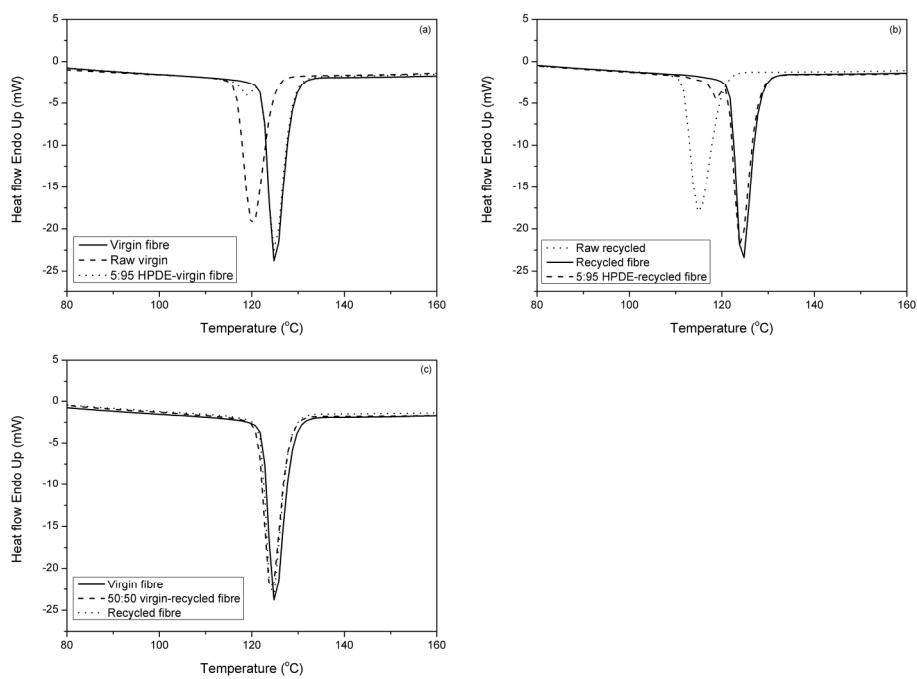


FIGURE 6 DSC heating curves of the PP fibres and their raw materials (cooling from 220 to 30 °C)
99x69mm (600 x 600 DPI)

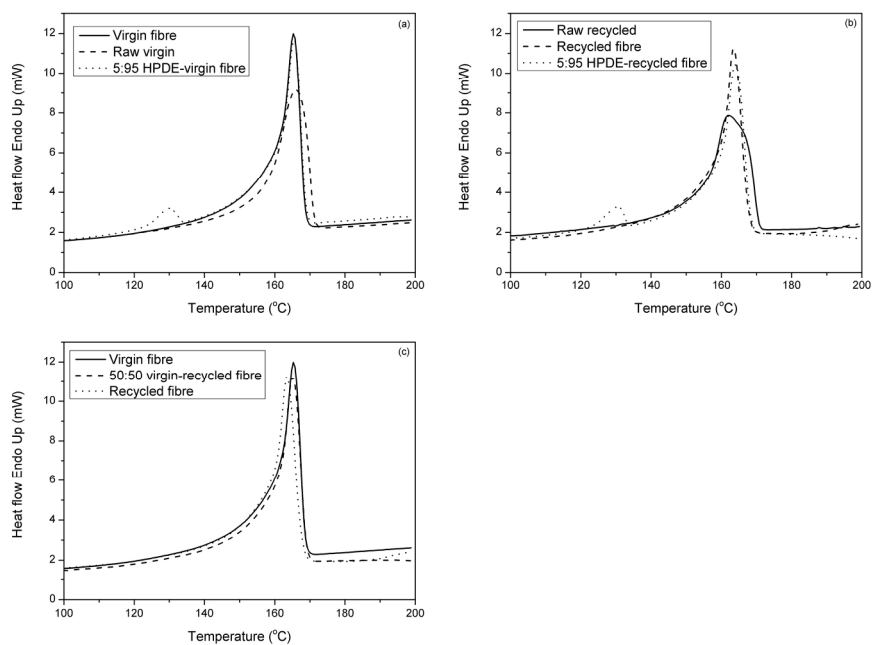


FIGURE 7 DSC heating curves of the PP fibres and their raw materials (second round of heating from 30 to 220 °C)
99x69mm (600 x 600 DPI)

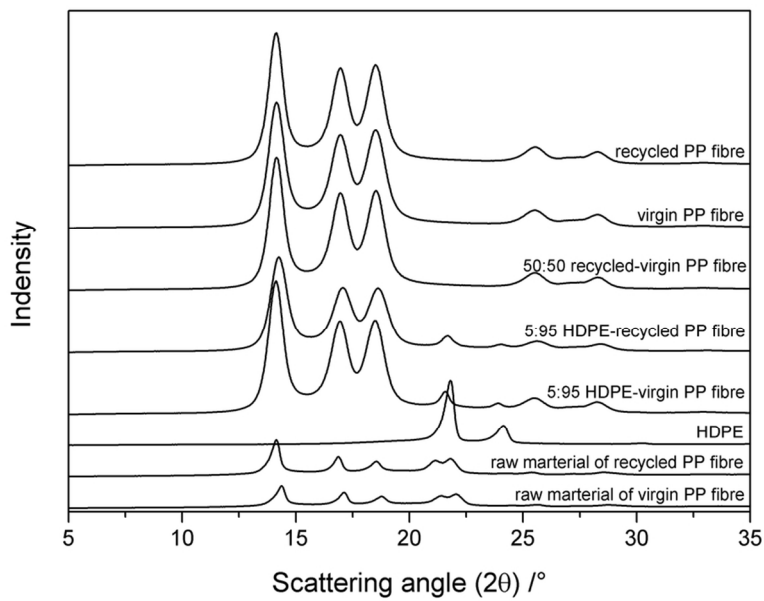


FIGURE 8 WAXS profiles of the polypropylenes
49x34mm (600 x 600 DPI)

TABLE 1 Characteristics of raw materials of plastic fibres

Raw material	Virgin PP granule	Recycled PP granule	HDPE granule
Density (g/cm ³)	0.90	0.90-0.92	0.957
Melt flow rate (MFI, 2.16 kg, dg/min)	3.5 (at 230 °C)	13 (at 230 °C)	0.4 (at 190 °C)
Tensile stress at yield (MPa)	31	35	31.4
Flexural modulus (GPa)	1.25	1.48	
Notched izod impact strength (23 °C, type 1, Notch A, kJ/m ²)	4.7	3.5	5.8

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TABLE 2 Tensile properties of the PP fibres

PP compositions	Tensile strength (MPa)		Young Modulus (MPa)		Tensile elongation (%)	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
	100 % virgin PP fibre	457.1	31.7	7526	2011	10.6
5:95 HDPE-virgin PP fibre	436.0	23.2	6837	1538	16.5	2
100 % recycled PP fibre	341.6	29.3	7115	2083	8.4	2.2
5:95 HDPE-recycled PP fibre	341.9	27.6	6467	2326	9.4	1.7
50:50 virgin-recycled PP fibre	435.5	26.5	9016	1919	8.1	1.4

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TABLE 3 Peak temperatures of melting and heat of fusion for the α - and β -form crystals (first heating from 30 to 220 °C)

PP compositions	T_m of α -form crystals (°C)	T_m of β -form crystals (°C)	Total ΔH (J/g)	Crystallinity (%)
raw material of virgin PP	166.3		76.2	36.8
100 % virgin PP fibre	170.3	152.8	106.7	51.5
5:95 HDPE-virgin PP fibre	169.8	153.3	100.5	48.6
raw material of recycled PP	167.8		85.9	41.5
100 % recycled PP fibre	166.3	156.3	105.4	50.9
5:95 HDPE-recycled PP fibre	169.2	157.3	99.7	48.2
50:50 virgin-recycle fibre	169.8	154.3	104.8	50.6

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TABLE 4 Peak temperature of crystallisation and heat of fusion (cooling from 220 to 30 °C)

PP compositions	T_c (°C)	ΔH (J/g)
raw material of virgin PP	119.8	88.4
100% virgin PP fibre	124.8	87.6
5:95 HDPE-virgin PP fibre	124.8	97.8
raw material of recycled PP	114.8	87.9
100% recycled PP fibre	124.8	89.4
5:95 HDPE-recycled PP fibre	123.8	93.8
50:50 virgin-recycle fibre	123.8	87.3

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TABLE 5 Peak temperature of melting and heat of fusion (second round of heating from 30 to 220 °C)

PP compositions	T_m (°C)	ΔH (J/g)
raw material of virgin PP	164.8	83.2
100% virgin PP fibre	165.3	90.9
5:95 HDPE-virgin PP fibre	165.3	94.6
raw material of recycled PP	161.8	84.3
100% recycled PP fibre	163.8	91.2
5:95 HDPE-recycled PP fibre	164.3	95.4
50:50 virgin-recycle fibre	165.3	92.8

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TABLE 6 Crystallinity of the polypropylenes

Composition	Crystallinity (X_c)	$K_\alpha X_c$	$X_c K_\beta$
Raw material of virgin PP	0.472	0.40	0.077
100 % virgin PP fibre	0.827	0.75	0.078
5:95 HDPE-virgin PP fibre	0.820	0.68	0.063
Raw material of recycled PP	0.512	0.43	0.078
100 % recycled PP fibre	0.817	0.74	0.074
5:95 HDPE-recycled PP fibre	0.799	0.66	0.060
50:50 recycled-virgin PP fibre	0.819	0.75	0.071

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