



INFLUENCE OF THE REPROCESSING CYCLES ON THE PROPERTIES OF POLYPROPYLENE

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ABSTRACT

To address issue with indiscriminate littering of polypropylene packaging material in environment, mechanical recycling is the most economically viable approach where end-of-life thermoplastics are mechanically crushed and reprocessed. However, compared to virgin material, the recycled thermoplastics show inferior performances due to degradation while reprocessing. Therefore, for detailed understanding of the thermo-mechanical degradation with reprocessing cycles, injection molding polypropylene homopolymer grade was reprocessed up to 12th cycles in a corotating twin screw extruder. Properties like physical, mechanical, optical, rheological were evaluated to understand the morphology. Compared to virgin, reprocessed polypropylene showed lower average molecular weight, narrower polydispersity index, higher melt flow index and lower melt viscosity at low shear region. The degradation phenomena was also supported by lower oxidation induction time and higher yellowness index value. Although in infrared spectra, a very feeble carbonyl characteristic peak was observed in virgin material, the peak was absent in reprocessed samples till 8th pass, then found to reappear due to oxidative degradation of the matrix. Tensile yield strength was found to be independent of reprocessing cycles, but elongation at break and izod impact strength found to decrease considerably with reprocessing cycles. However, stiffness and heat deflection temperature was found to increase with reprocessing cycles.

Keywords: degradation, environment, molecular weight, polypropylene, reprocessing

INTRODUCTION

Polypropylene is the second largest commodity thermoplastic due to its lower density, low cost, good processability, corrosion resistance and excellent resistance to water and CO₂ permeability [1-4]. Over the period, consumption of plastic packaging has been increased drastically due to improved population and standard of living of people. This advancement has led to another issue of plastic waste littering. Littering of waste impacts the environment negatively which leads to growing interest of academicians, industries & government bodies for minimizing waste and achieve the goal for cleaner environment. Large amount of polymer production and its inappropriate discharge have contributed significantly towards the damage of the environment in big cities. A surge in urban pollution and flooding is evident in the metro cities as a result of indiscriminate and improper plastic waste disposal [5-7].

To deal with such situation, a variety of techniques like chemical & mechanical recycling has emerged for recycling and reusing polypropylene & other polymer waste. Among these, mechanical recycling got more importance considering its focus specifically to re-value the polymer post processing [8]. If mechanical recycling is compared with plastic waste incineration for energy recovery and chemical recycling, mechanical recycling emerges to be the most reliable route to deal with plastic waste management which even can reduce greenhouse emissions by 80% [9-10]. However, one of the critical issues with use of recycled plastics is the deterioration of performance and property of polymer after recycling due to degradation of polymer [11-12]. Mechanical recycling crushes the end-of-life plastics mechanically, then further reprocessed to obtain an economically viable new structural part [13-15].

In polymer industry, mechanical recycling is well accepted to reprocess plastic waste using extruder and injection molding machine [16]. Recycled material can also be added in certain percentage with virgin material to get balanced properties at reduced cost leading reduction in waste accumulation and contributing directly towards cleaner environment [17-19]. Less amount of landfills and economics aspects justify the encouragement of mechanical plastic recycling [20-22]. This is well reflected in many focused research in the domain of polymer recycling via blending and composite routes as it results in stiffness-toughness balance [23-26]. Currently, there is a trend to replace certain percentage of virgin plastics with recycled polymer in designing fresh part for cost effective solution without compromising the property.

Although, there are research reported on polypropylene recycling, but very few articles are available with detailed investigation on the effect of recycling on molecular weight (MW), molecular weight distribution (MWD), flow behaviour, mechanical and optical properties of polypropylene. Hence, this present study will provide detailed data resource for polypropylene recycling covering the effect of recycling process on the aforesaid properties.

MATERIALS AND METHODS

Materials:

Polypropylene (PP) homopolymer pellets, Polysure® M12RR (MFI of 12 g/10 min at 2.16 kg & 230°C)

was chosen from HPCL-Mittal Energy Pvt. Ltd., India product portfolio. The PP resin contains both primary and secondary antioxidants along with mold release agent.

Reprocessing:

The polypropylene pellet was extruded up to twelve times in a modulated co-rotating twin-screw extruder (Omega-25 from Steer Engineering, India) with a screw diameter of 25 mm, L/D ratio of 32, assembled with a gravimetric feeder and pelletizing unit. A temperature profile of 215°C to 250°C, screw speed of 300 rpm, 40-50% (57-69 Nm) torque and output of 15 kg/h was maintained during the process. Higher temperature profile was chosen to facilitate the degradation process. Sample nomenclature has been done as per number of reprocessing cycles and denoted as “PPi,” where i = 0 to 12. Here, “0” represents the raw material directly processed by injection molding without any extrusion cycle (Table 1).

Sample ID	PP0	PP2	PP4	PP6	PP8	PP10	PP12
Reprocessing Cycles	0 th	2 nd	4 th	6 th	8 th	10 th	12 th
Polymer Resin	12 MFI Molding Grade PP Homo Polymer						

Table 1: Sample nomenclature as per number of reprocessing cycles.

One part of the re-processed pellets was used for the evaluation of thermal, rheological, and optical properties, whereas the remaining pellets was used or injection molded specimen preparation to evaluated mechanical and other properties. Injection molded specimens were prepared using Ferromatik Milacron injection molding machine (Nova Servo 80) of 80-ton capacity with a temperature profile of 190°C to 205°C, mold temperature of 60°C, injection speed of 10 mm/s, cooling time of 20 s and cycle time of 54 s. Prior to test, all molded specimens were conditioned as per ASTM D618 at 23±2°C and 50±10% RH for 48 h in an environmental chamber.

Characterization Techniques:

Melt rheology:

Melt flow index (MFI) is a measure of the flow properties of polymer melt at low shear rates and is inversely proportional to the average molecular weight of the resin, i.e., higher the MFI, lower the molecular weight and vice versa. The MFI of all the compositions was measured as per ASTM D1238 at 2.16 kg load and 230°C temperature using MI-4 Gottfert MFI tester.

Along with MFI, to study the effect of number of reprocessing cycles on molecular weight of polypropylene, high shear rheology was performed as per ASTM D3835 using RG-25 Gottfert capillary rheometer. Shear viscosity was measured as a function of shear rate at a specific temperature of 230°C.

High temperature gel permeation chromatography (HT-GPC):

To estimate the molecular weight of reprocessed PP, HT-GPC was carried out. About 8 mg of polypropylene sample was taken in a 10 ml glass vial and dissolved in 1,2,4-trichlorobenzene (TCB) solvent for 90 mins at 160°C. Before injecting the dissolved polymer into GPC separation column, it was filtered through a stainless-steel filter of 10 µm porosity to remove any contamination. The sample was then analyzed

as per ISO 16014 using GPC-IR6 instrument from Polymer Char with infrared (IR6) and viscometer detectors coupled in series. Polystyrene standards with four different molecular weight ranges were used for the calibration. The signals were processed with the GPC One® software to generate the chromatograph with molecular weight distribution.

Mechanical properties:

The room temperature ($23\pm 2^\circ\text{C}$) mechanical properties like tensile as well as flexural of all the neat and reprocessed samples were evaluated using Instron-5966 UTM. The room temperature tensile properties (e.g. elastic modulus, yielding behaviour and failure pattern) was measured as per ASTM D638 test method. Injection molded Type-I specimen was stretched unidirectionally along specimen axis at a constant speed of 50 mm/min. Grip to grip separation of 115 mm and gauge length of 50 mm was used for this purpose. 'Auto-X' extensometer was utilized to measure the deformation with more accuracy and precision.

The flexural properties like modulus (1% secant) and strength were determined as per ASTM D790 using a 3-point bending fixture. Injection molded rectangular bars of specified dimension was mounted on the cantilever support of span around 50.8 mm and loaded by means of a loading nose midway between the supports, the rate of deflection maintained at 1.30 mm/min.

To understand the toughness of the reprocessed material, notched izod impact test was carried out as per ASTM D256 using CEAST-9050 impact tester. Injection molded standard specimen of 64 mm (length) x 12.7 mm (width) x 3.2 mm (thickness) was used. The notching of each specimen was made in such a way that the depth of the plastic material remaining in the specimen under the notch was 10.16 ± 0.05 mm. Angle of notch was $45\pm 1^\circ$ with radius of curvature at the apex of 0.25 ± 0.05 mm. A hammer of 1J energy was used to strike the specimens at a speed of 3.5 m/s. The absorbed energy was reported in terms of J/m.

Thermal analysis:

Differential scanning calorimetry (DSC):

The % crystallinity, onset of crystallization and melting behaviour of the samples were evaluated as per ASTM D3418 using differential scanning calorimeter, DSC-250 (Discovery series) from TA Instruments. About 8 to 10 mg of sample was heated under a nitrogen atmosphere from 23°C to 225°C at a heating rate of $10^\circ\text{C}/\text{min}$ and held at that temperature for 5 mins for complete melting of the samples. It was then cooled down to 23°C with a cooling rate of $10^\circ\text{C}/\text{min}$ and then once again heated to 225°C with the same heating rate. The 1st heating was performed to remove the in-mold residual stress inside the sample, if any. The crystallization onset temperature was analyzed from the cooling curve, whereas melting point and % crystallinity were evaluated from the second heating cycle. The % crystallinity (X_c) was evaluated from endothermic melting enthalpy using the following equation:

$$X_c = [(\Delta H_m)/(\Delta H^0_m)*w]*100 \quad (1)$$

where ΔH_m is the melting enthalpy, ΔH^0_m is the melting enthalpy corresponding to 100% crystalline PP (i.e. 209 J/g) and w is the weight fraction of PP used [27-28].

Thermal stability:

Thermal stability was investigated from degradation onset temperature using thermogravimetric analysis (TGA) as per ASTM E1131 using TGA-550 (Discovery series) from TA Instruments. About 15 mg of sample was heated from 23°C to 900°C at a heating rate of 10°C/min under nitrogen atmosphere.

The oxidative stability of the samples was evaluated by oxidation induction time (OIT) as per ASTM D3895. About 10 mg of the sample was heated till 200°C at 20°C/min under nitrogen atmosphere (99.9% purity). At 200°C, sample was exposed to oxygen atmosphere with a purity of 99.9%. Under oxygen atmosphere, the time taken for initiation of oxidation exotherm was considered as the OIT. Higher is the OIT, higher is the oxidation stability of the polymer.

Heat deflection temperature (HDT) is known as the temperature at which a polymer sample deforms under a specified load. This test was conducted as per ASTM D648 by applying a load of 0.455 MPa on rectangular specimen in a flat-wise position. The specimen was immersed under the load in heat transfer medium and raised the temperature at $2 \pm 0.2^\circ\text{C} / \text{min}$. As the temperature increased, the specimen started deflecting under the load. HDT was measured as the temperature of the medium at which test bar was deflected by 0.25 mm.

Optical properties:

Yellowness index (YI) was measured using spectrophotometer Lab Scan XE from Hunter Lab as per ASTM E313. Before the test, a calibrated white tile was used to calibrate the instrument. After calibration, the specimen was placed at the reflectance port. The illuminant used was a standard D65 light placed at an observer angle of 10°. The illuminating light was reflected from the sample, collected by a lens and analyzed by the instrument.

FTIR spectroscopy:

Fourier transform infrared spectroscopy (FTIR) was used to determine formation of any functional groups due to oxidative degradation of the polymer. The samples were scanned in the mid infrared (IR) region of the spectrum i.e. from 400 cm^{-1} to 4000 cm^{-1} wavenumbers as per test method ASTM E1252 using Nicolet iS50 spectroscope from ThermoFisher Scientific. The recorded spectra was processed through OMNIC software to obtain the spectrograph.

RESULTS AND DISCUSSION

Melt rheology and flow properties:

Melt flow index shows the flow behaviour of the material under a constant load and temperature. Higher is the flow, lower is the molecular weight. As depicted in Figure 1a, the MFI found to increase with number of passes in the extruder. Esmizadeh et al. also reported a similar observation for polypropylene [29]. This increase in MFI can also be accounted for scission of molecular chains when exposed to shear force and temperature several times during reprocessing [30-31]. The pass-to-pass change in MFI found to be within

30% till 4th pass and it got increased exponentially to more than 40% after 4th pass.

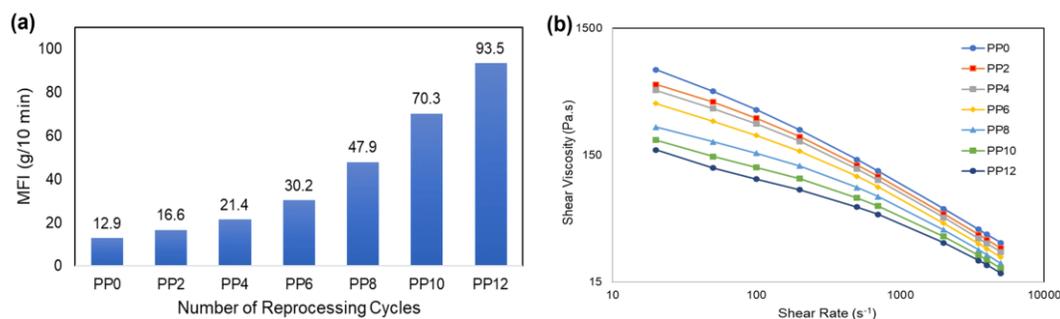


Figure 1: Melt rheology of various reprocessed samples: (a) Melt flow index (MFI) at 230°C and 2.16 kg load, and (b) shear viscosity as a function of shear rate at 230°C.

Capillary rheology is a very useful technique to study the flow behaviour of a polymer, as it simulates the similar shear profile of polymer processing like extrusion as well as injection molding. Viscosity is known to be the resistance to flow and parameters like shear rate, molecular weight & its distribution play a very critical role to control the viscosity. As per various research articles it is well known that there is an inverse correlation between MFI and viscosity, which also directly relates to polymer chain length. Higher is the molecular chain length of the polymer, higher is the molecular weight which promotes more entanglement of the chain resulting a higher resistance to flow and increase in melt viscosity. Figure 1b demonstrates how the shear viscosity changes with shear rate at a particular temperature. Being a thermoplastic, PP shows a shear thinning behaviour where melt viscosity decreases with increase in shear rate due to orientation of molecular chains along the flow. Also, it is evident that throughout the whole shear rate regime, viscosity found to decrease with increase in reprocessing cycle as the molecular weight decreases with increase in reprocessing cycles. However, this trend found more significant in low shear region.

This observation was also supported by the change in weight average molecular weight (M_w) and number average molecular weight (M_n) as determined using high temperature gel permeation chromatography (HT-GPC). Figure 2 represents the chromatograms which shows the molecular weight distribution for all reprocessed samples.

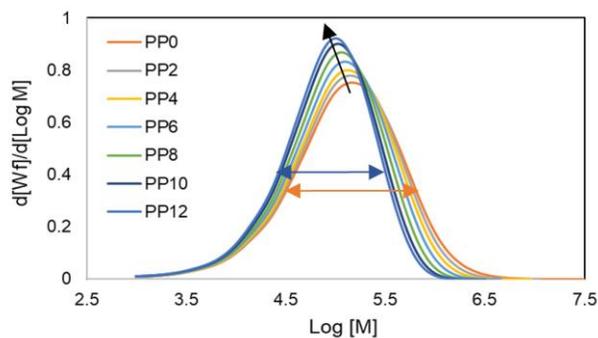


Figure 2: Molecular weight distribution of reprocessed samples as obtained by high temperature gel permeation chromatography (HT-GPC) at 160°C.

It is quite evident that, with increasing number of reprocessing cycles, the molecular weight distribution becomes narrower as indicated by the width of the middle point of distribution bell curve. Also, population of polymer chains found to shift towards lower molecular weight side due to reduction in weight average molecular weight resulted from molecular chain scission. The quantitative parameters as derived from the chromatogram is summarized in Table 2.

Sample ID	M_w (g/mol)	M_n (g/mol)	M_w / M_n (PDI)
PP0	2,48,200	40,100	6.20
PP2	2,16,700	39,800	5.44
PP4	1,95,400	39,700	4.93
PP6	1,69,700	35,000	4.85
PP8	1,48,100	34,500	4.29
PP10	1,30,600	33,700	3.88
PP12	1,22,300	34,200	3.57

Table 2: Average molecular weight and polydispersity index of reprocessed samples.

As summarized in Table 2, the weight average molecular weight (M_w) was found to decrease progressively with increase in numbers of reprocessing cycles [32-33]. The change was in between 9 to 13% from its previous cycles till 10th cycle except 12th cycle where the drop was about 6%. In case of number average molecular weight (M_n), the change in molecular weight was significant till 4th cycle. This decrease in molecular weight was more evident in case of M_w than M_n as chain scission occurs preferably at the centre of long polymer chains and therefore has a larger effect on M_w [34-35]. Chain scission also found to results in narrower molecular weight distributions for reprocessed polymers which is represented in Table 2 as M_w/M_n commonly known as Poly Dispersity Index (PDI). Lower PDI indicates narrower molecular weight distribution, whereas higher PDI indicates broader molecular weight distribution.

Mechanical properties:

Considering reuse of the recycled (or reprocessed) material as blend with the virgin polymer, retention of mechanical properties irrespective of reprocessing cycles plays a very crucial role. Figure 3a depicts the tensile properties of all the reprocessed materials.

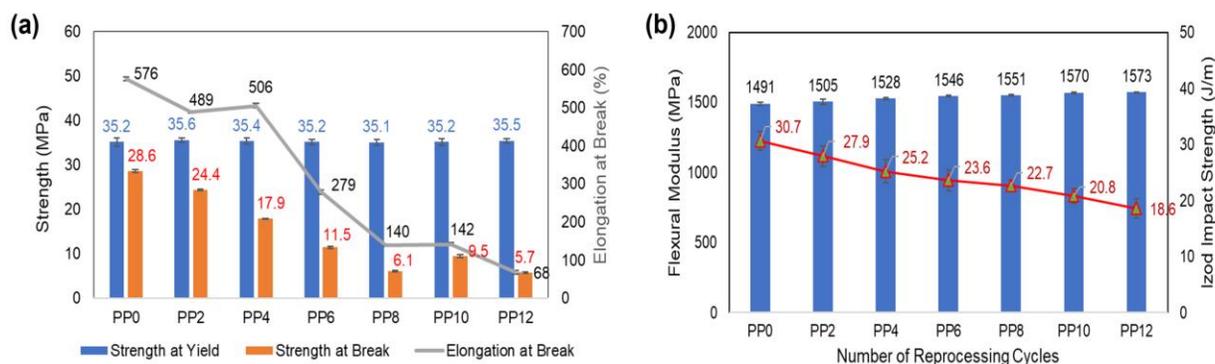


Figure 3: Mechanical properties of various reprocessed samples: (a) tensile strength at yield, tensile strength at break and tensile elongation at break, and (b) flexural modulus (stiffness) and notched izod impact strength.

Tensile yield strength is found to be independent of number of reprocessing cycles. However, elongation and tensile stress at break found to decrease considerably with increase in reprocessing cycles. The elongation values reduced from 576% to 68% after 12th reprocessing cycles. This decrease in tensile strength at break and elongation at break are related to reduction in molecular weight due to chain scission as a result of repetitive application of shear and thermal history altogether.

The higher elongation value of lower reprocessed material results from entangled higher macromolecules which have ability to get stretched under tensile force [36-37]. With increase in number of reprocessing cycles, elongation reduced mostly due to presence of lower molecular weight chains which are unable to provide proper stretching due to poor entanglement. The chain scission occurs at the amorphous regions of semi-crystalline polypropylene, whereas tie molecules are the ones responsible for mechanical integrity of the semi-crystalline polymers [38].

The effect of re-processing cycles on flexural modulus and impact strength has been illustrated in Figure 3b. The flexural modulus found to increase to some extent after each cycle and found to be about 5.5% higher compared to virgin PP after 12th pass. This may be due to the presence of lower molecular weight PP chain segments which facilitates the formation of compact crystals and enhances the stiffness. The impact strength was found to decrease linearly with reprocessing cycles because of reduction in molecular weight. As the molecular weight decreases, it refrains from the formation of chain entanglements resulting in an easily propagation of cracks during any sudden impact causing inferior impact properties. The effects of reprocessing and thermo-oxidative aging on post-consumption PP were investigated by Jansson et al. [39] and found that the different batches of recycled PP differed substantially in mechanical properties depending on stabilizing efficiency of antioxidants in order to reduce the degradative effects. So, in nutshell it can be said that thermomechanical degradation is controlled by both an increase in crystallinity and insertion of defects in the amorphous chains [40-41].

Thermal properties:

The thermal stability of the neat polypropylene and the reprocessed recyclates was evaluated from

their corresponding degradation onset temperature ($T_{d\text{-onset}}$) and the temperature at which maximum degradation rate ($T_{d\text{-peak}}$) was achieved using TGA as shown in Figure 4.

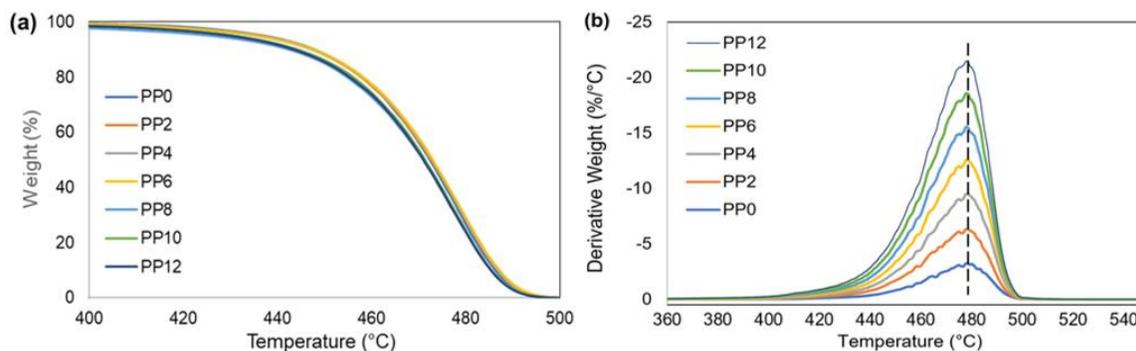


Figure 4: Thermogravimetric analysis of reprocessed samples: (a) % weight and (b) derivative % weight as a function of temperature.

The obtained results are summarized in Table 3.

Sample ID	$T_{d\text{-onset}}$ (°C)	$T_{d\text{-peak}}$ (°C)	OIT (min)	HDT (°C)	T_m (°C)	$T_{c\text{-onset}}$ (°C)	$T_{c\text{-peak}}$ (°C)	($T_{c\text{-onset}}$)- ($T_{c\text{-peak}}$) (°C)	% Crystallinity
PP0	456.5	480.9	7.8	93.2	162.6	120.3	117.6	2.7	53.3
PP2	456.4	479.9	6.8	94.6	161.7	120.3	117.9	2.4	52.3
PP4	456.9	478.2	6.8	95.6	161.2	120.3	117.8	2.5	50.8
PP6	456.4	479.6	5.3	96.4	161.6	120.4	117.7	2.7	53.0
PP8	454.1	477.8	3.9	97.8	160.7	120.5	118.1	2.4	51.1
PP10	454.9	477.5	3.9	98.1	160.3	120.7	118.2	2.5	52.3
PP12	454.3	476.2	3.6	100.3	161.1	120.5	117.9	2.6	53.4

Table 3: Characteristics parameters obtained from thermal analysis.

It was evident that the characteristic degradation temperatures (both $T_{d\text{-onset}}$ and $T_{d\text{-peak}}$) obtained for reprocessed PP were slightly lower than those of the virgin PP, suggesting that reprocessed PP samples are more susceptible towards thermal degradation than virgin PP. The thermo-mechanical scission of PP chains promotes formation of free radicals during reprocessing which further facilitates the acceleration of the degradation process by creating new sites susceptible to degradation. The shorter the polymer chains, the more susceptible those are towards thermal as well as oxidative degradation even at lower temperatures [42]. Although the change was not so significant but was in agreement with the higher MFI in reprocessed recyclates, as a consequence of the chain scission.

The oxidative degradation plays a very crucial role in polypropylene degradation [43-44]. Oxidation induction time (OIT) is used to measure the thermal oxidative stability of polymeric material. The initiation of exothermic reaction in oxygen atmospheres is a measure of OIT. Higher OIT value shows that material is more stable against oxidative degradation [45-46].

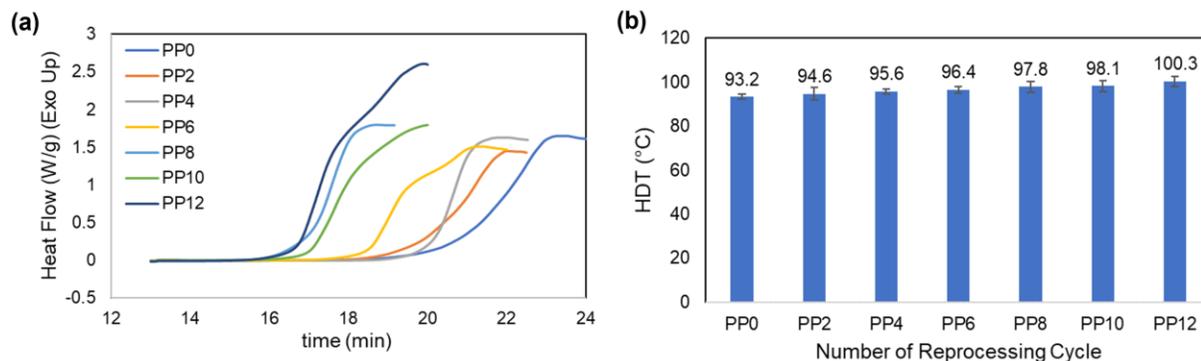


Figure 5: (a) Oxidation induction time (OIT), and (b) heat deflection temperature (HDT) as a function of number of reprocessing cycles.

As shown in Figure 5a, oxidation stability found to decrease with increase in number of reprocessing cycles. This is because of the fact that with increase in reprocessing cycles, the molecular weight of the polymer decreases resulting an inferior oxidative stability. Also, with increase in reprocessing cycles, there may be a possibility of increase in contamination level which may catalyse the degradation process in presence of oxygen [43].

Heat deflection temperature (HDT) is one of the very important property to measure dimensional stability of the polymer [47]. As shown in Figure 5b, with increase in number of reprocessing cycles, the HDT found to increase in slight incremental fashion. This increasing tendency of the HDT was similar with that of the flexural modulus (stiffness) as discussed earlier.

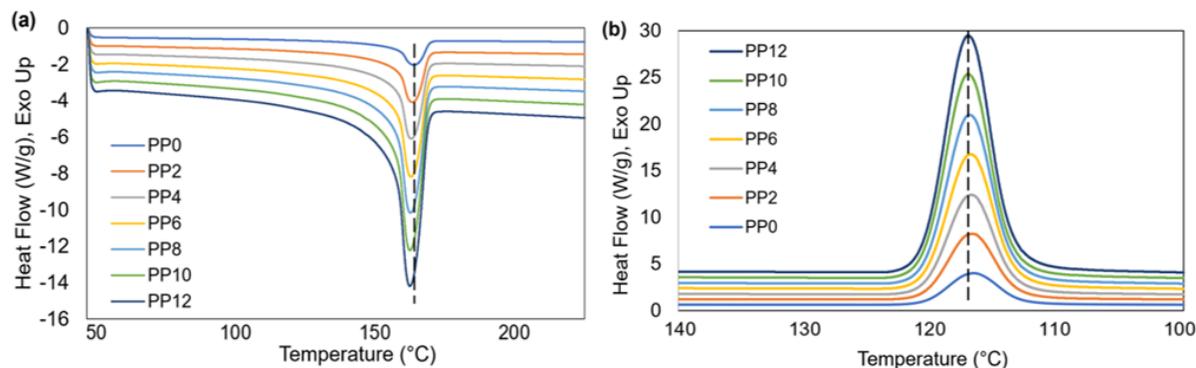


Figure 6: Differential scanning calorimetry (DSC): (a) heating cycle and (b) cooling cycle as a function of number of reprocessing cycles.

As shown in DSC thermogram, Figure 6a, the reprocessed samples showed a very minute decrease in melting temperatures (T_m) compared to neat PP. This slight decrease may attribute towards polymer chain scission in amorphous region. A slight decrease in % crystallinity was found till 4th reprocessing cycle and thereafter crystallinity found to increase to some extent. This increase in crystallinity can be attributed to the thermo-mechanical degradation of PP resulting in chain scission. A reduction in polymer chain length facilitated chain mobility and crystallization during cooling (Figure 6b). This phenomenon is also known as

chemi-crystallization process [48-51]. Although, reduction in molecular chain length was evident, but no significant change was observed in crystallization onset temperature (T_c -onset) and crystallization rate which is expressed as the difference between the crystallization peak temperature (T_c -peak) and crystallization onset temperature (T_c -onset).

Optical properties:

Yellowing of a polymer occurs typically due to thermo-mechanical degradation. During extrusion, the polymers undergo both heating and shearing over a period of time which leads to the initiation of degradation reaction. This degradation of polymer leads to color change caused by the polymer chain scission and formation of functional chromophores.

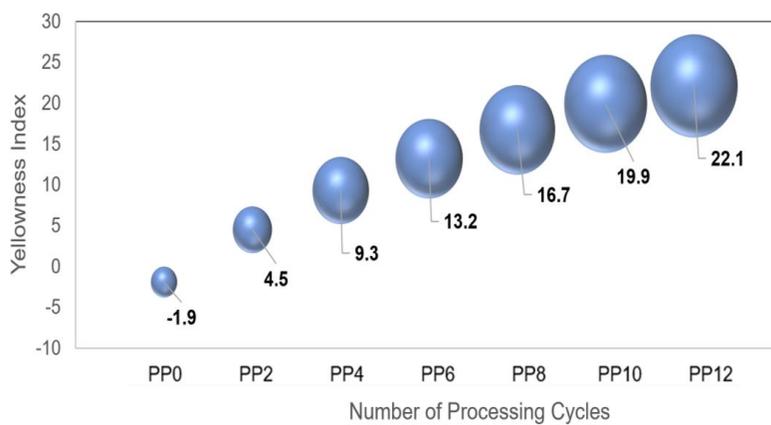


Figure 7: Yellowness Index (YI) as a function of number of reprocessing cycles.

As depicted in Figure 7, the yellowness index value found to increase steadily with the number of reprocessing cycles. The change in YI value was significant after 2nd reprocessing cycle (i.e. ~6) and continued till 4th reprocessing cycle (i.e. ~5). After that slope of change in yellowness index found to decrease slightly with increase in number of reprocessing cycles (around 2 to 3).

The thermal heating and heat released during shearing might have caused scission of polymer chains resulting formation of free radicals which can then scavenge the tertiary hydrogen of polypropylene chain to generate a polypropylene macro-radical. This macro-radical further undergoes β -scission, which causes the formation of an unsaturation resulting in a reduction in molecular weight [52]. This type of degradation reduces the thermal as well as color stability of the polymer, which is evident from the increase in yellowness index value with reprocessing cycles.

FTIR spectroscopy:

Being an aliphatic non-polar hydrocarbon, polypropylene doesn't contain any functional groups. The presence of any carbonyl group (C=O) in the samples likely arises from a combination of mechanical, thermal and oxidative degradation during processing in presence of relatively high shear or high screw rpm during extrusion, temperature and oxygen [53]. In FTIR spectra, the carbonyl group shows prominent characteristics peak around 1720-1740 cm^{-1} wavenumber which is free from any type of interference with other functional

groups present.

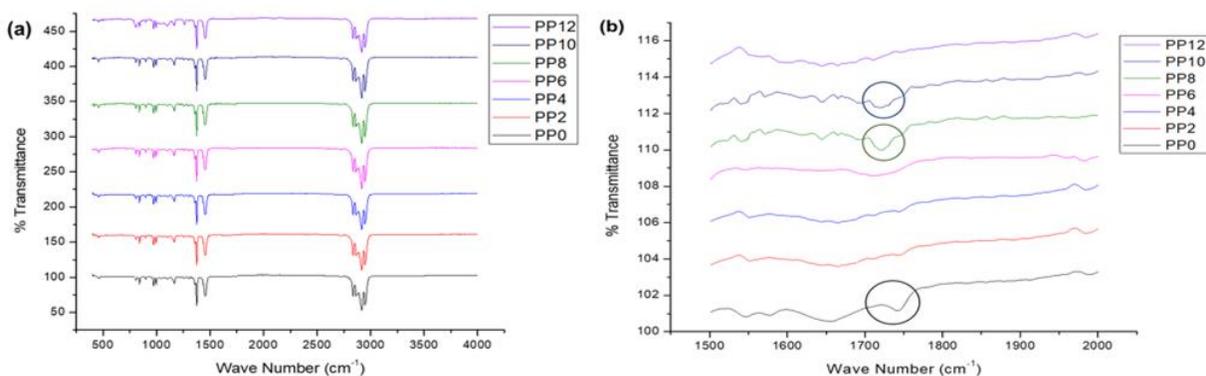


Figure 8: FTIR Spectroscopy of neat and reprocessed PP samples: (a) 400-4000 cm^{-1} wavenumber, and (b) 1500-2000 cm^{-1} wavenumber.

As shown in Figure 8a, FTIR spectra of all reprocessed as well as virgin polypropylene is compared. All the samples showed characteristic peaks of polypropylene like multiple C-H stretching around 2700 to 2950 cm^{-1} , $-\text{CH}_2$ stretching around 1464 cm^{-1} , peak due to symmetric deformation of $-\text{CH}_3$ group around 1378 cm^{-1} and peaks associated with polypropylene crystal around 976 to 1172 cm^{-1} . No additional peak corresponds to functional groups which may be generated during degradation was not visible prominently. Although, when the wavenumber region of 1500 cm^{-1} to 2000 cm^{-1} (Figure 8b) was scrutinized, a very feeble characteristic peak of carbonyl functional group was observed at 1724 cm^{-1} in neat PP sample which probably belongs to phenolic primary antioxidants present as a stabilizer. To stabilize the polymer, phenolic antioxidant sacrifices itself and converts itself to more stable chromophoric quinone structure containing keto or carbonyl group ($\text{C}=\text{O}$). This peak was not observed in reprocessed samples due to the consumption of phenolic primary antioxidant additive for stabilization of the polypropylene matrix [54]. However, after 8th reprocessing cycles, peak associated with carbonyl group further appeared which may be due to oxidative degradation of polypropylene in absence of phenolic primary antioxidants in the matrix. This presence of lower carbonyl concentration was also corroborated by a decrease in the shear viscosity and molecular weight with increase in reprocessing cycles suggested that instead of oxidation, the occurrence of chain scission reactions was the dominant factor.

CONCLUSION

In this present study, the effect of reprocessing cycle on the properties of polypropylene homopolymer was evaluated. With increase in number of passes in the extruder, the melt flow index (MFI) of polypropylene found to increase which is attributed to the molecular chain scissions caused by both the shear and thermal history. After 4th pass, MFI was event found to increase significantly event more than 40%. This observation was also supported by the obtained average molecular weight from GPC and melt viscosity at low shear regime. With increase in number of reprocessing cycles, both weight average molecular weight (M_w)

and number average molecular weight (M_n) found to decrease. However, the molecular weight change was more prominent in case of M_w which indicates towards uniformity of long chain scission showing narrower molecular weight distribution with reprocessing as represented by polydispersity index (PDI). A decrease in low shear viscosity also indicated the decrease in molecular weight with increase in number of reprocessing cycles.

The mechanical properties like tensile stress, elongation at break and izod impact strength were found to decrease with reprocessing cycles. However, the stiffness (flexural modulus) was found to increase with reprocessing cycles which may attribute to embrittlement of the material. This observation was also corroborated by the increase in heat deflection temperature with increase in reprocessing cycles.

The oxidation stability of reprocessed samples found inferior as compared to virgin PP material. Oxidation induction time (OIT) found to decrease as reprocessing in resulted in decrease in polymer chain length which promoted oxidation of the polymer. However, no significant change in onset of degradation was evident in TGA conducted in inert nitrogen atmosphere which justified the role of oxygen in degradation. In DSC, no significant change in melting temperature was observed which indicates that oxidative degradation occurs mainly in amorphous region of the PP molecular chains.

The yellowness index value found increase steadily with number of reprocessing cycles. Multiple thermal history under externally provided heat and shear heat generates lot of PP macro-free radicals in the matrix which further undergo β -scission creating unsaturation. With increase in reprocessing cycles, number of unsaturated sites also increase causing an increase in yellowness index values. It is well known that, with increase in oxidative degradation the intensity of carbonyl peaks at about $1720-1740\text{ cm}^{-1}$ wavenumber increases in FTIR spectroscopy. However, in this present study, a very feeble carbonyl characteristic peak was observed at 1724 cm^{-1} in neat PP sample due to consumption of phenolic primary antioxidants to stabilize the polymer and been converted to quinone structure containing carbonyl group (C=O). This characteristics peak was not observed in reprocessed samples till 8th pass as primary antioxidant got consumed for stabilization. Interestingly, after 8th pass, carbonyl group was further found to reappear due to oxidative degradation of PP in absence of antioxidants in the matrix.

Considering the industrial context, all these detailed understanding can be utilized to anticipate the effect of various processing conditions like temperature profile of the extruder as well as injection molding machine, screw rpm and stabilizer concentration to retain the optimum properties of the reprocessed material.

Acknowledgements:

All the authors have accepted responsibility for the entire content of this submitted manuscript. This research received no external funding.

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