# Influence of blending proportion on properties of melt spun monofilaments produced from virgin PET and recycled PET blend

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# Influence of blending proportion on properties of melt spun monofilaments produced from virgin PET and recycled PET blend

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## Abstract

Mechanical recycling of post-consumer polyethylene terephthalate (PET) bottles provides a sustainable, green, environmental friendly and cost-effective solution. In the present study, influence of blending recycled PET flakes with virgin PET on melt flow rate, boiling water shrinkage, tensile properties, melting behavior, crystalline behavior, molecular confirmation and yellowing effect is reported. The virgin-PET/recycled-PET blended yarn samples are produced by introducing R-PET in the proportions of 0%, 50%, 60%, 70%, 80%, 90% and 100%. The blend homogenization, melt spinning and drawing is carried out sequentially to produce monofilament yarn samples. The virgin PET sample has highest intrinsic viscosity, boiling water shrinkage stability, molecular weight, and crystallinity. The blended yarn samples with R-PET content of 50-80% have performed marginally similar in terms of tensile stress and strain. The loss of tensile stress and strain is significant when R-PET content in blend is above 80%. IR spectra confirmed presence of hydroxyl and carboxyl groups with –OH links which induces thermo-mechanical degradation of R-PET. The whiteness, brightness and reflectance values decreases in contrast to yellowing index which increases on introducing R-PET content in blend. This study recommends blend produced from mechanical recycling process should restrict the recycled PET content to 70-80%, in order to accomplish minimum desired yarn properties for average strength applications with cost-reduction, minimising environmental impact and raw material conservation.

## Keywords

PET bottle recycling, mechanical recycling, virgin PET, recycled PET, blending, PET monofilaments.

## Abbreviations

PET – polyethylene terephthalate

PP – polypropylene

PE – polyethylene

PA – polyamide

PC-PET (PET-bg) – post-consumer polyethylene terephthalate bottle grade

R-PET (rPET) – recycled polyethylene terephthalate bottle flake

V-PET (vPET) – virgin polyethylene terephthalate pellet

DMT – dimethyl terephthalate

TPA – terephthalic acid

EG – ethylene glycol

BHET – bis(hydroxyethyl) terephthalate

NREU – non-renewable energy use

GHG – greenhouse gas

GWP – global warming potential

V-PET/R-PET – virgin PET and recycled PET blend (proportions in weight)

MFR – melt flow rate (gram/10 minute)

IV – intrinsic viscosity (dL/gram)

## 1. Introduction

Polyethylene terephthalate (PET) is classified as a semi-crystalline thermoplastic polymer produced from either Dimethyl terephthalate method (DMT) or Terephthalic acid (TPA) method. In the former method, the product bis(hydroxyethyl) terephthalate (BHET) is obtained from ethylene glycol (EG) and dimethyl terephthalate (DMT) by transesterification reaction. In the latter method, bis(hydroxyethyl) terephthalate (BHET) is obtained from ethylene glycol (EG) and terephthalic acid (TPA) by esterification reaction. Further, the polymerization of BHET yields polyethylene terephthalate often recognized as PET. PET bottles are produced through blow moulding process by air blowing and stretching the amorphous PET perform (Awaja & Pavel, 2005).

PET possess good barrier, chemical, thermal and mechanical properties. It is used worldwide to produce range of products such as bottle and food containers, textiles (fiber, yarn and fabrics), nets, strappings, foils, films, resins, automotive parts, electrical insulation, acoustics, packaging material, civil engineering, geotechnical and industrial applications (American Chemistry Council, 2016). The identification of PET resin can be done with the code printed on various products as represented in Figure 1. The modest cost along with associated properties such as clear and transparent color, light weight, absence of Bisphenol-A, good impact behavior, shelf life, chemical resistance and barrier properties against light, gas, and microorganisms made PET favorable for application in water or beverage bottles. Food grade application recommends use of virgin PET due to health concern. Therefore, more often post-consumer PET (PC-PET) bottles are considered as a single use material. A major share of the PC-PET bottles are discarded which contributes in landfills and ocean pollution. The slow rate of natural decomposition of PET imposes challenge to manage the quantum of solid waste. The photolytic and hydrolytic degradation under natural environment more often alters surface chemistry; the bulk polymer under accelerated ageing requires a temperature closer to glass transition temperature for possible decomposition reaction (Sang et al., 2020). The biological degradation entails intricate process and is economically not viable (Awaja & Pavel, 2005). The PET waste management can be regulated by opting for either incineration or recycling process. The incineration process with energy recovery is an acceptable solution considering its lower acidification potential with reduced burden on fossil fuel requirement (Aryan et al., 2019). However, recycling is advantageous in contrast to incineration considering low emission of pollutant particles, greenhouse gas, heavy metal,

and dioxins with considerable quantity of raw material savings (Aryan et al., 2019; Chilton et al., 2010). The thermoplastic nature of PET polymer makes it worthy for remolding and recycling process. There is a growing intent towards sustainability by implementing 3-R concept – reduce, recycle and reuse. Recycling of PET into fibers and filaments is advisable considering improved societal awareness, responsibility and imposition of stringent law and regulations for environmental protection. PC-PET recycling provides a sustainable solution by second life to product, solid waste management, availability of R-PET at cheaper rates, limits virgin raw material dependency, reduced energy requirement, and lower processing cost.

According to the data obtained from National Association for PET Container Resources (NAPCOR), PET bottle recycling in United States stands at 29.2% in 2017. The major share 47% of the R-PET produced was used in fiber production. The other uses includes 21% as food and beverage bottles, 19% in sheet and film production, 8% as strappings, 4% in non-food bottles and 1% others (NAPCOR (National Association for PET Container), 2018). Globally, out of the total PC-PET flakes collected, fiber production and bottle to bottle conversion contributes to 72% and 10%, respectively (Shen et al., 2010, 2011). The European nations have made significant progress in PET recycling compared to the rest of the world. The recycling of PC-PET bottle is greatly influenced by the type and the concentration of foreign matter (contaminants) such as water, coloring matter, acetaldehyde, PVC, PA, PP, PE, acid generating substances, pesticides, and detergents (Awaja & Pavel, 2005; Itim & Philip, 2015). Appropriate means of waste collection system, sorting and segregation methods is of utmost importance involved in PET recycling. According to (Gomes et al., 2019), there is a need for consideration of social and economic analysis and energy efficient recovery routes apart from the environmental impact for selecting PET recycling methods.

The recycling of PC-PET is broadly categorized into primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (incineration with energy recovery) recycling methods. The mechanical recycling method is again sub-categorized as – flake to fiber conversion process (mechanical recycling), flake to pellets and pellets to fiber conversion process (semi-mechanical recycling) (Shen et al., 2010). The tertiary recycling method is sub-categorized as – hydrolysis (disintegration into TPA and EG), methanolysis (break down into monomers – DMT and EG), glycolysis (disintegration into oligomer-BHET), aminolyis and ammonolysis (Shen et al., 2010; Sinha et al., 2010). Among the chemical recycling methods, glyclolysis method is the elementary, and economical method and it should be assisted by catalyst (Campanelli et al., 1994; Chen & Chen, 1999). Methanolysis process yields superior PET grade, but has the highest environmental impact compared to glycolysis, mechanical and semi-mechanical recycling methods (Shen et al., 2010). The chemical recycling involves disintegration of PET molecule into the monomers or oligomers. This process can yield PET with high purity and has a wider application range. The chemical recycling method is recommended for bottle to bottle recycling due to fulfilment of food grade packaging safety standards. The PC-PET to fiber conversion using chemical recycling is expensive in contrast to mechanical recycling process (Shen et al., 2010). The bottle to bottle recycling through super-clean recycling processes is not a very economical means considering insignificant cost reduction in contrast to the processing cost involved for bottle production from virgin PET. However, the major push to bottle to bottle recycling is due to increased awareness and reforms for environmental conservation and sustainability (Welle, 2011). Implementation of European Recycling Regulation 282/2008 in Europe has made it mandatory for individual recycling process to get acceptance from

European Food Safety Authority (EFSA). Different nations are implementing new laws and regulations to motivate recycling practices for environment conservation. The super-clean recycling processes involving bottle to bottle recycling has been considered hazard-free (Welle, 2013). The life cycle analysis and social life cycle analysis of PC-PET bottles in Mauritius was studied (Foolmaun & Ramjeeawon, 2013). The option included landfilling, incineration with energy recovery, flake production and their combinations. They reported that, environmental and social impacts were least for case considering 75% PC-PET flake production and 25% landfilling.

Mechanical recycling is recognized as green technology due to its considerable lower environmental impact. The chemistry of material is not changed during mechanical recycling process. It involves collection of PC-PET bottles, segregation, bailing, flake conversion, cleaning, and melt extrusion. Shen et al. (2010) studied life cycle analysis of PC-PET bottle to fiber conversion. They reported that compared to virgin PET fiber production, PC-PET flake to fiber conversion has a reduced NREU and GWP impact by 40-85% and 25-75% respectively, subjected to recycling method and boundary conditions. Mechanical and semi-mechanical recycling has lower environmental impact in contrast to chemical recycling (via glycolysis method). The mechanical recycling offers substantial environmental protection by regulating parameters such as abiotic depletion, acidification, eutrophication, human toxicity and aquatic toxicity, GWP, and NREU (Shen et al., 2010). Shen et al. (2011) further reported PC-PET to fiber recycling has lesser environmental impact compared to PC-PET to bottle recycling. The use of bio-based feedstock for PET production minimizes NREU by 21% and GHG by 25%. The recycled bio-based PET has the least impact of NREU and GHG by 35% and 37% respectively. The increase in R-PET content when used for PET production will have positive impact on environment. Multiple recycling of R-PET can have 26% reduction in environmental impacts, which is insignificant after third time recycling (Shen et al., 2011). However, there are certain limitations of mechanical recycling method such as reduction in molecular weight which is assisted by presence of water and other impurities causing chain-scission reactions. They are less often recommended for food-grade applications (Sinha et al., 2010).

Mechanical recycling of PET offers advantage in form of environment and economic considerations. Fann et al. (1997) reported V-PET has higher crystallinity in contrast to R-PET when both are spun at similar speed. However, at high spinning speed crystallinity reduces with increase in R-PET content due to strain induced crystallization. They reported marginal boiling water shrinkage for crystalline structures. The tensile strength increases and elongation decreases when R-PET is spun at higher speed. The drawing process improves tensile properties, but R-PET possesses poor ability for drawing as compared to V-PET. The fully drawn R-PET irrespective of possessing 70% of tensile strength compared to V-PET can be suitably used to meet requirements of industrial applications (Fann et al., 1997). V-PET/R-PET blend has exhibited good compatibility and miscibility without phase separation. The static, dynamic and cyclic fatigue behavior of V-PET/R-PET blend offers acceptable properties. Increase in R-PET content has offered an increase in tensile strength with minor enhancement in crystallinity and reduced elongation (Elamri et al., 2007). According to the investigation by Lee et al. (2013) R-PET exhibited a faster rate of crystallization and lower thermal stability as compared to V-PET. Melting temperature decreases on increasing R-PET content in blend. Drawn fiber yield higher tensile strength, modulus and birefringence with lower elongation, attributed to improved orientation. The V-PET/R-PET blend with 70% composition exhibited similar mechanical behavior as compared to 100% V-PET (Lee et al., 2013).

The increase in number of extrusion cycles causes break in ester bond of PET dominated chain scission leads to reduced molecular weight of polymer, viscosity, modulus and toughness. PET degradation is associated with formation of cyclic oligomeric species (with glycol unit) increases evident from forth reprocessing cycle (López et al., 2014). Repeated reprocessing cycle leads to increase in crystallinity, reduced melt flow rate with reduction of plastic deformation ability was reported (Badía et al., 2009). The thermal behavior of R-PET contaminated with PP was studied along with the effect of multiple extrusion cycles (Itim & Philip, 2015). Reduction in nucleation rate, spherulite development and crystallinity with increase in molecular movement (melt flow) was observed both for PP contaminated R-PET and multiple extrusion cycles and was attributed to cross-linking of PP with R-PET, copolymer grafting, chain scission and extension. Eccentric rotor extruder based on elongational flow field was employed to recycle PET was reported (Wu et al., 2019). The R-PET produced was found to have superior mechanical properties except toughness, retaining molecular weight of polymer in contrast to R-PET processed on a twin-screw extruder with shear flow field. Another study investigated the possibility of R-PET flakes to be reused for food packaging applications. They observed yellowing of the R-PET, without any hazardous metal traces. They suggested use of R-PET is safe to consider for food grade packaging application (Masmoudi et al., 2018). An intensive study was carried out by Berg et al. (2016) to understand the discoloration of R-PET. The presence of grey color in R-PET is attributed to the presence of antinomy metal based catalyst residues. However, yellow color is associated with the either thermo-oxidative reaction during PET extrusion or formation of azomethine structures on exposing polyamide (used as barrier layers in PET bottles) to higher temperature (Berg et al., 2016).

Efforts were made by different researchers to understand the mechanical, thermal, and rheological behavior of R-PET material. This objective of this paper is to investigate the influence of R-PET content in blended yarn subjected to melt flow rate analysis, viscosity measurement, hot water thermal stability, tensile test, melting and crystallization, absorption behavior and molecular confirmation through IR spectrum, and color change (yellowing effect). This study is intended to estimate the optimum amount of R-PET which can be accommodated in V-PET/R-PET blend without compromising the minimum property requirement suited for average tenacity applications.



Figure 1. Resin code for identification of PET product (American Chemistry Council, 2016).

## 2. Materials and methods

### 2.1 Raw materials

The virgin PET fiber grade polymer pellets was scoured from Reliance Industries, Gujarat, India. The R-PET bottles (transparent in color) were supplied by a local supplier.

## 2.2 Material processing

### 2.2.1 Impurities removal

The process for R-PET bottles into flakes conversion followed by decontamination and cleaning of R-PET flakes has been shown in Figure 2. The removal of impurities and moisture from R-PET flakes has a significant contribution towards mechanical properties of R-PET yarn.
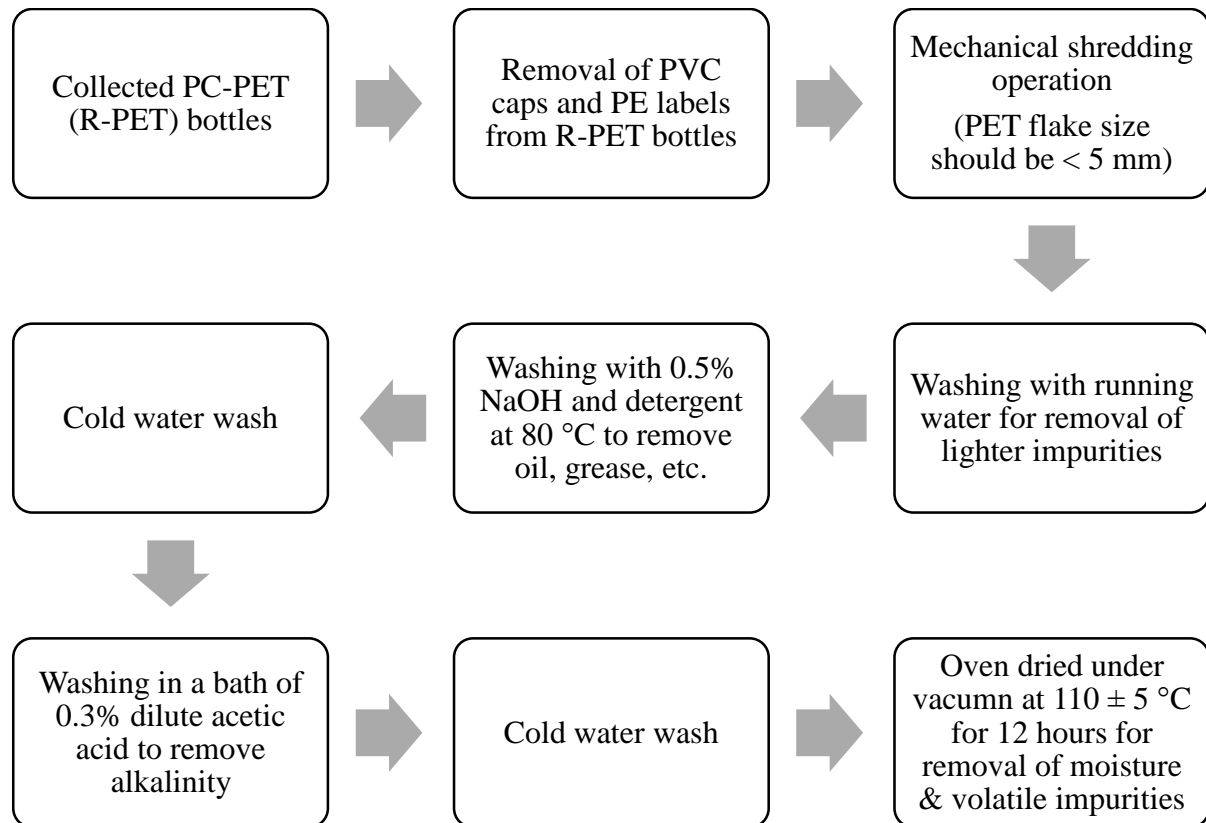


Figure 2. Process flow showing R-PET bottle to flake conversion and removal of impurities (decontamination) from R-PET flakes (Barman et al., 2015).

### 2.2.2 Pelletizing

The pilot scale twin screw extruder was employed to ensure good blend homogenization of V-PET pellets and R-PET flakes. A total of five V-PET/R-PET samples were produced at blending proportions of 50/50, 40/60, 30/70, 20/80, and 10/90. The screws with 20 mm diameter were rotating in coaxial direction with 30 rpm speed and temperature was set at 270 ± 5 °C. This was followed by pelletizing process where V-PET/R-PET pellets were formed. The pellets were oven dried at 100 °C for 12 hours to remove the residual moisture.

### 2.2.3 Monofilament production

Melt spinning is carried out for seven samples out of which five samples were in blended pellet form and two additional samples of V-PET/R-PET in following compositions 100/0 (100% V-PET) and 0/100 (100% R-PET). A single extruder pilot melt-spinning machine with a single spinneret hole (0.5 mm nozzle diameter) was employed. The screw was set to rotate at 100 rpm, spinning speed 1500 mpm and temperature was set for extrusion and spinning

regions at 275 and 280 °C, respectively. The filament was passed through a cold water bath for filament quenching treatment. To improve the molecular orientation inside the PET monofilament it was drawn with the aid of hot godet rollers (draw ratio 2.5) and finally wound on package. The melt spinning prototype machine and different zones of the screw extruder are shown in Figures 3 and 4, respectively.
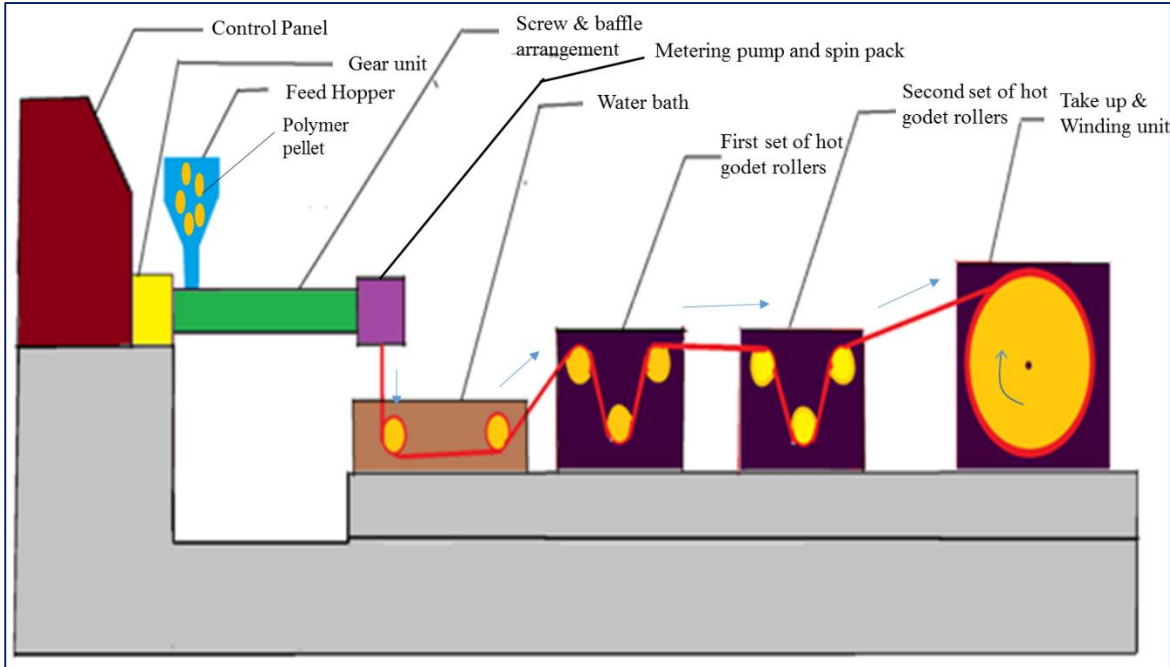


Figure 3. Schematic representation of a pilot scale melt-spinning machine for producing PET mono-filament.
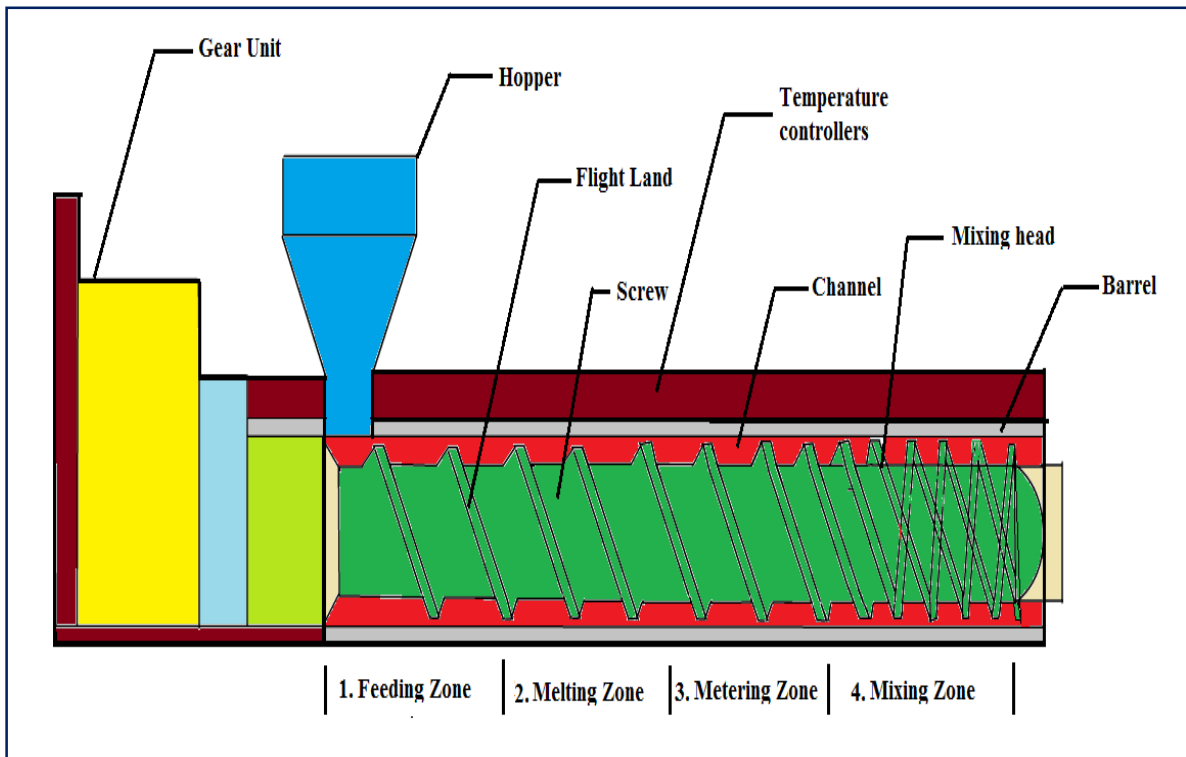


Figure 4. Schematic representation of the different regions inside the screw extruder.

## 2.3 Material test methods

### 2.3.1 Denier measurement

The test was carried out as per ASTM D1907 test method using a wrap reel and weighing balance. It is a representation of linear density of the yarn sample. It is defined as the weight in grams of 9000 meters yarn length. Average of ten reading was considered. The linear density of the yarn sample was 400±3 denier.

### 2.3.2 Melt flow rate and intrinsic viscosity

This melt flow analysis was performed as per ASTM D1238 using extrusion plastometer by Hem- Tech Corporation. The melt flow rate (grams/10 min) was recorded and average of five readings was considered.

Polymer viscosity was measured as per ASTM D4603 test method in an Ubbelohde viscometer. A dilute solution (0.5%) of phenol and 1,1,2,2- tetrachloroethane was formed at 60/40 (v/v) composition at temperature of 30 °C for dissolution of PET polymer. The intrinsic viscosity was computed using Billmeyer equation as followed in previous research (Berkowitz, 1984).

### 2.3.3 Boiling water shrinkage

This test was performed as per ASTM D2259 on A-one Scientific equipment. The percentage shrinkage (%) of the different monofilament yarn samples was observed when subjected to hot water immersion at 90 °C for 30 minutes.

### 2.3.4 Tensile properties

The test was performed as per ASTM D2256 method on Lloyd LRX material testing machine. Test parameters includes gauge length of 250 mm, test speed of 25 mm/min, breaking time was set at $20 \pm 3$ sec. Average of ten reading was considered.

### 2.3.5 Thermal characterisation

Thermographs of different blended samples were obtained using differential scanning calorimeter of make and model − Perkin Elmer DSC 6000. The test involves a heating run from 20-300 °C, followed by a thermal treatment at 300 °C for 180 seconds to eradicate the previous history and thereafter cooling run (crystallisation) back to 30 °C. The heating and cooling cycle was carried out at a rate of 10 °C/minute, 3 bar pressure and gas flow of 10 mL/minute. The crystallinity (% Xc) of the blended samples was computed using the standard equation (1).

$$X_c(\%) = \frac{\Delta H_m - |H_c|}{\Delta H_m^\circ} \times 100 \quad \dots (1)$$

Where, $\Delta H_m^\circ$ is the heat of fusion of 100% crystalline PET ($\Delta H_m^\circ = 135.8$ J g$^{-1}$) (Starkweather et al., 1983), enthalpy of crystallization ($\Delta H_c$), and enthalpy of melting ($\Delta H_m$).

### 2.3.6 Fourier Transform Infrared (FTIR) Spectroscopy

A computer-assisted Fourier Transform Infrared (FTIR) Nicolet-10 Spectrophotometer (Thermo Scientific) is used in the absorption mode and was set in the range 4000-400 cm$^{-1}$.

### 2.3.7 Whiteness, yellowness, brightness indices reflectance

The whiteness, yellowness, brightness indices, and reflectance value of the different PET blended yarn samples were measured using Premier Colour Scan – 5100 Spectrophotometer connected with computer colour matching (CCM) system. The test was performed with following test methods- Stephensen (for whiteness), ASTM D1925 (for yellowness) and TAPPI 452/ ISO 2470 (for brightness). The sample was prepared by wrapping the PET monofilament yarn samples on a white hard paper board (50 mm x 40 mm). The yarn was wrapped in parallel configuration with no interspacing between the adjacent yarn wraps, and that can be correlated as a close packed structure.

### 3. Results and discussion

### 3.1 Influence of V-PET/R-PET blending on melt flow rate and intrinsic viscosity

The melt flow rate analysis shows an upward trend with increase in R-PET content in the blend, opposite behaviour is found for intrinsic viscosity as shown in Figure 5. The 100% R-PET sample has offered highest MFR value of 85 grams/10 min and lowest IV value of 0.59 dL/grams, respectively. The increase in MFR values is associated with lower molecular weight of R-PET which is attributed to thermo-mechanical degradation and shortening of molecular structure due to chain scission reactions of PET caused during reprocessing which is confirmed through IR analysis. This effect is more evident when PET is subjected to higher reprocessed cycles (Badía et al., 2009).
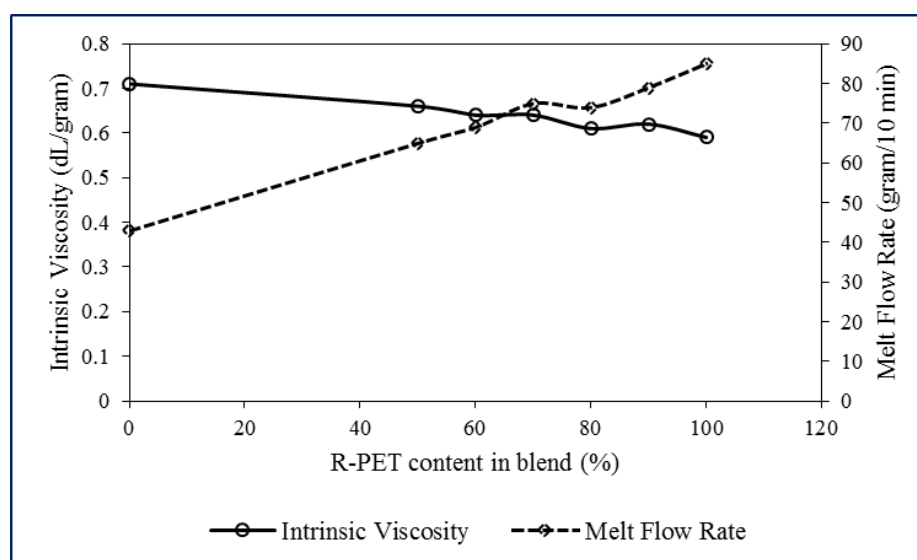
Figure 5. The influence of R-PET content (%) on IV and MFR for V-PET/R-PET blended pellet samples.

## 3.2 Influence of V-PET/R-PET blending on boiling water shrinkage

There is a marginal change in shrinkage behaviour of blended yarn samples when subjected to hot water as shown in Figure 6. The shrinkage was highest for 100% R-PET yarn sample and lowest for 100% V-PET sample at 6.7% and 5.1%, respectively. This behaviour is attributed to lower thermal stability, orientation and crystallinity of R-PET sample which is confirmed through DSC, and IR analysis. On the contrary, R-PET sample has lower molecular weight, shorter length chains and increased molecular mobility due to chain scission reactions which makes the specimen sensitive to boiling shrinkage. The raw material characteristics and composition in blend also influences shrinkage behavior (Fann et al., 1997).

## 3.3 Influence of V-PET/R-PET blending on tensile properties

The change in tensile stress and strain values with increasing R-PET content in blended yarn has been shown in Figure 7. The 100% V-PET sample has exhibited the highest tensile stress and strain at 306.70 MPa and 30.17%, respectively. The effect is attributed to the presence of higher molecular weight in V-PET, ordered and crystalline structure, and relatively longer molecular chain. On the contrary, 100% R-PET sample has offered the lowest tensile stress and strain at 114.40 MPa and 13.24%, respectively. The explanation to this behavior is R-PET has lower molecular weight, short molecular chains due to thermo-mechanical degradation, and reprocessing under higher temperature has caused removal of plastic deformation ability. The blended yarn samples with R-PET content of 50%, 60%, 70% and 80% have performed comparable in terms of tensile stress and strain. The loss of tensile stress and strain is significant when blend possess V-PET content less than 20%.
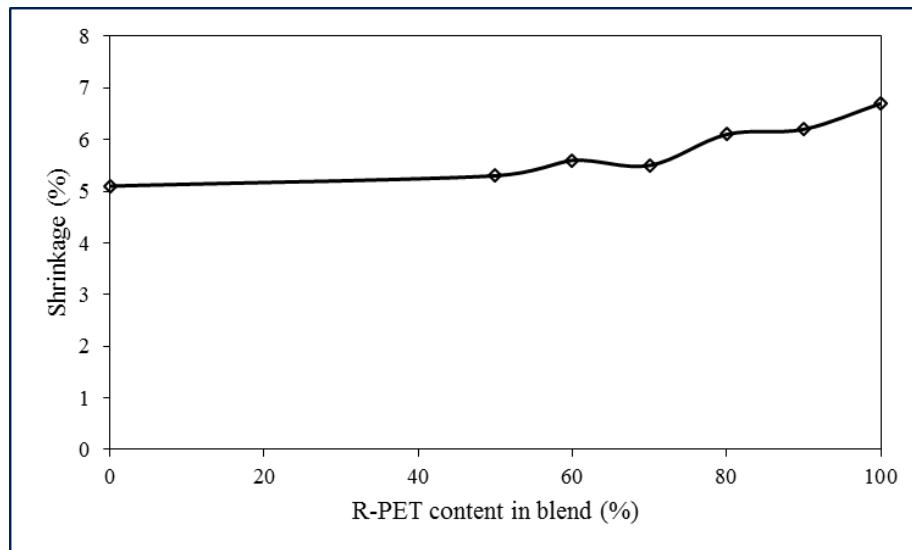


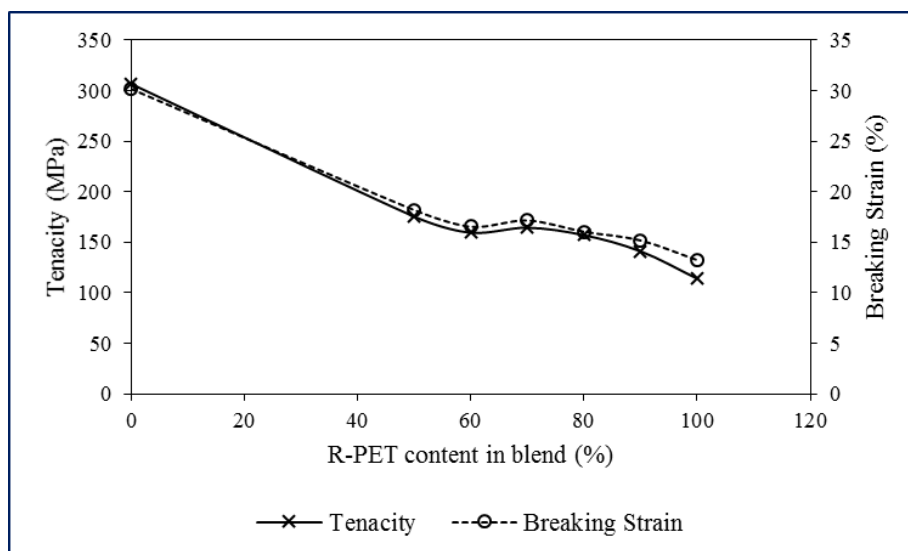Figure 6. The influence of R-PET content (%) on boiling shrinkage (%) for V-PET/R-PET yarn.

Figure 7. The influence of R-PET content (%) on tenacity (MPa) and breaking strain (%) for V-PET/R-PET yarn.

## 3.4 Influence of V-PET/R-PET blending on melting and crystallisation behavior

The DSC thermographs involving heating and cooling scan for different blend compositions has been shown in Figure 8. The effect of increasing R-PET content in blend on glass transition temperature, crystalline temperature and melting temperature has been graphically represented in Figure 9. The crystallisation temperature marginally increases with increase in R-PET content in blend. The thermographs reveal that increasing amount of R-PET content in blend causes formation of narrow and long melt-crystallisation peaks. This behaviour is attributed to the faster rate of crystallisation for the R-PET samples in contrast to the V-PET samples. The presence of contaminants such as traces of metals, chain scission reaction products and oligomers and associated thermal treatment during recycling process opens up the molecular chain to release the residual strain leads to rapid crystallisation of R-PET (Lee et al., 2013). There is a marginal increase in melting temperature with increase in R-PET content in blend. This behavior may attributed to the chain scission reaction occurred during reprocessing of R-PET which may induce crystallization with modification and separation of crystal populations based on crystal dimensions (Badía et al., 2009). Another explanation to this behavior is shorter length molecular chains get accommodated in the long chain polymer network, require high temperature for melting phenomena (Sängerlaub et al., 2020). The glass transition temperature which constitute molecular movement in amorphous region remains almost unaffected except higher glass transition temperature for 100% R-PET sample. The thermographs of all the blended samples have single prominent crystallization and melting peak which confirms the good compatibility and homogeneity within a single phase for both V-PET and R-PET components (Elamri et al., 2007).
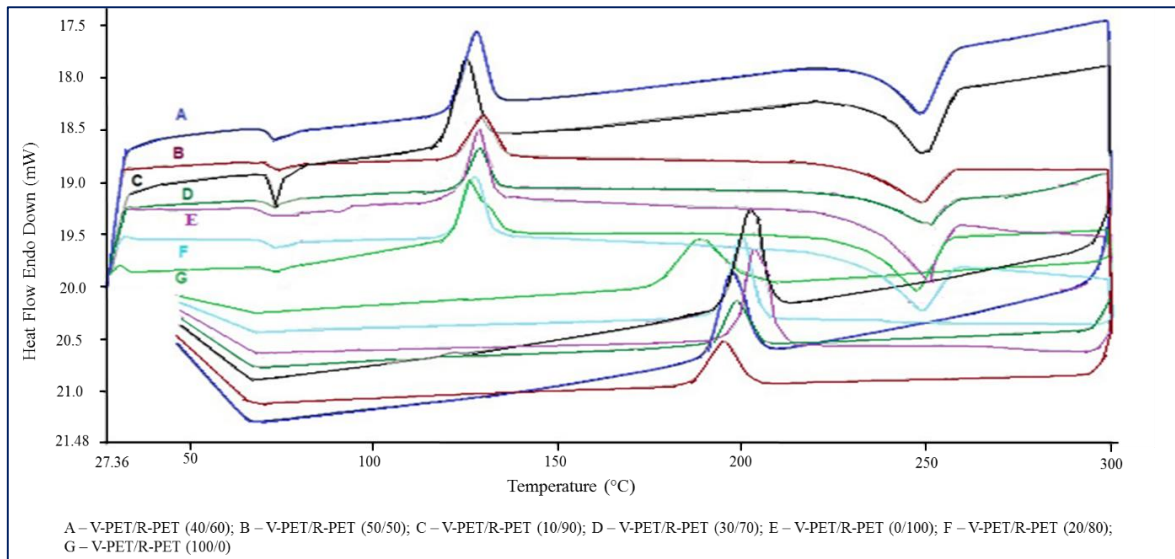
Figure 8. DSC Thermographs showing heating and cooling scan for V-PET/R-PET pellets.

The crystallinity (%) of the samples obtained from DSC indicates that crystallinity content in sample gradually reduces with incorporation of R-PET in blend as shown in Figure 10. The 100% V-PET sample have exhibited highest crystallinity of 36.55%, and 100% R-PET sample has lowest crystallinity of 17.19%. This result is attributed to the presence of dense closely packed molecular configuration, higher molecular weight and longer molecular chain in V-PET. V-PET achieves high degree of crystallinity through strain induced crystallization during thermal drawing and spinning operation (Fann et al., 1997).
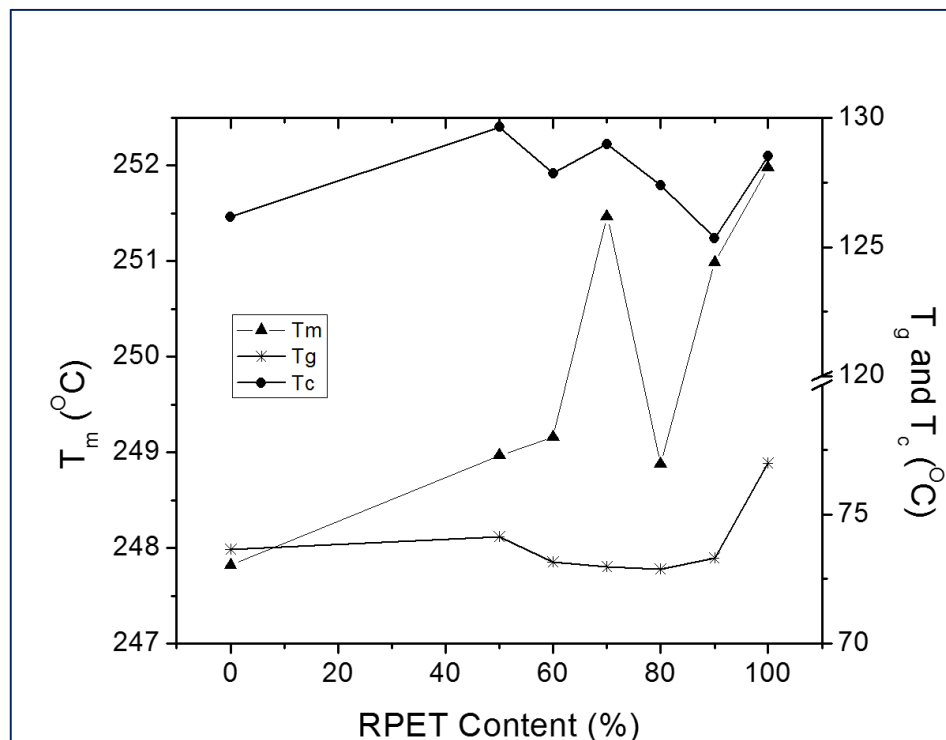


Figure 9. The influence of R-PET content (%) on glass transition temperature, crystalline temperature and melting temperature for V-PET/R-PET pellets.
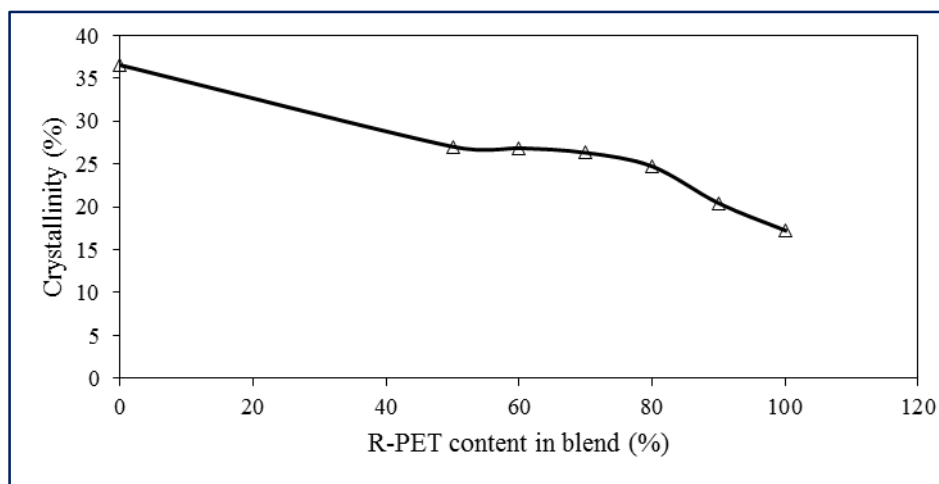
Figure 10. The influence of R-PET content (%) on crystallinity (%) of the V-PET/R-PET pellets.

**3.5 Influence of V-PET/R-PET blending on Fourier Transform Infrared (FTIR) Spectroscopy**

The FTIR spectra of the 100% V-PET and 100% R-PET samples are shown in Figure 11 and 12, respectively. The IR spectrum is helpful to investigate molecular conformation of PET, presence of functional groups, orientation, and change in molecular structure (stretching, vibration, bending of bonds).

The IR spectra for 100% V-PET and 100% R-PET show almost similar absorption peaks. The spectra confirm the presence of characteristic absorption peak for PET as shown in Table 1. In contrast to the 100% R-PET sample, 100% V-PET has exhibited higher absorption value at all the corresponding absorption peaks. This behaviour is attributed to presence of higher crystallinity (%) in V-PET, also confirmed by DSC result analysis. Similar findings was reported by (Acar et al., 2006).

Table 1. IR peak detection in FTIR spectra for V-PET and R-PET specimen.

| Absorption peak detection at corresponding Wavenumber (cm$^{-1}$) for | Absorption peak detection at corresponding Wavenumber (cm$^{-1}$) for | Explanation (Acar et al., 2006; Badia et al., 2012; Holland & Hay, 2002; Varma et al., 1998) |
|---|---|---|
| 100% V-PET sample | 100% R-PET sample | |
| 723.50 | 723.39 | Out of plane distortion or bending of two carbonyl substitute on aromatic ring |
| 872.91 | 872.98 | Vibration of aromatic ring with C − H deformation of adjacent hydrogen atoms |
| 1016.20 | 1016.32 | In plane vibration of aromatic ring |

| | | |
|---|---|---|
| 1041.71 | | 1, 4-substitution of aromatic ring |
| 1092.31 | 1092.22 | Stretching vibration of C − O bonds associated with semi-crystalline structure of PET |
| - | 1174.38 | Bending vibration of − CH$_2$ group |
| 1239.06 | 1239.17 | Stretching vibration of C − O bonds, associated with parallel dichroism |
| 1339.37 | 1339.28 | Bending vibration of − CH$_2$ group, trans, extended, crystalline. Wagging of the ethyl unit |
| 1370.95 | 1370.96 | CH$_2$ wagging mode of the gauche-conformer, relaxed, amorphous. |
| 1408.24 | 1408.26 | Vibration of aromatic ring |
| 1456.11 | 1456.66 | Reduced intensity in crystallisation process, gauche-conformation of the EG. |
| 1505.50 | 1506.01 | Formation of conjugated aromatic structure |
| 1577.22 | 1577.16 | Formation of conjugated aromatic structure |
| 1715.22 | 1715.46 | Stretching vibration of carbonyl C=O bonds in ester linkage, connected with perpendicular dichroism |
| 2958.21 | 2962.22 | Aliphatic C − H stretching vibration |
| - | 3566.76 | Associated with moisture absorption or availability of hydroxyl and carboxyl groups with − OH links due to thermo-mechanical degradation |
| - | 3613.14 | Associated with moisture absorption or availability of hydroxyl and carboxyl groups with − OH links due to thermo-mechanical degradation |

Formation of new absorption peaks were observed for 100% R-PET sample at 3566 cm$^{-1}$ and 3613 cm$^{-1}$. This behaviour is due to the availability of hydroxyl and carboxyl groups with − OH links, which may be produced due to chain scission (chain cleavage) reaction. This acts as catalyst and causes thermo-mechanical degradation of PET with reduction of molecular weight and viscosity associated with higher polymer mobility (Badia et al., 2012).

The increase in − OH species are also responsible for presence of yellow hue in sample and causes discoloration of PET sample. Hydroxyl ions induces hydroxylation of terephthalate ring (Ladasiu Ciolacu et al., 2006).
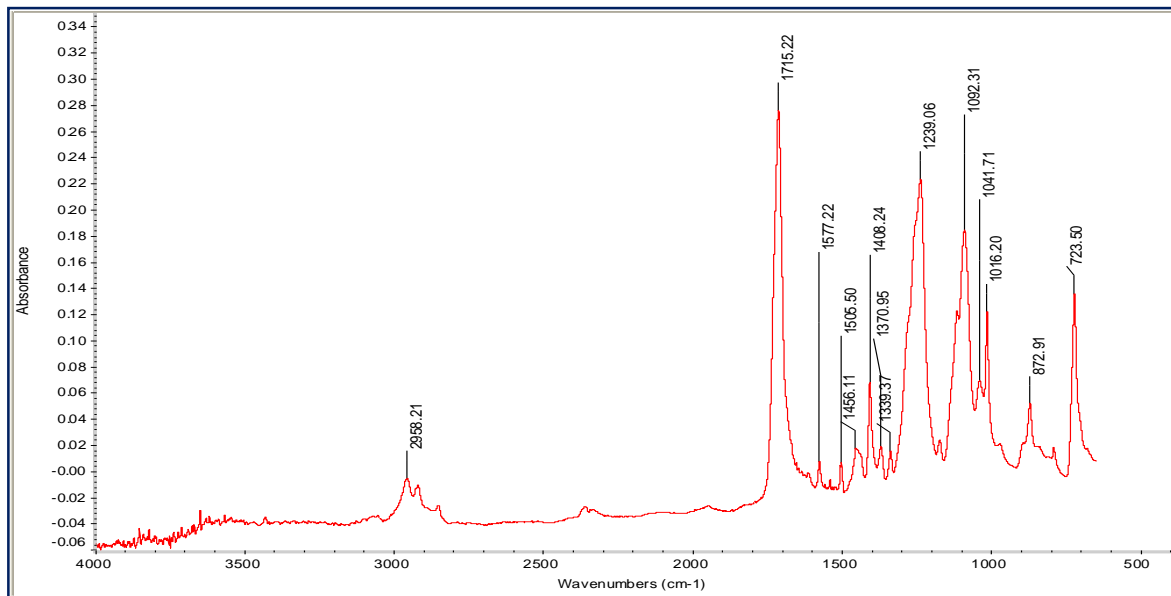


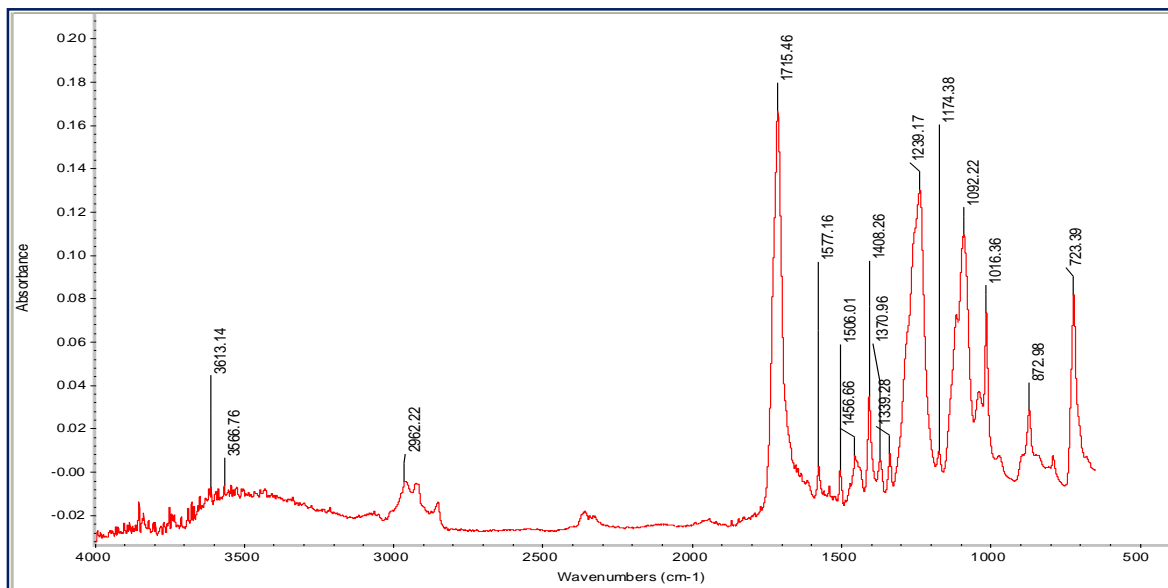Figure 11. Infra-red spectrum for 100% V-PET sample.



Figure 12. Infra-red spectrum for 100% R-PET sample.

**3.6 Influence of V-PET/R-PET blending on whiteness, yellowness, brightness indices and reflectance**

The influence of increasing R-PET content in the whiteness, yellowness and brightness values of the samples is shown in Figure 13. Moreover, influence of increasing R-PET content in the reflectance values of the blended samples is shown in Figure 14. It is evident from the graphs that, whiteness, brightness and reflectance values reduces on increase in R-PET content in blend. Contrary behaviour is observed for yellow index, which increases with incorporation of R-PET in blend. Yellowing of R-PET makes it less acceptable in food grade

packaging applications. The yellowness hue in R-PET is attributed to the chain scission reaction or thermo-oxidative reaction during PET extrusion which produces – OH species which causes hydroxylation of terephthalate ring (Badia et al., 2012; Ladasiu Ciolacu et al., 2006). This behaviour was also confirmed through FTIR analysis. Another reason for yellowing of R-PET is formation of azomethine structures on exposing polyamide (used as barrier layers in PET bottles) to higher temperature (Berg et al., 2016).
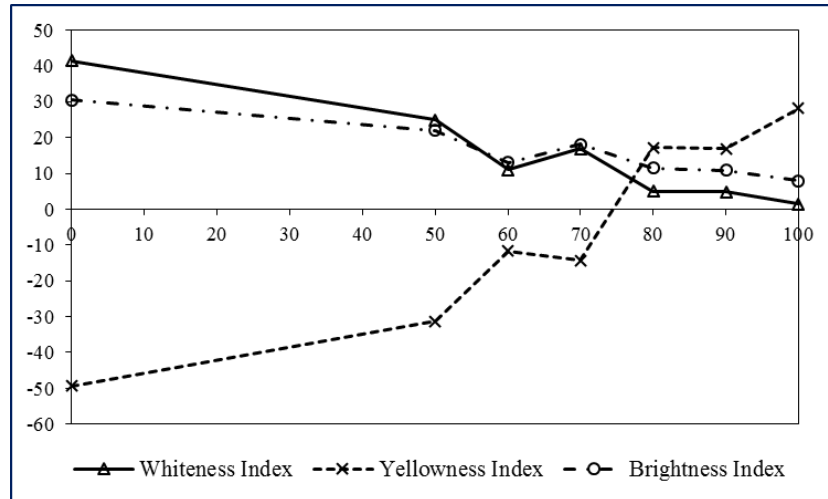


Figure 13. The influence of R-PET content (%) on whiteness, yellowness and brightness indices of the V-PET/R-PET monofilaments.
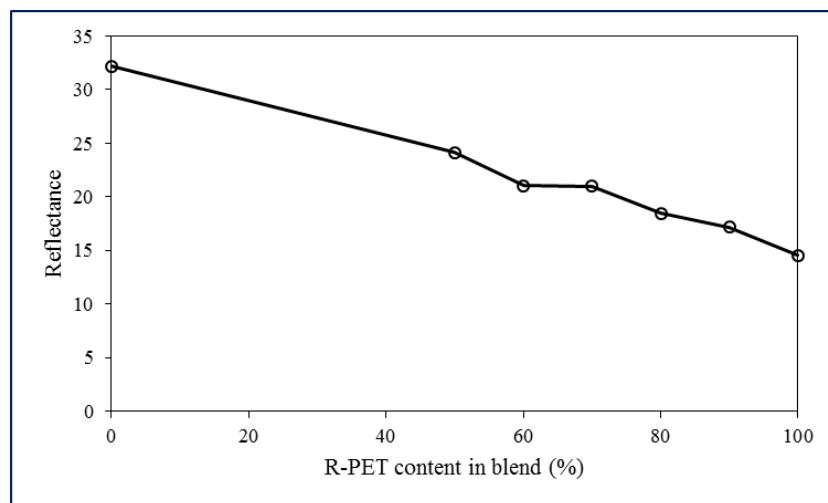


Figure 14. The influence of R-PET content (%) on reflectance value of the V-PET/R-PET monofilaments.

## 4. Conclusions

The V-PET/R-PET yarn properties were investigated by varying the proportion of R-PET content in blend (0%, 50%, 60%, 70%, 80%, 90% and 100%). The 100% R-PET sample has offered highest MFR and lowest IV, confirming the reduction in molecular weight and increase molecular mobility of specimen due to chain scission reaction occurred during thermo-mechanical degradation, also supported through IR analysis. The thermal stability of V-PET sample was highest which is attributed to the presence of higher molecular weight, longer molecular chains and high crystallinity and more oriented structure. The tensile stress

and strain are recorded lowest for 100% R-PET sample. This explanation to this behavior is R-PET has lower molecular weight, short molecular chains, and reprocessing under higher temperature has led to removal of plastic deformation ability. The blended yarn samples with R-PET content of 50-80% have performed marginally similar in terms of tensile stress and strain. The loss of tensile stress and strain is significant when R-PET content in blend is above 80%. Thermal characterisation of R-PET specimen confirmed presence of narrow and long melt-crystallisation peaks, which indicates faster rate of crystallisation for R-PET in contrast to V-PET. The thermographs of all the blended samples have single prominent crystallization and melting peak which confirms the good compatibility and homogeneity within a single phase for both V-PET and R-PET components. The crystallinity (%) of the samples obtained from DSC, indicates that crystallinity content in sample gradually reduces with increase in R-PET content. The IR analysis suggested a higher absorption value for 100% V-PET at all the corresponding absorption peaks. This behaviour is attributed to presence of higher crystallinity (%) in V-PET. New absorption peaks were detected for 100% R-PET sample at 3566 cm$^{-1}$ and 3613 cm$^{-1}$. This is attributed to the presence of hydroxyl and carboxyl groups with – OH links causes thermo-mechanical degradation of PET. There is a decrease in whiteness, brightness and reflectance values and increase in yellow index on incorporation of R-PET content in blend. The yellowness is attributed to the chain scission reaction or thermo-oxidative reaction during PET extrusion which produces – OH species which incite hydroxylation of terephthalate ring.

The 100% V-PET sample have performed superior in comparison to other V-PET/R-PET blended samples. However, in order to reduce cost, environmental impact, and raw material requirement it is advisable to incorporate R-PET in such a manner that the minimum desired property requirement is achieved. In this study it was found that, V-PET/R-PET blended yarn produced through mechanical recycling process should not contain less than 20-30% of V-PET, suitable for average tenacity applications. Optimizing V-PET/R-PET blend ratio in mechanical recycling provides a sustainable alternative to obtain minimum desirable filament characteristics with significant cost reduction.

## References

Acar, I., Kaşgöz, A., Özgümüş, S., & Orbay, M. (2006). Modification of Waste Poly(Ethylene Terephthalate) (PET) by Using Poly(L-Lactic Acid) (PLA) and Hydrolytic Stability. *Polymer-Plastics Technology and Engineering*, *45*(3), 351–359. https://doi.org/10.1080/03602550600553267

American Chemistry Council. (2016). *Plastic Packaging Resins*. 3. https://plastics.americanchemistry.com/Plastic-Resin-Codes-PDF/ (accessed online on 30th January 2021)

Aryan, Y., Yadav, P., & Samadder, S. R. (2019). Life Cycle Assessment of the existing and proposed plastic waste management options in India: A case study. *Journal of Cleaner Production*, *211*, 1268–1283. https://doi.org/10.1016/j.jclepro.2018.11.236

Awaja, F., & Pavel, D. (2005). Recycling of PET. *European Polymer Journal*, *41*(7), 1453–1477. https://doi.org/10.1016/j.eurpolymj.2005.02.005

Badia, J. D., Strömberg, E., Karlsson, S., & Ribes-Greus, A. (2012). The role of crystalline, mobile amorphous and rigid amorphous fractions in the performance of recycled poly (ethylene terephthalate) (PET). *Polymer Degradation and Stability*, *97*(1), 98–107. https://doi.org/10.1016/j.polymdegradstab.2011.10.008

Badía, J. D., Vilaplana, F., Karlsson, S., & Ribes-Greus, A. (2009). Thermal analysis as a quality tool for assessing the influence of thermo-mechanical degradation on recycled poly(ethylene terephthalate). *Polymer Testing*, *28*(2), 169–175.

https://doi.org/10.1016/j.polymertesting.2008.11.010

Barman, N. K., Bhattacharya, S. S., & Mandot, A. (2015). Mechanical Properties of melt-spun Monofilaments Produced From Virgin and Recycyled Poly (ethylene terephthalate ) Blends. *International Journal of Recent Scientific Research*, 6(6), 4517–4525.

Berg, D., Schaefer, K., Koerner, A., Kaufmann, R., Tillmann, W., & Moeller, M. (2016). Reasons for the Discoloration of Postconsumer Poly(ethylene terephthalate) during Reprocessing. *Macromolecular Materials and Engineering*, 301(12), 1454–1467. https://doi.org/10.1002/mame.201600313

Berkowitz, S. (1984). Viscosity–molecular weight relationships for poly(ethylene terephthalate) in hexafluoroisopropanol–pentafluorophenol using SEC–LALLS. *Journal of Applied Polymer Science*, 29(12), 4353–4361. https://doi.org/10.1002/app.1984.070291264

Campanelli, J. R., Kamal, M. R., & Cooper, D. G. (1994). Kinetics of glycolysis of poly(ethylene terephthalate) melts. *Journal of Applied Polymer Science*, 54(11), 1731–1740. https://doi.org/10.1002/app.1994.070541115

Chen, J.-W., & Chen, L.-W. (1999). The glycolysis of poly(ethylene terephthalate). *Journal of Applied Polymer Science*, 73(1), 35–40. https://doi.org/10.1002/(SICI)1097-4628(19990705)73:1<35::AID-APP4>3.0.CO;2-W

Chilton, T., Burnley, S., & Nesaratnam, S. (2010). A life cycle assessment of the closed-loop recycling and thermal recovery of post-consumer PET. *Resources, Conservation and Recycling*, 54(12), 1241–1249. https://doi.org/10.1016/j.resconrec.2010.04.002

Elamri, A., Lallam, A., Harzallah, O., & Bencheikh, L. (2007). Mechanical characterization of melt spun fibers from recycled and virgin PET blends. *Journal of Materials Science*, 42(19), 8271–8278. https://doi.org/10.1007/s10853-007-1590-1

Fann, D.-M., Huang, S. K., & Lee, J.-Y. (1997). Processing Characteristics of Recycled Poly(Ethylene Terephthalate) as Melt Spun Fibers. *Textile Research Journal*, 67(12), 891–896. https://doi.org/10.1177/004051759706701205

Foolmaun, R. K., & Ramjeeawon, T. (2013). Comparative life cycle assessment and social life cycle assessment of used polyethylene terephthalate (PET) bottles in Mauritius. *The International Journal of Life Cycle Assessment*, 18(1), 155–171. https://doi.org/10.1007/s11367-012-0447-2

Gomes, T. S., Visconte, L. L. Y., & Pacheco, E. B. A. V. (2019). Life Cycle Assessment of Polyethylene Terephthalate Packaging: An Overview. *Journal of Polymers and the Environment*, 27(3), 533–548. https://doi.org/10.1007/s10924-019-01375-5

Holland, B. ., & Hay, J. . (2002). The thermal degradation of PET and analogous polyesters measured by thermal analysis–Fourier transform infrared spectroscopy. *Polymer*, 43(6), 1835–1847. https://doi.org/10.1016/S0032-3861(01)00775-3

Itim, B., & Philip, M. (2015). Effect of multiple extrusions and influence of PP contamination on the thermal characteristics of bottle grade recycled PET. *Polymer Degradation and Stability*, 117, 84–89. https://doi.org/10.1016/j.polymdegradstab.2015.04.004

Ladasiu Ciolacu, C. F., Roy Choudhury, N., & Dutta, N. K. (2006). Colour formation in poly(ethylene terephthalate) during melt processing. *Polymer Degradation and Stability*, 91(4), 875–885. https://doi.org/10.1016/j.polymdegradstab.2005.06.021

Lee, J. H., Lim, K. S., Hahm, W. G., & Kim, S. H. (2013). Properties of recycled and virgin poly(ethylene terephthalate) blend fibers. *Journal of Applied Polymer Science*, 128(2), 1250–1256. https://doi.org/10.1002/app.38502

López, M. del M. C., Ares Pernas, A. I., Abad López, M. J., Latorre, A. L., López Vilariño, J. M., & González Rodríguez, M. V. (2014). Assessing changes on poly(ethylene terephthalate) properties after recycling: Mechanical recycling in laboratory versus postconsumer recycled material. *Materials Chemistry and Physics*, 147(3), 884–894.

https://doi.org/10.1016/j.matchemphys.2014.06.034

Masmoudi, F., Fenouillot, F., Mehri, A., Jaziri, M., & Ammar, E. (2018). Characterization and quality assessment of recycled post-consumption poly(ethylene terephthalate) (PET). *Environmental Science and Pollution Research*, *25*(23), 23307–23314. https://doi.org/10.1007/s11356-018-2390-7

NAPCOR (National Association for PET Container). (2018). *Report on postconsumer PET container recycling activity in 2017*. 13. https://napcor.com/wp-content/uploads/2018/11/NAPCOR_2017RateReport_FINAL.pdf (accessed online on 30th January 2021)

Sang, T., Wallis, C. J., Hill, G., & Britovsek, G. J. P. (2020). Polyethylene terephthalate degradation under natural and accelerated weathering conditions. *European Polymer Journal*, *136*(July), 109873. https://doi.org/10.1016/j.eurpolymj.2020.109873

Sängerlaub, S., Glas, C. E., Schlemmer, D., & Müller, K. (2020). Influence of multiple extrusions of blends made of polyethylene terephthalate and an oxygen scavenger on processing and packaging-related properties. *Journal of Plastic Film & Sheeting*, *36*(3), 260–284. https://doi.org/10.1177/8756087919886893

Shen, L., Nieuwlaar, E., Worrell, E., & Patel, M. K. (2011). Life cycle energy and GHG emissions of PET recycling: change-oriented effects. *The International Journal of Life Cycle Assessment*, *16*(6), 522–536. https://doi.org/10.1007/s11367-011-0296-4

Shen, L., Worrell, E., & Patel, M. K. (2010). Open-loop recycling: A LCA case study of PET bottle-to-fibre recycling. *Resources, Conservation and Recycling*, *55*(1), 34–52. https://doi.org/10.1016/j.resconrec.2010.06.014

Sinha, V., Patel, M. R., & Patel, J. V. (2010). Pet Waste Management by Chemical Recycling: A Review. *Journal of Polymers and the Environment*, *18*(1), 8–25. https://doi.org/10.1007/s10924-008-0106-7

Starkweather, H. W., Zoller, P., & Jones, G. A. (1983). The heat of fusion of poly(ethylene terephthalate). *Journal of Polymer Science: Polymer Physics Edition*, *21*(2), 295–299. https://doi.org/10.1002/pol.1983.180210211

Varma, P., Lofgren, E. A., & Jabarin, S. A. (1998). Properties and kinetics of thermally crystallized oriented poly(ethylene terephthalate) (PET). I: Kinetics of crystallization. *Polymer Engineering & Science*, *38*(2), 237–244. https://doi.org/10.1002/pen.10184

Welle, F. (2011). Twenty years of PET bottle to bottle recycling—An overview. *Resources, Conservation and Recycling*, *55*(11), 865–875. https://doi.org/10.1016/j.resconrec.2011.04.009

Welle, F. (2013). Is PET bottle-to-bottle recycling safe? Evaluation of post-consumer recycling processes according to the EFSA guidelines. *Resources, Conservation and Recycling*, *73*, 41–45. https://doi.org/10.1016/j.resconrec.2013.01.012

Wu, H., Lv, S., He, Y., & Qu, J. P. (2019). The study of the thermomechanical degradation and mechanical properties of PET recycled by industrial-scale elongational processing. *Polymer Testing*, *77*(December 2018), 105882. https://doi.org/10.1016/j.polymertesting.2019.04.029