

Effects of Recycling Processes on Physical, Mechanical and Degradation Properties of PET Yarns

Hyun Jin Koo*, Gap Shik Chang, Seong Hun Kim¹, Wan Gyu Hahm², and Seong Yoon Park³

Reliability Division, FITI Testing and Research Institute, Seoul 130-864, Korea

¹Department of Organic Nano Engineering, Hanyang University, Seoul 133-791, Korea

²Technical Textile Technology Center, Korea Institute of Industrial Technology, Ansan 426-171, Korea

³HUVIS Corporation, Daejeon 306-230, Korea

(Received April 10, 2013; Revised July 3, 2013; Accepted July 9, 2013)

Abstract: Mechanical properties and the long-term degradation properties of the recycled PET yarns are typically lower than the virgin PET yarns due to the contaminants coming from non-PET bottles, labels and caps etc. For environmental reasons, recycling of post-consumer polyester bottles into textile fibers has become commercially attractive. We studied mechanical and chemical recycling processes and examined their effects on yarn properties such as tensile properties, thermal characteristics, hydrolysis and photo-degradation. It was found that the virgin and the chemical recycled yarns with sufficient purification show similar processability, physical and mechanical properties, and long-term degradation behavior. The results provide useful information on recycled PET yarns for processability and serviceability for the high-end use.

Keywords: Mechanical recycling, Chemical recycling, Depolymerization, Hydrolysis, Photo-degradation

Introduction

In mechanical recycling the waste bottles are recycled directly as polymer feed through the process of grinding, cleaning, separating, dehydrating, drying, and re-melting. The waste bottles collected in domestic regions have lower quality than those of foreign countries due to the fact that those have much more contaminants such as labels, general wastes, etc. Therefore the cleaning process is very important to increase the physical and mechanical properties of recycled PET flakes.

In chemical recycling shown in Figure 1, they are depolymerized to give chemical intermediates (monomers or oligomers), which can then be re-polymerized. PET may be depolymerized using a range of chemical agents and processing conditions, the most important methods of which are methanolysis, hydrolysis and glycolysis [1]. Total depolymerization process to monomers such as methanolysis

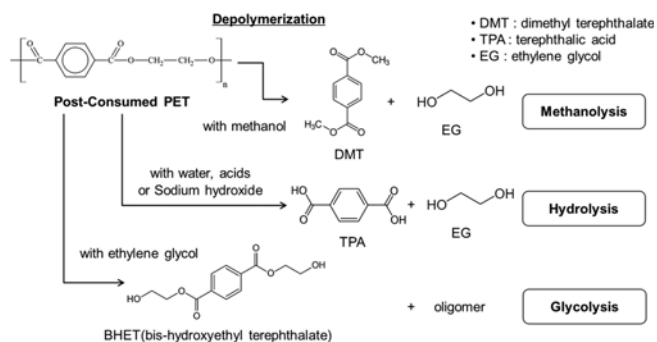


Figure 1. Chemical recycling process.

is more tolerant of contamination while it is more expensive than glycolysis. For this reason, the glycolysis process is widely used for thermoplastic polymers such as PET and Polyurethane [2].

Chemical recycling process allows any contaminants bound to the polymer chain to be removed by purification of the monomers and oligomers while mechanical recycling process can separate inorganic contaminants and therefore the organic contaminants are remelted in extrusion process.

The mechanical properties and long-term degradation properties of recycled PET yarns are known to be lower than virgin PET yarns due to the contaminants coming from non-PET bottles, labels and caps etc. which cause the reduction in intrinsic viscosity (IV) during the remelting or spinning processes [1,3]. Contaminants such as PVC, PVDC, glues, EVA, paper etc. generate acidic compounds which catalyze the hydrolysis of the PET's ester linkages while thermal degradation reaction is catalyzed by metal compounds such as residues of the transesterification or polycondensation

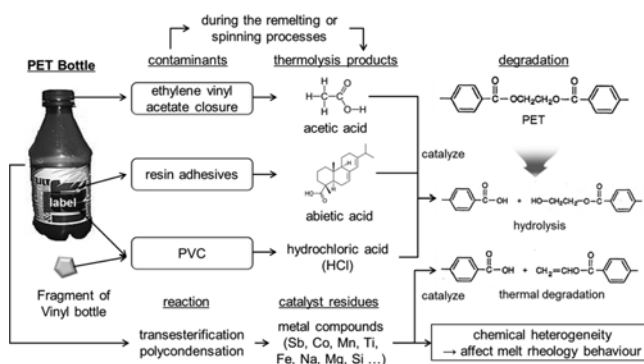


Figure 2. Effect of contaminants on the degradation of recycled PET.

*Corresponding author: koohh@fiti.re.kr

catalysts [4,5] as shown in Figure 2.

In addition, residual moisture in PET must be below 0.02 % in order to avoid molecular weight reduction by hydrolysis. The rate of hydrolysis of ester links has been reported to be several orders of magnitude higher than their thermal breakdown rate [6]. Therefore, the recycled PET should conform to the minimal contamination requirement in order to be able to be used in high-value applications.

In this study, we have compared virgin PET, mechanical recycled PET and chemical recycled PETs with different degree of purification in the aspect of processability, physical, mechanical and long-term degradation properties.

Experimental

Sample Preparation

The waste bottles were cleaned in bottle state before grinding process, and re-cleaned in flake state to improve the purity of mechanical recycled PET flakes. Also, aluminum and floating materials were removed and the moisture regain in recycled PET flakes was reduced to 0.8 % by applying the advanced dehydration process. The PET flakes were reprocessed into granules by melt extrusion. After the filtration of inorganic contaminants, the mechanical recycled chips were obtained. The detailed mechanical recycling process is shown in Figure 3.

The chemical recycled PET chips were obtained using glycolysis of PET with purification of bis-hydroxyethyl terephthalate (BHET) at relatively low temperature to virgin PET processes in order to reduce CO₂ emissions. In details,

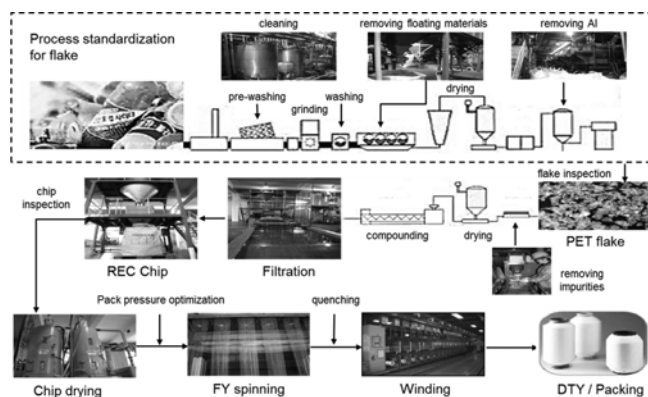


Figure 3. Mechanical recycling process.

glycolysis of PET flake was performed under pressure at around 200 °C to give BHET and oligomers. The metal catalyst used in depolymerization is eliminated by an ion exchange resin at about 140 °C. Purification of BHET was achieved by melt filtration under pressure to remove physical impurities using pilot and full scale purification facilities in order to compare the degree of purification. Even though the purification processes are the same for pilot and full scale facilities, the efficiency of pilot scale facility is lower than that of full scale facility due to the shorter treatment time and smaller filter size. Accordingly, the recycled chips contained more inorganic contaminants which cause the higher pack pressure during the spinning process. This was followed by treatment with activated carbon to selectively desorb those impurities responsible for poor color and also oxidative degradation promoters.

Virgin PET chips, mechanical recycled PET (MR-PET) chips and chemical recycled PET (CR-PET-P, CR-PET-F) chips were melt spun to produce a drawn textured yarn (DTY) composed of 72 multi-filaments with 1 denier of linear density. The recycled PET chips show higher IV than virgin PET chips since PET bottles are based on copolyesters, such as isophthalic acid modified PET and required a higher IV than fiber application. The samples used in this study are summarized in Table 1.

Test Methods

Tensile properties, intrinsic viscosity, and melting temperature were measured according to the standard test methods given in Table 2. Tensile properties were measured in accordance with KS K 0412 at (30±2) cm/min of a strain rate with 25 cm of the gauge length between the yarn grips. The intrinsic viscosity was measured according to ASTM D 4603 which is a dilute solution viscosity measurement in a solvent mixture of phenol-tetrachloroethane. The melting temperature

Table 2. Test methods for physical and mechanical properties

Properties	Unit	Test methods
Linear density	denier	KS K ISO 2060
Tenacity	g/d	KS K 0412
Tensile strain	%	
Melting temp.	°C	DSC
Intrinsic viscosity	-	ASTM D 4603

Table 1. PET samples used in this study

Recycling process	Chips	Yarns
Virgin PET	Virgin PET (IV 0.645)	Virgin PET DTY 75/72
Mechanical recycled PET	MR-PET (IV 0.674)	MR-PET DTY 75/72
Chemical recycled PET(P)*	CR-PET-P (IV 0.659)	CR-PET-P DTY 75/72
Chemical recycled PET(F)**	CR-PET-F (IV 0.652)	CR-PET-F DTY 75/72

*Chemical recycled PET(P) purified using pilot-scale facility and **chemical recycled PET(F) purified using full-scale facility.

Table 3. Test conditions for long-term degradation

Long-term properties	Test conditions			Duration time (h)
	Temp. (°C)	Humidity (% R.H.)	Irradiance (W/m ²)	
Hydrolysis	90	95	-	360
Photo-degradation*	70	50	1.5	24

*Xenon arc lamp, S-borosilicate (inner)/S-borosilicate (outer) filter combination and temperature of BPT (black panel thermometer), spectral irradiance at 340 nm.

was measured by differential scanning calorimetry (DSC) through measuring energy differences by temperature change. The melting profile is that temperature was increasing 40 °C to 300 °C at 40 °C/min and cooling.

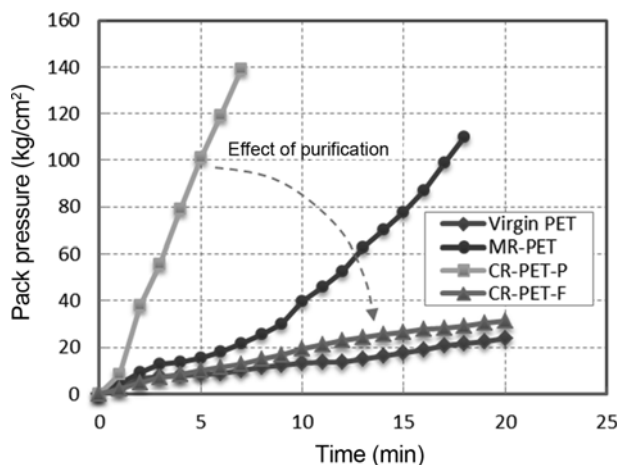
In addition, the long-term degradation properties were measured for hydrolysis and photo degradation in order to conform to the serviceability. For hydrolysis and photo degradation testing, PET yarns were arrayed in the specially designed yarn holders to prevent entanglement and then tested in the equipment. The test conditions for long-term degradation were summarized in Table 3.

Results and Discussion

Processability

Usually, more broken filaments and higher pack pressure took place in the melt spinning process of recycled PET. The processability of various recycling processes was examined by plotting the pack pressure along with time as shown in Figure 4.

The pack pressure of CR-PET-P increases largely followed by MR-PET and CR-PET-F. It indicates that more contaminants left in the chemical recycled PET chips without enough purification than mechanical recycled PET chips. On the other hand, the increases in pack pressure are similar for

**Figure 4.** Pack pressure vs. time for various recycled PET during the melt spinning process.**Table 4.** Effects of recycling processes on IV drops during melt spinning

Samples	IV		IV drop (%)
	Chip	Yarn	
Virgin PET	0.645	0.608	5.7
MR-PET	0.674	0.621	7.9
CR-PET-P	0.659	0.573	13.1
CR-PET-F	0.652	0.626	4.0

virgin PET and CR-PET-F. The glycolysis with purification of BHET is found to be the most important process to decrease the chemical heterogeneity and to improve spinnability and yarn quality.

The intrinsic viscosity may be reduced during the recycling process due to the contaminants. In order to have a sign of changes in the molecular weight and possible degradation during melt spinning process, IV values of chips and yarns were compared. As it can be seen in Table 4, IV losses of MR-PET and CR-PET-P are considerably higher than that of virgin PET. It might be due to the contaminants remain in the MR-PET and CR-PET-P chips. However the IV drop of CR-PET-F has improved dramatically than that of CR-PET-P, and shows similar behavior of virgin PET. These results agree well with low processability with high pack pressure due to contaminants during the melt spinning process described in Figure 4.

Physical and Mechanical Properties

The effects of recycling methods on yarn properties were investigated through comparing the tensile properties and thermal characteristics. The test results were shown in Table 5 and Figure 5. The linear densities are around 75 denier for all PET yarns. The tenacity of CR-PET-F yarn is highest and the rest of PET yarns have similar tenacities. The tensile strains of mechanical and chemical recycled PET yarns are lower than that of virgin PET yarn. The tenacities show positive relationship with IV values of yarn samples. It means that the tensile properties can be optimized by controlling IV values of recycled chips.

The decreases in melting temperature of MR-PET and CR-PET-P yarns might be due to the chemical heterogeneity. However the melting temperature of CR-PET-F yarn increases

Table 5. Physical and mechanical properties of PET yarns used in this study

Samples	Linear density (denier)	Tenacity (g/d)	Tensile strain (%)	Melting temp. (°C)
Virgin PET DTY 75/72	77.8	4.54	25.4	253
MR-PET DTY 75/72	74.5	4.76	17.7	249
CR-PET-P DTY 75/72	75.8	4.52	18.0	248
CR-PET-F DTY 75/72	76.0	5.19	19.4	251

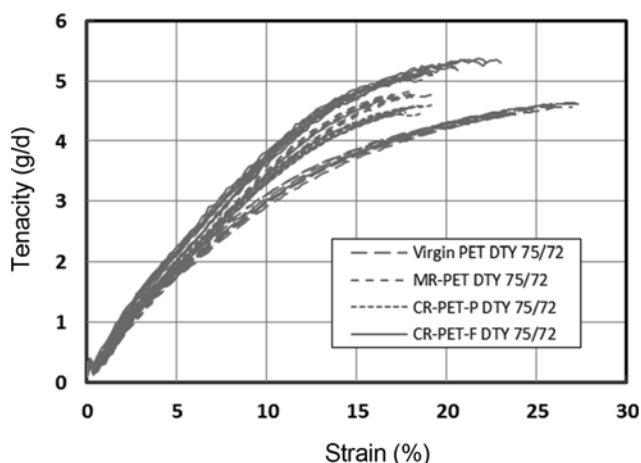


Figure 5. Tensile properties of PET yarns.

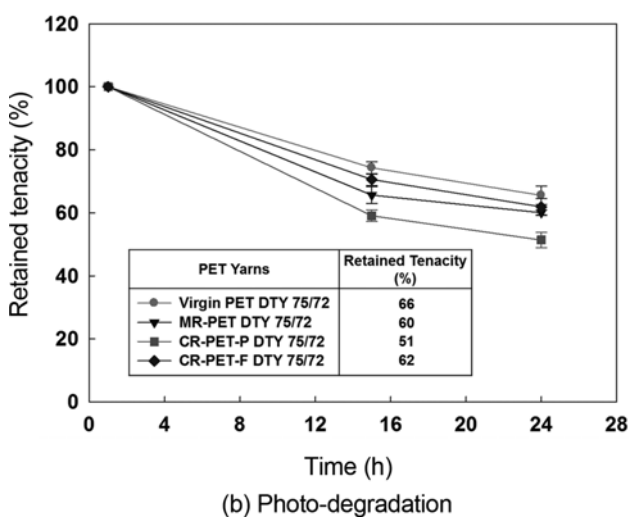
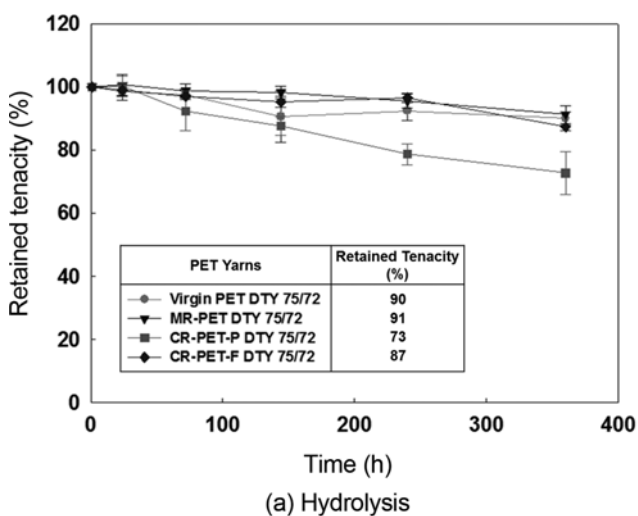


Figure 6. Long-term degradation properties for the virgin and recycled PET yarns.

up to 251 °C by improving the degree of purification.

Long-term Degradation Properties

The hydrolysis and photo-degradation behaviors of the virgin and recycled PET yarns are shown in Figure 6 and the test conditions are given in Table 3. The thermal degradation was combined with hydrolysis and photo degradation since the high temperature accelerates hydrolysis and photo-degradation, effectively.

The photo-degradation is more severe than hydrolysis and the tenacities decrease up to (34-49)% after photo-degradation given in Table 6. The CR-PET-P yarn shows the lowest retained tenacity after photo-degradation and hydrolysis while the CR-PET-F yarn shows the similar degradation behaviors to virgin PET yarn. The MR-PET yarn shows similar resistance to hydrolysis to virgin PET yarn while more photo-degradation than virgin PET yarn. In case of CR-PET yarns, the degree of purification is positively correlated with processability, physical, mechanical and long-term degradation properties. The MR-PET yarn shows, however, different degradation behaviors for hydrolysis and photo-degradation with respect to CR-PET. It contains more remelted organic contaminants which might accelerate photo degradation rather than hydrolysis. This indicates that the differences in the long-term degradation properties of recycled PET yarns compared with virgin PET yarn can be attributed mainly to the additional thermal history experienced by the recycling process and contaminants [7].

Conclusion

Losses of IV and increases in pack pressure during melt spinning are the highest for CR-PET-P followed by MR-PET, virgin PET and CR-PET-F. The processability agrees well with the losses of IV since more broken filaments and higher pack pressure ($\Delta\text{bar/hr}$) took place along with the losses of IV due to the contents of contaminants and the chemical heterogeneity for recycled PET.

The virgin and CR-PET-F yarns show similar processability, physical, mechanical and long-term degradation properties while the CR-PET-P yarn shows insufficient resistance to long-term degradation properties with low processability worse than MR-PET yarn. It proved that more contaminants left in the chemical recycled PET chips without enough purification than mechanical recycled PET chips.

In this study, the most significant finding is that the chemical recycled yarns can be used for high-value applications to conform the full purification of BHET during the glycolysis process and consistent batch-to-batch quality.

Acknowledgement

This work was supported by the Ministry of Trade, Industry and Energy (Project No. 10035180).

References

1. M. Abbasi, M. R. M. Mojtahedi, and A. Khosreshahi, *J. Appl. Polym. Sci.*, **103**, 3972 (2007).
2. X. Wang, H. Chen, C. Chen, and H. Li, *Fiber. Polym.*, **12**, 857 (2011).
3. M. Mannhart, *Synthetic Fibers*, **27**, 9 (1998).
4. H. Zimmermann in "Development in Polymer Degradation" (N. Grassie Ed.), Vol.5, p.112, Applied Science Publishers, 1984.
5. J. Scheirs, "Polymer Recycling-Science, Technology and Applications", p.119, John Wiley & Sons, Ltd., 1998.
6. K. S. Seo and J. D. Cloyd, *J. Appl. Polym. Sci.*, **42**, 845 (1991).
7. H. J. Koo, S. H. Kim, and G. S. Chang, *Proc. of ATC-11*, 199 (2011).