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AN EXPLORATION INTO THE USE OF STEPWISE REGRESSION ANALYSIS TO DETERMINE POST-CONSUMER RECYCLED PET CONTENT IN PET SHEET

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AN EXPLORATION INTO THE USE OF STEPWISE REGRESSION ANALYSIS TO DETERMINE POST-CONSUMER RECYCLED PET CONTENT IN PET SHEET

By

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ABSTRACT

AN EXPLORATION INTO THE USE OF STEPWISE REGRESSION ANALYSIS TO DETERMINE POST-CONSUMER RECYCLED PET CONTENT IN PET SHEET

By

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The aim of this research was to explore the use of a stepwise regression analysis to determine the post-consumer recycled polyethylene terephthalate (PET) content in PET sheets. Six kinds of PET sheets with varying percent of virgin (V) and recycled (R) PET contents were produced at Peninsula Packaging Company (Exeter, CA, USA). The optical, thermal, barrier and thermo-mechanical properties of the PET sheets were evaluated as function of RPET contents. There was a statistically significantly difference between the UV and visible light absorption in the region between 200 and 350 nm and 670 and 700 nm, respectively. Color measurement indicates that more RPET contents in PET sheets lead to greyer, greener and more yellow color. DSC indicates that the melting (T_m) and cold crystallization temperatures follow a semi-linear trend with the amount of RPET in the blends. Intrinsic viscosities were statistically significantly different between 100%V and 100%R PET sheets. The results of ^1H NMR indicates that protons of end groups in 60V40R, 40V60R and 20V80R PET were higher than 100V PET ($\alpha=0.05$). A tentative stepwise regression model emerged with an adjusted R^2 of 0.9740 for predicting the amount of RPET, with intrinsic viscosity, UV, color, T_m, and oxygen permeability values as predictor variables. This model was developed for a specific mechanical RPET stream provided by the ECO2 company (Modesto, CA, USA). At this stage, it is not applicable for other recycled PET streams and products without new studies.

Dedicated to my family and friends

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TABLE OF CONTENTS

LIST OF TABLES ix

LIST OF FIGURES xii

KEY TO ABBREVIATIONS OR SYMBOLS xiv

1. INTRODUCTION 1

2. LITERATURE REVIEW 4
  2.1 Introduction 4
  2.2 Virgin PET 5
    2.2.1 PET synthesis 6
    2.2.2 Morphology of PET 8
    2.2.3 PET applications and processing 9
  2.3 Municipal solid waste of virgin and recycled PET resin 10
    2.3.1 Continued high price for virgin PET 13
    2.3.2 Increasing demand for PET 14
    2.3.3 Increasing demand for Recycled PET (RPET) 16
    2.3.4 Low environmental footprint of RPET 17
  2.4 Management method of PET 19
    2.4.1 Packaging in municipal solid waste 22
    2.4.2 Source reduction of PET packaging 24
      2.4.2.1 Lightweight 25
      2.4.2.2 Reuse and refill 27
    2.4.3 Recycling of PET packaging 29
  2.5 Legislation of PET recycling for food use 30
  2.6 Recycled PET 31
    2.6.1 Collection 32
    2.6.2 Recyclables processing of PET 34
      2.6.2.1 Materials recovery facilities (MRFs) 34
      2.6.2.2 Mixed waste processing 35
    2.6.3 Conventional recycling process 35
      2.6.3.1 Chemical recycling 36
      2.6.3.2 Mechanical recycling 37
    2.6.4 Effects of contaminants on recycling of PET 38
      2.6.4.1 Acid producing contaminants 39
      2.6.4.2 Water 39
      2.6.4.3 Coloring contaminants 39
      2.6.4.4 Acetaldehyde 40
      2.6.4.5 Other contaminants 40
    2.6.5 End use applications of recycled PET 40

3. METHODOLOGY 43

3.1 Materials......43
3.2 Optical properties......43
3.3 Mechanical properties......44
3.4 Thermal properties......45
3.5 Barrier properties......46
3.6 Nuclear Magnetic Resonance (NMR) Spectroscopy......46
3.7 Viscosimetry......47
3.8 Statistic Analysis......47

4. RESULTS AND DISCUSSION......49
4.1 Optical analysis......49
4.1.1 UV-Visible Spectroscopy......49
4.1.2 Colorimeter......53
4.2 Mechanical analysis......54
4.2.1 Dynamic Mechanical Analysis (DMA)......54
4.2.2 Universal Material Testing......55
4.3 Thermal analysis......57
4.4 Intrinsic viscosity......59
4.5 Barrier properties......60
4.6 Nuclear Magnetic Resonance analysis (NMR)......61
4.7 Stepwise regression analysis......65
4.8 Preliminary verification of the model......72
4.9 Limitation of the study and the model......76

5. CONCLUSION......77

6. APPENDICES......80
6.1 Appendix A- Description of sample production and processing conditions......80
6.1.1 Processing condition of 80R20V PET sheet......83
6.1.2 Processing condition of 100R PET sheet......85
6.1.3 Processing condition of 60R40V PET sheet......87
6.1.4 Processing condition of 40R60V PET sheet......89
6.1.5 Processing condition of 20R80V PET sheet......91
6.1.6 Processing condition of 100V PET sheet......93
6.2 Appendix B – Description of stepwise regression analysis and SAS code......95
6.2.1 Multiple linear regression analysis......95
6.2.2 Pearson correlation coefficient......95
6.2.3 R, R Square and adjusted R Square......96
6.2.4 Stepwise regression......97
6.2.4.1 Forward selection......97
6.2.4.2 Backward selection......97
6.2.4.3 Stepwise selection......98
6.2.5 SAS code for this study......98
6.3 Appendix C – Description for each linear regression and estimated parameter for each step......103
6.3.1 Description for simple linear regression between TG and dependant variables103
6.3.2 Description for simple linear regression between TM and dependant variables104

6.3.3 Description for simple linear regression between χc and dependant variables106
6.3.4 Description for simple linear regression between UV380 and dependant variables........107
6.3.5 Description for simple linear regression between IV and dependant variables109
6.3.6 Description for simple linear regression between OTR and dependant variables110
6.3.7 Description for simple linear regression between WVTR and dependant variables........112
6.3.8 Description for simple linear regression between NMR424 and dependant variables........113
6.3.9 Description for simple linear regression between 'L*' and dependant variables114
6.3.10 Description for simple linear regression between 'a*' and dependant variables116
6.3.11 Description for simple linear regression between 'b*' and dependant variables117
6.3.12 Description of the estimated parameter for each step........119

7. REFERENCES........120

LIST OF TABLES

Table 2-1. Trade names of PET and their manufacturers [22] 6

Table 2-2. Common properties of PET 8

Table 2-3. Required intrinsic viscosity for different PET applications [20, 22] 10

Table 2-4. Values of damage categories for 100V, 50V50R and 100R PET bottle 19

Table 2-5. Generation and recovery of products in MSW, 2007 [8] 23

Table 2-6. Energy and material saving of lightweight PET bottles compared to traditional PET bottles [36] 25

Table 2-7. Examples of lightweight bottle productions with company [38-40] 27

Table 2-8. Costs of 500 ml refillable and one-way glass and PET beverage containers in Europe [41] 28

Table 2-9. Refillables as a portion of total beverage sales and policies in some countries [41] 29

Table 2-10. Examples of recommended surrogates [42] 30

Table 2-11. US FDA no objection letters, until December 2008 [43] 31

Table 2-12. Minimum requirements for PCR-PET flakes to be used for sheet applications [13, 24] 32

Table 2-13. Number and population served by curbside recyclables collection programs in the U.S. 2007 [8] 33

Table 2-14. Material recovery facilities in U.S., 2007 [8] 35

Table 2-15. U.S. consumption of recycled PET as different product categories [1] 41

Table 4-1. Light transmission (%) for PET sheets with varying percent of virgin and recycled PET contents 52

Table 4-2. Results of color measurement for varying percent of virgin and recycled PET sheets 54

Table 4-3. Maximum loss, tan delta curve and onset of rubbery plateau as temperature values 55

Table 4-4. Mechanical properties for PET sheets with varying percent of virgin and recycled PET contents 56

Table 4-5. DSC data for PET sheets with varying percent of virgin and recycled PET contents 57

Table 4-6. Intrinsic viscosity and viscosity molecular weight 60

Table 4-7. Water vapor permeability for PET sheets with varying percent of recycled PET as SI units 61

Table 4-8. Composition ratio of PET sheets with varying percent of recycled and virgin PET contents 63

Table 4-9. Pearson correlation of predictor variables for PET sheets with varying percent of virgin and recycled PET contents 65

Table 4-10. p-value, skewness, mean, median for the simple regression analysis for the predictor variables for PET sheets with varying percent of virgin and recycled PET content. (α and β values for the equation $y=\alpha*X+\beta$ and the normal distribution of the standard errors are shown in appendix C.) 68

Table 4-11. Backward elimination sequence for PET sheets with varying percent of virgin and recycled PET as function of results from each different technique 69

Table 4-12. Proposed linear model ($PET= \alpha+\beta*IV+\chi*OTR+\delta*Tm+\eta *b+\varepsilon$) 70

Table 4-13. Results of each predictor parameter for 4 different kinds of unknown PET samples 74

Table 4-14. Comparison between predicted fraction of virgin PET and company specification 75

Table 6-1. Description of extruder zone 81

Table 6-2. The condition of two extruders for 80R20V PET sheet 83

Table 6-3. The temperature of dryer and plant for 80R20V PET sheet 83

Table 6-4. The condition of roller for 80R20V PET sheet 84

Table 6-5. The condition of two extruders for 100R PET sheet 85

Table 6-6. The temperature of dryer and plant for 100R PET sheet 85

Table 6-7. The condition of roller for 100R PET sheet 86

Table 6-8. The condition of two extruders for 60R40V PET sheet 87

Table 6-9. The temperature of dryer and plant for 60R40V PET sheet 87

Table 6-10. The condition of roller for 60R40V PET sheet 88

Table 6-11. The condition of two extruders for 40R60V PET sheet 89

Table 6-12. The temperature of dryer and plant for 40R60V PET sheet 89

Table 6-13. The condition of roller for 40R60V PET sheet 90

Table 6-14. The condition of two extruders for 20R80V PET sheet 91

Table 6-15. The temperature of dryer and plant for 20R80V PET sheet 91

Table 6-16. The condition of roller for 20R80V PET sheet 92

Table 6-17. The condition of two extruders for 100V PET sheet 93

Table 6-18. The temperature of dryer and plant for 100V PET sheet 93

Table 6-19. The condition of roller for 100V PET sheet 94

Table 6-20. Estimated parameter, P value and 95% confidence interval for step 0 119

Table 6-21. Estimated parameter, P value and 95% confidence interval for step 1 119

LIST OF FIGURES

Figure 2-1. PET synthesis reactions: (a) Esterification reaction and (b) *trans*-Esterification reaction 7

Figure 2-2. Materials generated in MSW, 1960 to 2007 [8], Others includes electrolytes in batteries and fluff pulp, feces, and urine in disposable diapers 11

Figure 2-3. Total plastics in MSW, by resin, 1996 to 2007 [8], Others includes electrolytes in batteries and fluff pulp, feces, and urine in disposable diapers.................. 12

Figure 2-4. Recovery of plastics in MSW, by resin, 1996 to 2007 [8], others includes electrolytes in batteries and fluff pulp, and plastic in disposable diapers.......................... 13

Figure 2-5. U.S. price trends of gasoline and crude oil, according to the Energy Information Administration (Data released on 07/13/2009 for gasoline and 07/15/2009 for crude oil) 14

Figure 2-6. Total weight of bottles on U.S. shelves and collected with gross recycling rate, from 1995 to 2007 [1] 15

Figure 2-7. Price of recycled and virgin PET, 1997 to 2009, according to the report of Innovation Group “Chemical Profile-PET” and Plastics News.com “PET resin prices”.. 17

Figure 2-8. Comparison of damage categories for production of 100V, 50V50R, 100R PET bottle; 100V PET bottle , 50V50R PET bottle , 100%R PET bottle 18

Figure 2-9. Diagram of solid waste management [32] 20

Figure 2-10. MSW generation, recycling and % recycling in U.S., 1960 to 2007 [8] 21

Figure 2-11. Municipal solid waste management, 1960 to 2007 [8] 21

Figure 2-12. Total MSW generation by category, 2007 [8] 22

Figure 2-13. Depolymerization of PET: (a) Hydrolysis (b) Methanolysis (c) Glycolysis [19, 22] 37

Figure 2-14. Degradation of PET: (a) hydrolysis (b) thermal degradation [14, 25]..........38

Figure 2-15. U.S. converter consumption of recycled PET as different product categories [1]; Fiber (•), Sheet & Film (o), Strapping (▼), Engineering resin (Δ), Food & Beverage bottles (■), Non-food Bottles (□), Other (♦) 42

Figure 4-1. Constitutional unit of PET 49

Figure 4-2. Light transmission of PET sheets with varying percent of virgin and recycled PET contents between 323 and 450nm 50

Figure 4-3. Light transmission of PET sheets with varying percent of virgin and recycled PET contents between 650 and 750nm 50

Figure 4-4. 500 MHz ^{1}H-NMR spectrum of 100V PET samples measured in TFA/$CDCl_3$ 62

Figure 4-5. Predicted percentage of PET contents in PET sheets as function of experimental PET contents in PET sheets (left), Standardized residual vs percentage of PET contents in PET sheets (right) 71

Figure 6-1. The flow chart of PET sheet processing 82

KEY TO ABBREVIATIONS OR SYMBOLS

ABBREVIATIONS

ANOVA	Analysis of variance
APR	Association of Postconsumer Plastic Recyclers
ASTM	American Society for Testing and Materials
BHET	Bis (hydroxyethyl) terephthalate
CIWMB	California Integrated Waste Management Board
CSD	Carbonate soda
DALY	Disability Adjusted Life Years
DC	Dietary concentration
DMA	Dynamic mechanical analysis
DMT	Dimethyl terephthalate
DP	Degree of polymerization
DSC	Differential scanning calorimeter
EDI	Estimated daily intake
EG	Ethylene glycol
EPA	Environment Protection Agency
FDA	Food and Drug Administration
HDPE	High density poly (ethylene)
HSD	Honestly significant differences
LDPE	Low density poly (ethylene)

LLDPE	Linear low density poly (ethylene)
MRFs	Materials recovery facilities
MSW	Municipal Solid Waste
NAPCOR	The National Association for PET Container Resources
NMR	Nuclear magnetic resonance
OTR	Oxygen transmission rate
PCR	Post-consumer recycled
PDF	Potentially Disappeared Fraction
PET	Poly (ethylene trepthalate)
RPET	Recycled poly (ethylene terepthalate)
PP	Poly (propylene)
PS	Poly (styrene)
PVC	Poly (vinyl Chloride)
RH	Relative humidity
RPPC	Rigid Plastic Packaging Container
SSP	Solid state polymerization
TFA	Trifluoroacetic acid
TPA	Terephthalic acid
WVTR	Water vapor transmission rate

SYMBOLS

α	Thermal expansion coefficient, Scalar for Mark-Hauwink Equation Significant level, Intercept of multi-linear model
atm	Atmosphere
β	Estimated parameter for intrinsic viscosity
βi	Parameters or regression coefficients
^0C	Celsius
¢	Cent
$CDCl_3$	Chloroform
CO_2	Carbon dioxide
-COOR	Ester group
dl	Deciliter
ε	Residue
^1H	Hydrogen proton
hr	Hour
IV	Intrinsic viscosity
J	Joule
K	Kelvin, Constant for Mark-Houwink Equation
kPa	Kilopascal
ksi	Kilopound per square inch
kWh	kilowatt hour
l	Thickness

MHz	Megahertz
mmlbs	Million pounds
$\overline{M}_V$	Viscosity molecular weight
MPa	Megapascal
η	Estimated parameter for 'b' value
$[\eta]$	Intrinsic viscosity
nm	Nanometer
NMR424	Intensity ratio of δ 4.2 combined with 4.0 peak
ppb	Part per billion
ppm	Part per million
psi	Pounds per square inch
q	Quantity
r	Pearson correlation coefficient
R	Recycled
std	Standard deviation
Tc	Crystallization temperature
Tcc	Cold crystallization temperature
Tg	Glass transition temperature
TM	Trademark
Tm	Melting temperature
µm	Micrometer
UV	Ultra violet
UV350	Light transmission at 350 nm

UV380	Light transmission at 380 nm
UV678	Light transmission at 678 nm
V	Virgin
χ	Estimated parameter for oxygen permeability value
χc	Percent of crystallinity
$\overline{X}$	Sample mean of independent variables
Y	Dependant variables
Y'	Predicted value
$\overline{Y}$	Sample mean of dependent variables
ΔHm	Heat of melting
ΔHc	Heat of crystallization
ΔH_m^o	Heat of fusion of 100% crystalline polymer
λ	Wavelength
δ	Difference of NMR spectrum between standard and sample intensity, Estimated parameter for melting temperature
●	Fiber
○	Sheet & Film
▼	Strapping
Δ	Engineering resin, delta
■	Food & beverage bottles
□	Non-food bottles
♦	Other

1. INTRODUCTION

Poly (ethylene terephthalate) (PET) is one of the most widely used thermoplastic polyesters in the U.S. and around the world. In 2007, 5.7 billion pounds of PET bottle resin were used by the U.S. bottle manufacturers utilizing recycled sources; excluding post industrial regrind, and including exported bottles and pre-forms as well as bottles less than eight ounces in sizes [1]. Since PET has good chemical, physical and mechanical properties, and provides good oxygen and carbon dioxide barrier properties, it is successfully being used in applications such as beverage bottles, fibers, moldings and sheets. The most widely used application of PET in the U.S. is the manufacture of bottles [2]. PET beverage bottles sales in the U.S. have grown approximately 9% annually, from 1995 to 2007 [1].

As the demand for non-renewable PET is increasing, recovering of post-consumer PET (RPET) is also increasing. Recovering of PET is being managed by collection, separation, cleaning and reprocessing it as new products. Total recycled bottle grade PET production by the U.S. reclaimers was recorded at 1,079 million pounds in 2007 compared to 588 million pounds in 1995, representing an increase of 83% [1]. The main application of recycled PET is the manufacture of fiber (383 million pounds), beverage bottles (136 million pounds), and sheet & film (128 million pounds) non-food bottles (60 million pounds) [1].

RPET from bottles can be recycled via mechanical and chemical recycling. During mechanical recycling, PET is melt processed into other parts [3]. Chemical recycling, on the other hand, by glycolysis, methanolysis, hydrolysis, amninolysis and ammonolysis can recover the PET monomers (i.e., terephthalic acid and ethylene glycol)

[4]. According to David Cornell, technical director of the Association of Postconsumer Plastic Recyclers (APR), at least 95% of PCR-PET was mechanically recycled in 2007. On the other hand, the amount of PCR-PET chemically recycled was very small due to higher processing cost than mechanical recycling. Cost efficiency of chemical recycling can be achieved in quantities of 50,000 tons/year, whereas mechanical recycling is more cost efficient with plant capacities within a range of 5,000 to 20,000 tons/year [5].

Generally, RPET recycling is performed by collecting scraps from homogeneous deposits like carbonated and non-carbonated bottled drinks, and from heterogeneous deposits contaminated by polyvinyl chloride (PVC) nylon and various additives. Among the problems met in the reprocessing of PET bottle scraps, the degradation caused by the simultaneous presence of retained moisture and the contaminants is a main drawback for obtaining high quality RPET [6]. The retained moisture and contaminants generate problems during processing, such as chain cleavage, an increase in carboxylic end groups, a reduction in molecular weight and a decrease in intrinsic viscosity [6-7]. Thus, the final quality of the RPET resin is lower than virgin PET indicating that RPET products obtained from mechanical recycling have reduced physical, mechanical and chemical properties.

Several approaches have been established to replace products containing virgin PET with post-consumer recycled PET due to environmental responsibility. The incentive to have a lower environmental footprint motivates producers to make claims of higher recycled PET content in the final package. Hence, there is a need to know the amount of RPET in the final product. However, to the best of authors' knowledge, there is not a current technique or model able to determine the post-consumer recycled content of PET film, sheet and containers.

Thus, the aim of this study was to explore the use of stepwise regression analysis to determine the amount of recycled PET content, which was previously recycled by mechanical recycling, in PET/RPET sheets. The model includes the optical, physicomechanical, thermal and barrier properties of PET sheets with varying percent of recycled (R) and virgin (V) PET. The model was developed only considering a single recycled PET stream obtained from the bottle deposited program and provided by the ECO2 company (Modesto, CA, USA). Therefore, at this stage it is not applicable for other recycled PET streams and products without new studies.

2. LITERATURE REVIEW

2.1 Introduction

Plastic materials are currently used for various applications, such as food containers, beverage bottles, and electronic products. Due to their diverse usage and large fraction by volume, plastic materials are treated as one of the important municipal solid waste categories. In 2007, plastic materials composed over 12% of total MSW generation [8]. The predominant method of waste disposal in U.S. has been and remains landfill, representing 54% of total MSW generation [8-9]. However, discarding plastic waste to landfill is undesirable due to legislation pressures, rising costs and the lack of biodegradability of commonly used polymers [9]. As an alternative to landfill, recycling of plastic waste has been proposed as a way to reduce the amount of plastic that ends in the landfill. There are several methods for recycling of plastic waste, such as primary recycling (e.g., plastic bottle to plastic bottle), mechanical recycling, chemical recycling and energy recovery. Among those recycling techniques, mechanical recycling is dominantly used in the U.S. for PET, poly (ethylene terephthalate).

PET is one of the most popular plastics, and it is widely used in various applications, such as soft drink bottles and food containers. Although PET has the highest recovery rate (18.1%) compared to other plastics, such as HDPE, LDPE, PP, and PS, recycling of PET is still developing to satisfy economic benefit and environmental responsibility. The main obstacle for the effective recycling of PET is contaminants, such as a variety of additives, aluminum, polypropylene (PP) closures, and PVC. Therefore, in mechanical recycling systems, the developments have been focused on effective management of the different waste streams, such as selective sorting and automatic separation [10].

The majority of current research focuses on comparison of various properties between recycled PET and virgin PET [7, 11-13], analysis and the improvement of the quality of recycled PET [6, 14-18] and evaluation and improvement of the current PET recycling system [9, 19].

2.2 Virgin PET

PET, polyester, was developed by a small English company in 1941 as laboratory samples. In the 1950s, polyester research was based almost entirely on textiles – DuPont's Dacron™ and ICI's Terylene™. In 1962, Goodyear introduced the first polyester tire fabric, and it was in the late 1960s that polyesters were developed specifically for packaging; film, sheet, coatings, and bottles [20]. Nowadays, PET is one of the most important commodity plastics. Since PET has excellent tensile and impact strength, chemical resistance, clarity, processability, and reasonable thermal stability, it is widely used for many applications, especially drink bottles [21]. Commercial PET has a wide range of intrinsic viscosity $[\eta]$ that varies from 0.45 to 1.2 dl/g with a polydispersity index generally equal to 2. Above the glass transition temperature (T_g), the PET chains are stiff, unlike many other polymers. The low flexibility of the PET chain is a result of the nature of the short ethylene group and the presence of the *p*-phenylene group [22]. Some of the trade names of commercialized PET are shown in Table 2-1 [22].

Table 2-1. Trade names of PET and their manufacturers [22]

Trade name	Manufacturer
Arnite	DSM Engineering Plastics
Diolen	ENKA-Glazstoff
Eastapac	Eastman chemical company
Hostadur	Farbwerke Hoechst AG
Mylar	E. I. Du Pont de Nemours & Co., Inc.
Melinex	Imperial Chemical Industries Ltd.
Rynite	E. I. du Pont de Nemours and Company, Inc.

2.2.1 PET synthesis

PET is a condensation polymer, and it is produced from para-xylene and ethylene. The para-xylene is converted into either dimethyl terephthalate (DMT) or terephthalic acid (TPA), and the ethylene into ethylene glycol (EG) [2]. In an esterification reaction, the TPA reacts with EG at a temperature between 240 and 260 °C and a pressure between 300 and 500 kPa, producing water as the byproduct molecule (Figure 2-1). In *trans*-Esterification, DMT is reacted with EG between 150 and 220 °C and 100 kPa, producing methanol as a byproduct molecule [23-25] (Figure 2-1). *trans*-Esterification is more preferred than esterification due to easier purification. In both processes, bis (hydroxyethyl) terephthalate (BHET) is produced. Next in the the pre-polymerization step, BHET is polymerized to a degree of polymerization (DP) of up to 30 at 250-280 °C and 2-3 kPa [24]. About the next step is the condensation polymerization where the DP is further increased to 100 at 270-290 °C and 50-100 Pa. Up to this stage, PET is suitable for fibers and sheets which do not require high molecular weight or intrinsic viscosity [η]. For the application of bottle grade PET which requires high molecular weight or [η] of

0.7-0.81 dl/g, solid state polymerization (SSP) is applied to increase the DP to 150. Operating conditions for SSP are 200-240 °C at 100 kPa and 5-25 hr [25].

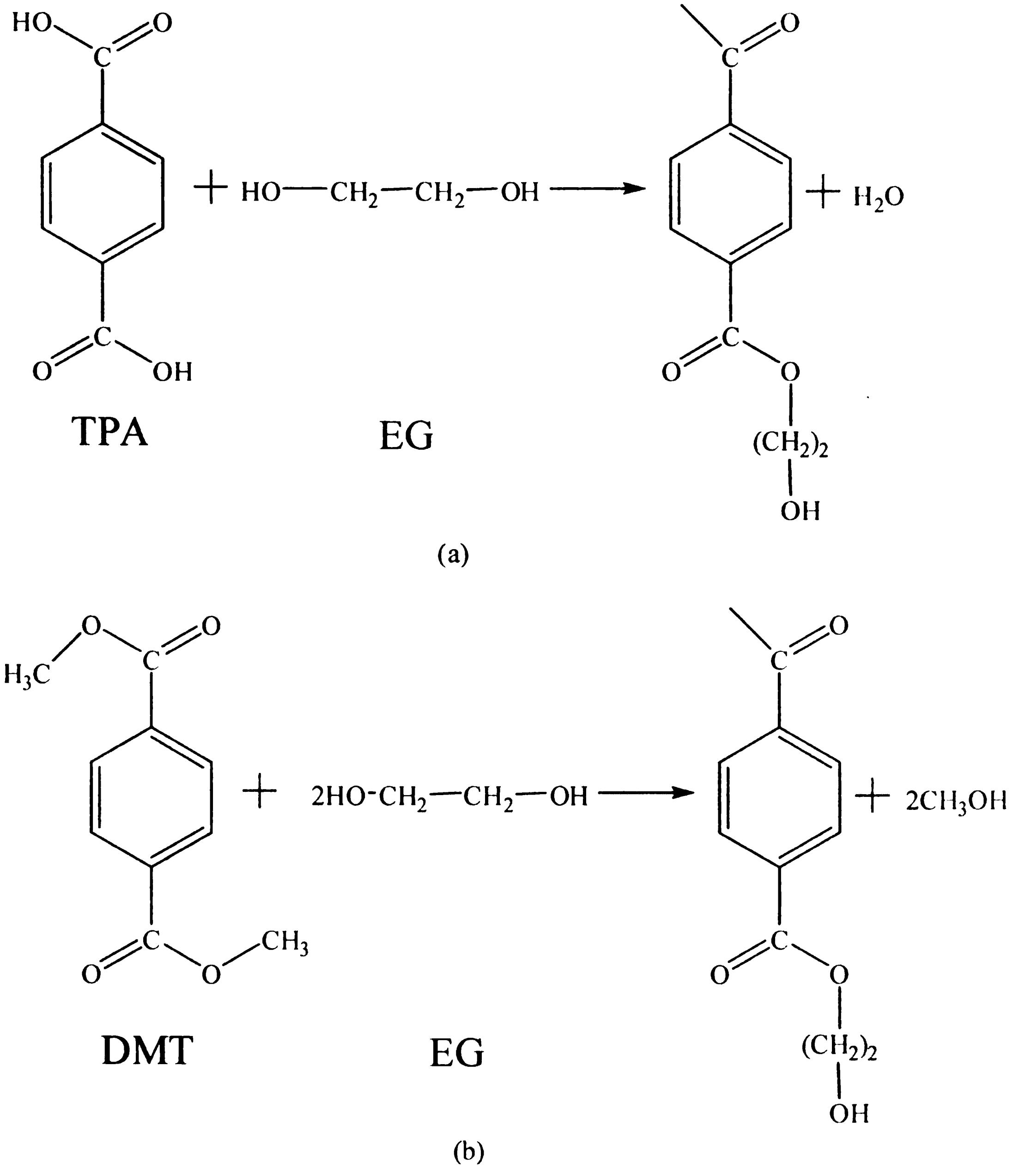

Figure 2-1. PET synthesis reactions: (a) Esterification reaction and (b) *trans*-Esterification reaction

2.2.2 Morphology of PET

PET is a linear molecule that exists either in an amorphous or a semi-crystalline state. In the semi-crystalline state, the molecules are highly organized and form crystallites. The maximum crystallinity level of PET may be no more than 55%. The rate of crystallinity of virgin PET depends on processing conditions, molecular weight, the presence of nucleating agents, the degree of chain orientation and the nature of the polymerization catalyst. Virgin PET is well known for having a very slow crystallization rate. The highest crystallization rate can be achieved between 170 and 190 °C [23, 26]. Since PET can be produced with high crystallinity, processing conditions for PET depends on its application. Cooling PET rapidly from the melting temperature to a temperature below T_g can produce an amorphous, transparent PET for films or bottles. On the other hand, slow cooling of the molten resin can produce semi-crystalline, opaque PET. Semi-crystalline PET deforms much less under stress, especially at elevated temperatures, than amorphous PET [2]. Common properties of PET are shown in Table 2-2.

Table 2-2. Common properties of PET

Property	Value (unit)	Reference
Molecular weight (of repeating unit)	192 (g/mol)	[27]
Mark-Houwink parameters	k = 3.72×10^{-4} (dl/g), $\alpha = 0.73$ at 30°C	[27]
	k = 7.44×10^{-4} (dl/g), $\alpha = 0.65$ at 25°C	[7]
Weight average molecular weight	30,000-80,000 (g/mol)	[27-28]
Density	1.29-1.40 (g/cm^3)	[2]
Glass transition temperature (T_g)	69-115 (°C)	[24, 28]
Melting temperature (T_m)	255-265 (°C)	[23]
Heat of fusion	166 (J/g)	[24]
Thermal expansion coefficient (α)	9.1×10^{5} (K^{-1})	[28]

Heat deflection temperature	336 (K) at 264 (psi) 344 (K) at 66 (psi)	[27, 29]
Break strength	48.2-72.3 (MPa)	[2]
Tensile modulus (Young's modulus)	2756-4135 (MPa)	[2]
	1700 (MPa)	[29]
Elongation at break	30-3000 (%)	[2]
Yield strain	4 (%)	[29]
Impact strength	90 (J/m)	[29]
Water vapor transmission rate	390-510 g $\mu m/m^2$ day at 37.8 ^{o}C 90%RH	[2]
O_2 permeability at 25 °C	$1.2\text{-}2.4 \times 10^3$ cm^3 $\mu m/m^2$ day atm	[2]
CO_2 permeability at 25 °C	$5.9\text{-}9.8 \times 10^3$ cm^3 $\mu m/m^2$ day atm	[2]
Water absorption after 24h	0.1-0.2 (%) at 0.32 cm thick	[2]
	0.5 (%)	[29]

Table 2-2. (*Continued*)

2.2.3 PET applications and processing

PET is used broadly in products such as bottles, electrical and electronic instruments, automobile products, housewares, lighting products, power tools, material handling equipment, and sporting goods [24]. After PET was introduced into the market as fiber in 1962, it has been developed for packaging such as film, sheet, coating, and bottles. Films are produced by biaxial orientation through heat and drawing. PET film does not require the use of solid-stated resin. PET film is used in various applications such as X-rays sheet, recording tapes and food packaging [20, 23]. PET is also used as an electrical insulator due to the severe restriction of the dipole orientation at room temperature which is well below the glass transition temperature [23]. Another important application of PET is fibers where strength is achieved by applying tension to align the chains through uniaxial stretching. Since PET can be used in various applications, different application requires different properties, especially intrinsic viscosity of PET. Table 2-3 shows the required intrinsic viscosity for different PET applications. The main PET processes are extrusion, injection molding and blow molding.

Table 2-3. Required intrinsic viscosity for different PET applications [20, 22]

Application	[η] (dl/g)
Common PET film	0.6-0.65
Recording tape	0.6
Fibers	0.65
Carbonated soft drink bottles	0.71-0.84
Industrial tire cord	0.85

2.3 Municipal solid waste of virgin and recycled PET resin

Plastics are a rapidly growing segment of total MSW in the United States. In 2007, 30.7 million tons of plastic MSW was generated in U.S. compared to 29.48 million tons in 2006, representing 4.2% increased (Figure (2-2)) [8]. Specifically, the containers and packaging category in used the most plastics, representing 30.9% of total plastic MSW. Among the total plastic MSW, 3.76 million tons of PET MSW were generated (Figure (2-3)) [8]. A big amount of PET resin was used for soft drink bottles. Even though total plastic MSW has rapidly increased, overall recovery of plastics for recycling is relatively small, amounting to 2.1 million tons, or 6.8 % of plastics generation in 2007 [8]. PET resin had the highest recovery rate (18.1 %), compared to HDPE, PP, LDPE/LLDPE and other resins in 2007 (Figure (2-4)). PET soft drink bottles (including water bottles) were recovered at a rate of 36.6 % in 2007 [8].

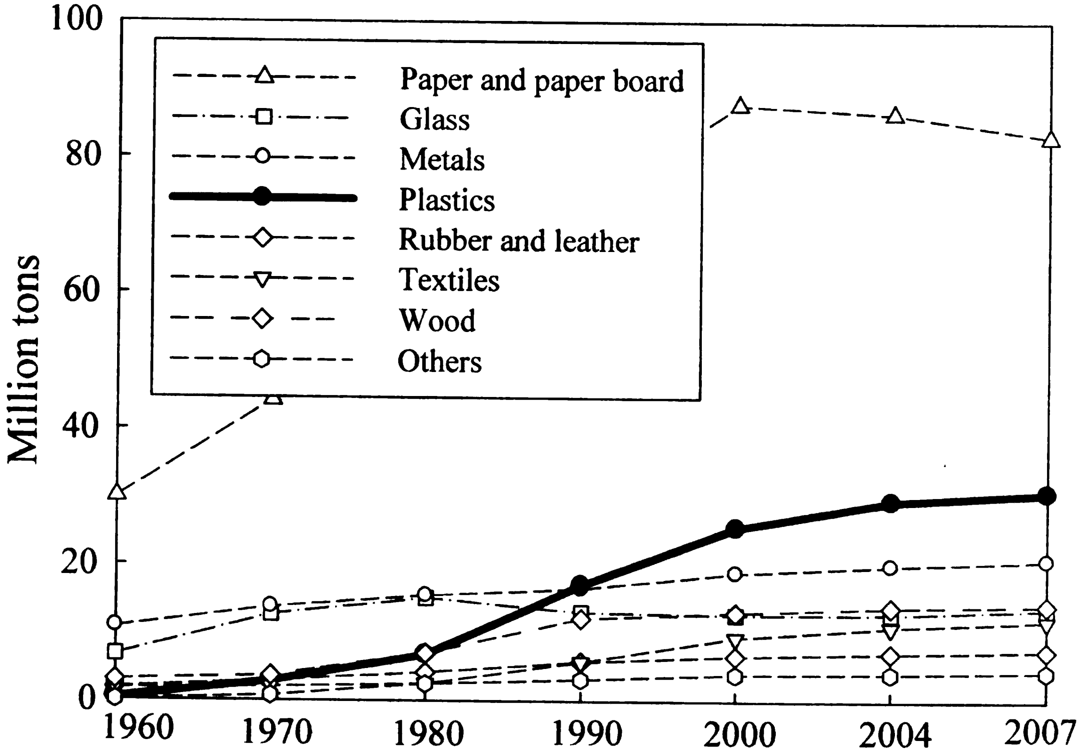

Figure 2-2. Materials generated in MSW, 1960 to 2007 [8], Others includes electrolytes in batteries and fluff pulp, feces, and urine in disposable diapers

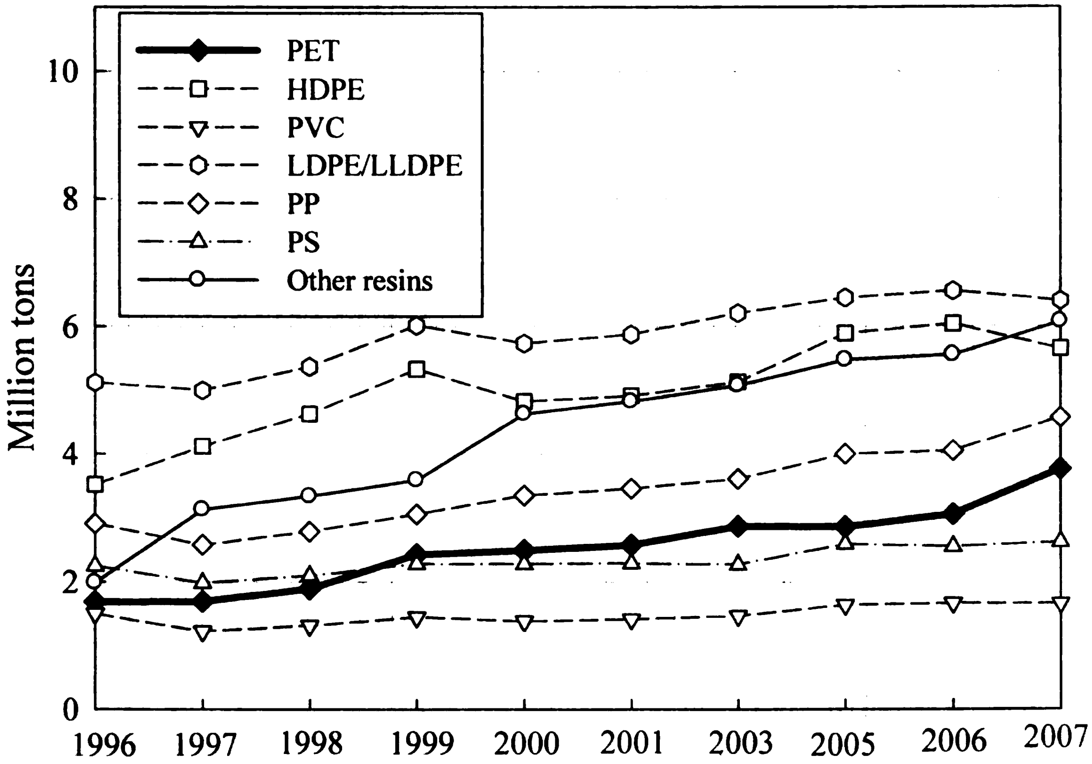

Figure 2-3. Total plastics in MSW, by resin, 1996 to 2007 [8], Others includes electrolytes in batteries and fluff pulp, feces, and urine in disposable diapers.

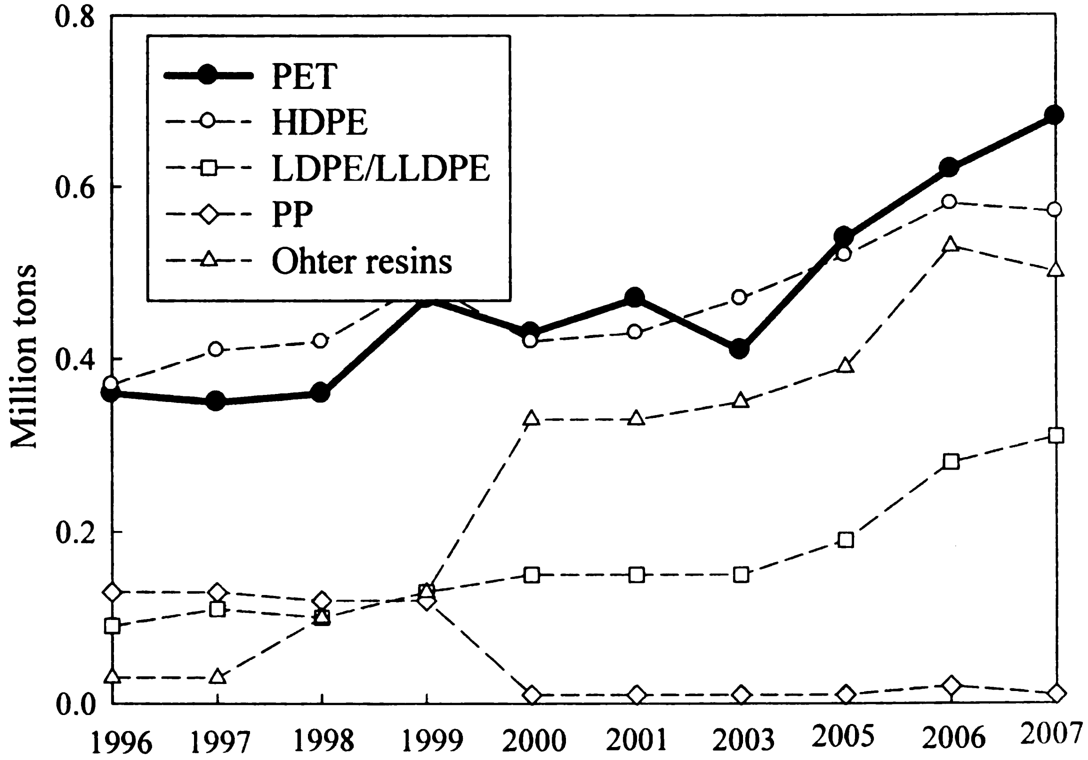

Figure 2-4. Recovery of plastics in MSW, by resin, 1996 to 2007 [8], others includes electrolytes in batteries and fluff pulp, and plastic in disposable diapers.

In this situation, the market dynamics of both virgin and recycled PET (RPET) are continually changing. The key factors impacting PET recycling are discussed below.

2.3.1 Continued high price for virgin PET

The price of virgin PET has remained high due to the high price of petroleum. Both virgin PET and gasoline production compete for the same petroleum precursor, paraxylene. Therefore, as long as gasoline prices remain high, virgin PET prices will remain high. Another PET precursor, isopthalic acid, was also in short supply in the spring of 2007, which further increased virgin PET pricing [30]. In general, high virgin

PET prices also allow PET reclaimers to charge higher prices for recycled PET flakes. As shown in Figure 2-5, the price of both crude oil and gasoline had been increasing until September, 2008. Following the trend for gasoline pricing, virgin PET prices are expected to remain high, even in the presence of excess supply.

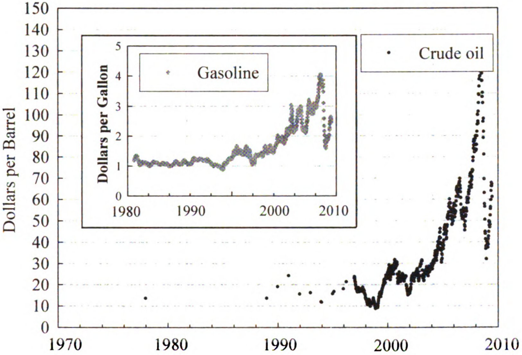

Figure 2-5. U.S. price trends of gasoline and crude oil, according to the Energy Information Administration (Data released on 07/13/2009 for gasoline and 07/15/2009 for crude oil)

2.3.2 Increasing demand for PET

According to a report of The National Association for PET Container Resources (NAPCOR), illustrated in Figure 2-6, 5,683 million pounds of PET bottles were on U.S. store shelves in 2007 compared to 1,950 million pounds in 1995, representing a 191 % increase [1]. However, market growth of about 4.8% for PET bottles and jars sold in the

U.S. during 2007 slowed down from 6.9% in 2006 [30]. The staggering sale of bottled water in the past decade is predicted to slow down as the market saturates. In 2006, isotonic drinks, tea, and the energy drink segments led the market growth of PET bottles and jars. In 2007, not only did those segments continue to perform well, but the first luxury wine bottle was offered in PET bottles. "Not only were 375 ml bottles used to access away-from-home markets, but 750 ml bottles were introduced at retail, primarily by Australian vineyards selling in North America [1]." The overall global PET demand is expected to grow at a rate of 7% per year between 2006 and 2011, with most of the new virgin PET production capacity in Asia and the Middle East.

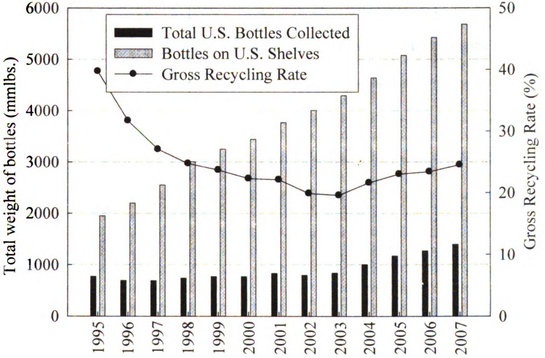

Figure 2-6. Total weight of bottles on U.S. shelves and collected with gross recycling rate, from 1995 to 2007 [1]

2.3.3 Increasing demand for Recycled PET (RPET)

Demand for RPET is at a record high due to increasing demand for all end-use applications such as carpets, filters, fabrics, roofing, paintbrushes and brooms, and packaging. David Cornell, the technical director of the Association of Postconsumer Plastics Recyclers (APR), believes that "demand will grow from the current 1 billion pounds per year to between 2 and 2.5 billion pounds per year [30]." This demand is driven by manufacturers of PET products who, by using RPET, obtain a cost advantage as high as 40 cents per pound when compared to virgin PET (Figure (2-7)) [30]. In addition, environmental concerns, as evidenced by the Wal-Mart (Bentonville, AR) packaging sustainability initiative, are motivating some packaging manufacturers to shift substrates from polystyrene (PS) and PVC towards recycled content PET. In September 2008, The Coca-Cola Co. (Atlanta, GA, USA), partnered with United Resource Recovery Corp. (Spartanburg, SC, USA), spent $45 million to build what the company is calling the largest plastic bottle-to-bottle recycling plant. One of the Coke officials expects that the company may achieve a recycle or reuse rate of at least 30 % by 2010. Moreover, California has passed a Rigid Plastic Packaging Container (RPPC) law (amended 2005), which requires that non-food plastic packaging be source - reduced (light-weighted) by at least 10%, reused a minimum of 5 times, or contain a minimum of 25% recycled content [30]. Therefore, increased enforcement of the RPPC by the California Integrated Waste Management Board (CIWMB), which has been eliminated, would further increase RPET demand.

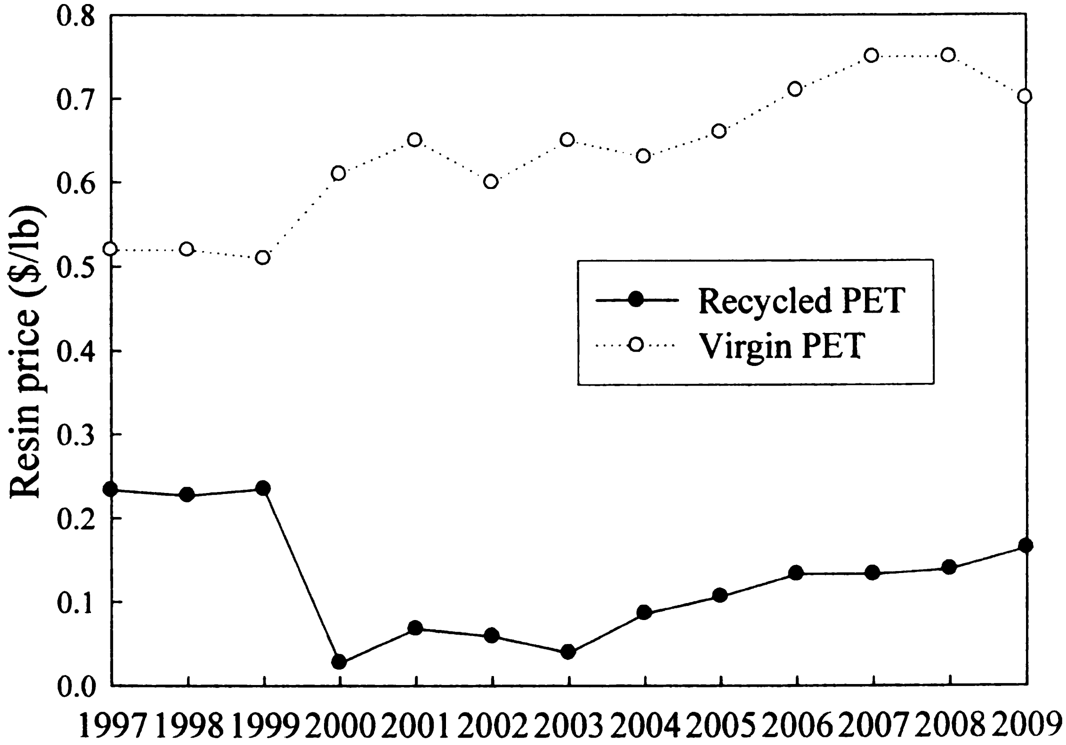

Figure 2-7. Price of recycled and virgin PET, 1997 to 2009, according to the report of Innovation Group "Chemical Profile-PET" and Plastics News.com "PET resin prices"

2.3.4 Low environmental footprint of RPET

Figure 2-8 show the environmental burden of 100V, 50V 50R and 100R PET as damage categories obtained from Simapro software (Amersfoort, Netherlands). Even though several assumptions were applied to simplify the model such as that the same transportation vehicles were applied for all scenarios and distances between every step of manufacturing, reprocessing and bottling process were assumed to be same for every scenario, the data support the advantage of using recycled PET. Among damage categories, human health represent several midpoint categories such as human toxicity (carcinogenic and non-carcinogenic effects), respiratory effects (inorganics and organics), ionizing radiation, and ozone layer depletion [31]. Ecosystem quality is composed of terrestrial acidification, terrestrial nutrification, and land occupation. The global warming was considered as a stand-alone endpoint category affected by carbon dioxide. The two midpoint categories contributing to resources were mineral extraction and non-renewable energy consumption [31]. The results indicate that 50% recycled PET contents in PET sheets reduce approximately 15 to 18% of value of each damage category.

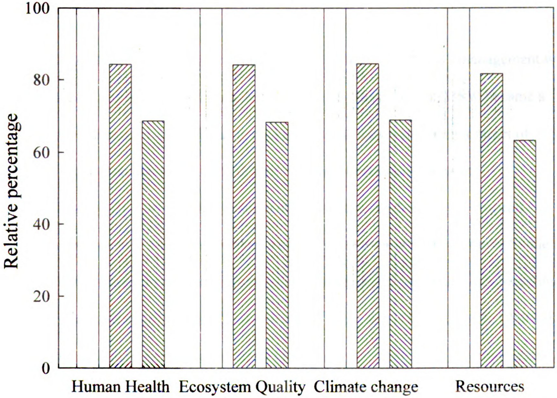

Figure 2-8. Comparison of damage categories for production of 100V, 50V50R, 100R PET bottle; 100V PET bottle □ , 50V50R PET bottle ▨, 100%R PET bottle ▧

Table 2-4. Values of damage categories for 100V, 50V50R and 100R PET bottle

	Human Health (DALY *) × 10^{-6}	Ecosystem quality ($PDF \times m^2 \times yr/kg$ □)	Climate change (kg CO2 eq ▼)	Resources (MJ primary $^{\Delta}$)
100V	3.80	0.141	3.95	93.3
50V50R	3.21	0.191	3.34	76.1
100R	2.61	0.096	2.73	58.9

* Disability Adjusted Life Years

□ Potentially Disappeared Fraction over a certain area and during a certain time per kg of emitted substance

▼ Amount of $CO_{2\,eq}$ that equal the impact of a considered pollutants into the air

Δ Amount of additional primary energy required per unit of mineral and of total non-renewable primary energy for energy carriers

2.4 Management method of PET

In the mid 1980s, the majority of municipal solid waste (MSW) management was landfill, accounting for 88.6% of total MSW. Soon, the land used for MSW became a public environmental issue, and plastic packaging industries were a major target of proposed legislation due to large fraction by volume of materials and poor biodegradability [2]. Furthermore, in some other countries such as most European countries and Japan in Asia, this problem was much more serious than in the U.S. due to lack of available land. In order to minimize landfill disposal, incineration and recycling were considered as alternative methods. However, in the late 1980s and early 1990s, the effort on the incineration resulted in many failures due to public concern about heavy metals in incinerator ash, and the poor economical efficiency to build and manage these facilities. In consequence, source reduction and recycling were rapidly increased, and packaging materials were the primary initial target.

According to the report of the Environmental Protection Agency (EPA), integrating waste management strategies, such as source reduction (or waste prevention), recycling, combustion with energy recovery and disposal through landfills (Figure 2-9), are still ongoing [32]. Source reduction has the effect of reducing MSW generation, whereas other management methods just deal with MSW once it is generated. Figure 2-10 indicates that total MSW generation of U.S. is about 254 million tons of trash and recycled and composted 85 million tons of this material, equivalent to a 33.4 % recycling rate. Among these 85 million tons, 63 million tons were recovered through recycling, representing 1.9 million tons more than in 2006. Composting recovered almost 22 million tons of waste [8]. The recovery rate of recycling and composting is continuously increased, while combustion with energy recovery and landfill of MSW are steady or somewhat decreased since the mid-1980s (Figure 2-11) [8].

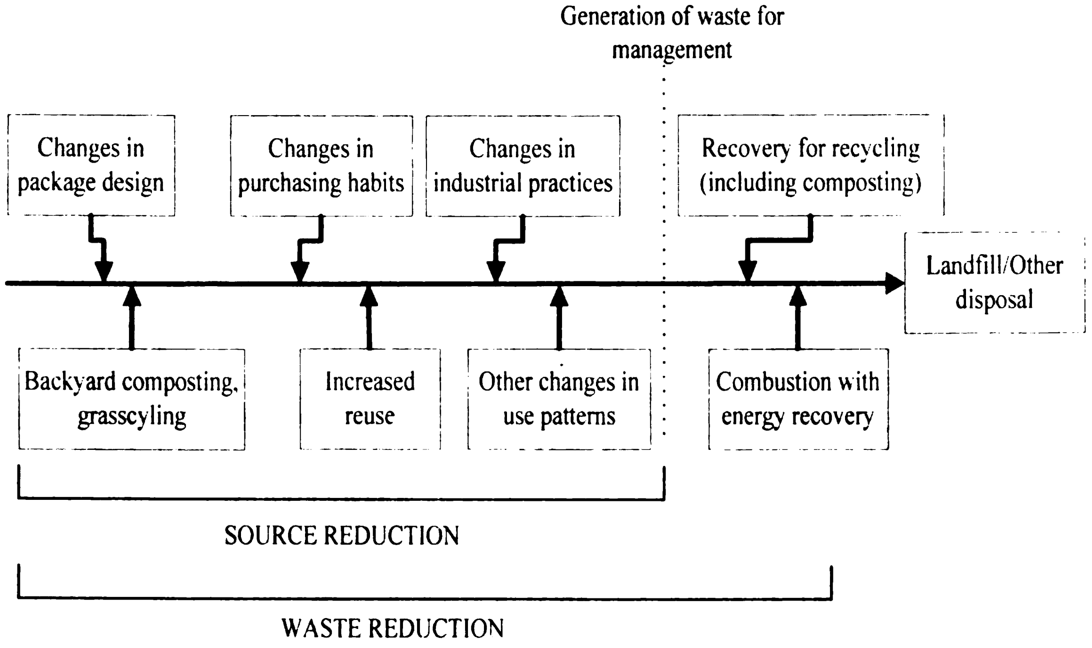

Figure 2-9. Diagram of solid waste management [32]

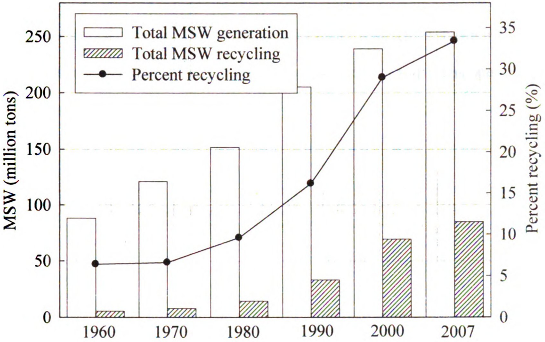

Figure 2-10. MSW generation, recycling and % recycling in U.S., 1960 to 2007 [8]

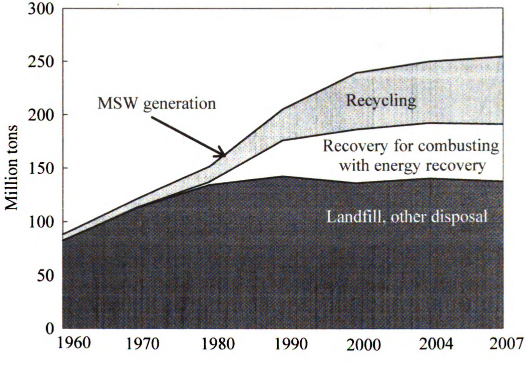

Figure 2-11. Municipal solid waste management, 1960 to 2007 [8]

2.4.1 Packaging in municipal solid waste

Data of waste generated in 2007 by product items by weight is shown in Figure 2-12 [8]. Containers and packaging made up the largest portion of waste generated, 30.9 %, or 78 million tons.

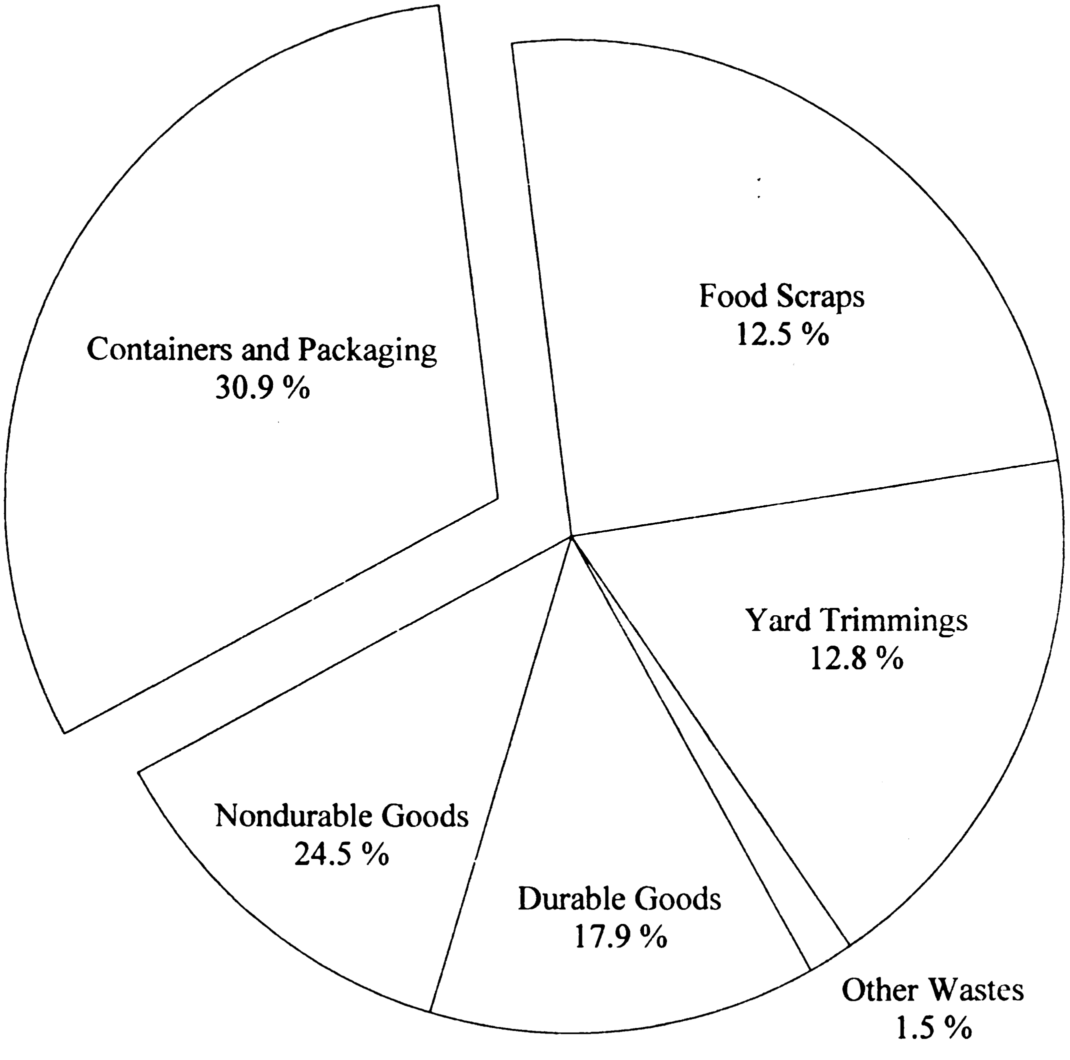

Figure 2-12. Total MSW generation by category, 2007 [8]

As shown in Table 2-5, total MSW recovered was about 33.4 % in 2007. Steel, paper products and aluminum were the highest recycled materials. The recycling percentage for steel packaging (mostly cans) was more than 64 %, and 62 % of paper and paperboard containers and packaging was recycled. In the case of aluminum packaging, it was recycled at a rate of 39 % [8]. Among the 11.7% recovery of plastic packaging waste, PET soft drink bottle (including water bottles) was the highest recovery rate at 36.6 %, and HDPE milk and water bottle was the next highest recovery rate at 28 % [8]. There are several reasons that the recovery rate of plastic packaging is relatively smaller than other packaging materials. One reason is that the recovery process requires that plastic materials undergo decontamination [33]. Another reason is that present recycling, sorting and cleaning techniques cannot handle all kinds of plastic packaging because many common packages do not consist of a single-type polymer but rather of polymer mixtures or copolymers.

Table 2-5. Generation and recovery of products in MSW, 2007 [8]

	Products	Weight Generated (millions of tons)	Weight Recovered (millions of tons)	Recovery (%)
Durable goods	Steel	13.0	3.55	27.3
	Aluminum	1.26	Negligible	Negligible
	Glass	2.11	Negligible	Negligible
	Plastics	10.5	0.50	4.8
	Rubber and leather	6.48	1.10	17.0
	Wood	5.63	Negligible	Negligible
	Textiles	3.33	0.46	13.8
	Other materials	3.17	2.38	75.1
	Total durable goods	45.4	7.99	17.6
Nondurable	Paper and paperboard	43.1	20.3	47.1

goods	Plastics	6.68	Negligible	Negligible
	Rubber and leather	0.97	Negligible	Negligible
	Textiles	8.34	1.44	17.3
	Other materials	3.15	Negligible	Negligible
	Total nondurable goods	62.2	21.8	35.0
Containers and packaging	Steel	2.68	1.73	64.6
	Aluminum	1.87	0.73	39.0
	Glass	11.5	3.22	28.1
	Paper and paperboard	39.9	24.9	62.4
	Plastics	13.6	1.59	11.7
	Wood	8.54	1.32	15.5
	Other materials	0.31	Negligible	Negligible
	Total containers and packaging	78.4	33.5	42.7
Other wastes	Food, other	31.7	0.81	2.6
	Yard trimmings	32.6	20.9	64.1
	Miscellaneous inorganic wastes	3.75	Negligible	Negligible
	Total other wastes	68.0	21.7	31.9
	Total municipal solid waste	254.1	85.0	33.4

Table 2-5. (*Continued*)

2.4.2 Source reduction of PET packaging

Source reduction, called "waste prevention," is defined by the EPA as "any change in the design, manufacturing, purchase, or use of materials or products (including packaging) to reduce their amount or toxicity before they become MSW. Prevention also refers to the reuse of products or materials" [8]. Source reduction can be achieved by a broad range of activities by private citizens, communities, commercial establishment, institutional agencies, and manufacturers and distributors [8]. Redesigning products or packages to reduce the amount of materials by replacing lighter materials for heavier ones is one of the examples of source reduction actions. Reusing products or packages is another action. Redesigning and reusing are considered better, according to the EPA, than recycling because the product does not need to be reprocessed before it can be used again. The efforts on refilling and light weighting of PET bottles are good examples.

2.4.2.1 Lightweight

The lightweighting of PET bottles started in the mid 90s with developments in PET resin technology and conversion equipment. By the mid 90s, 2-liter, 1.5-liter and 500 ml PET water bottles were 58, 40 and 22 g, respectively. By 2006, the lightest 1.5-liter PET water bottles weighed 30 g, and 2-liter PET water bottles were 47 g, while 500 ml bottles had slimmed down to 12.5 g [34-35]. In the last few years, the concern of lightweighting has continually increased as one of the source reduction actions.

Lightweight PET bottles must satisfy bottle specifications. Table 2-6 shows energy and material saving of lightweight PET bottles compared to traditional PET bottles.

Table 2-6. Energy and material saving of lightweight PET bottles compared to traditional PET bottles [36]

	Per million 500 ml PET bottles (Using 20g rather than 25g preforms)	Per million 2 liter PET bottles (Using 40g rather than 42g preforms)
PET weight savings	5 tonnes	2 tonnes
PET material cost savings at $1,300/t	$6,503	$2,601
Carbon emission savings	0.41 tonnes	0.10 tonnes
Energy savings	4,133 kWh	1,653 kWh

In theory, lightweighting involves removing weight from the neck finish area and the body. However, in practice, there are several issues, especially for lightweight PET bottles [35]. One of the problems is that product rigidity and top load resistance is decreased with decreasing wall thickness. Another possible problem is nesting of preforms (body of preform is less than opening of the neck) in the blow stage. Moreover, decreasing bottle weights affects not only bottle production and product filling speed but also shelf life of bottles. In order to solve these issues, three major technologies can be applied in practice. Redesigning preform shape, moulds and injection-stretch blow machine can be one of the technologies. Another technology is to develop a new PET material that is able to achieve light weighting along with improved processing and barrier performance. Eastman chemical introduced a new PET resin series named "Vorcalor PET CB11E, 9921W, and AQUALOR PET 18696," which can get up to 30 % energy saving and is very compatible with recycling processes [37]. The third developing technology is preform re-heat profile in an IR oven that obtains a perfect heat distribution between the inside and outside temperature of the preform, and the PET bottle can achieve the same stiffness at reduced material thickness. Table 2-7 show commercialized lightweight PET bottles by company.

Table 2-7. Examples of lightweight bottle productions with company [38-40]

Company	Product	Description
Colgate-Palmolive	Softsoap® hand soap pouch refill	50% weight reduction compared to like-sized PET bottle
Easterform Packaging	CSD bottles	500 ml CSD bottle (25g to 20g) 2 L CSD bottle (42g to 40g)
Kraft	Salad dressing PET bottle	19 % weight reduction by process refinement
Coca-Cola	CSD bottles	23% less PET in 600 ml CSD bottles in Mexico
	Dasani water bottle	35% less PET in 500 ml Dasani bottle
	Cap for PET bottle	38% smaller cap for PET bottles
Sidel	NoBottle	9.9 g per 500 ml bottle
Krones	PET lite 6.6	6.6 g per 500 ml bottle (lightest bottle on the market)
Filmatic	-	16 g per 500 ml bottle compared to traditional 26g

2.4.2.2 Reuse and refill

In the U.S. today, most consumer packages are not designed to be returned for reuse because the design and implementation of the collection, return and cleaning are not considered. Two-thirds of consumer packages are landfilled, and the remaining one-third are reprocessed and recycled into new products. Not too long ago, refilling systems gained popularity as a more efficient way of handling used containers, especially beverage containers, than recycling systems. In some European countries, refillable PET bottles are common for soft drinks, water and beer. One of the most general refillable PET bottles is the 1.5 liter soft drink bottle, which has enabled refilling system to package beverages in plastic that is more light-weight than glass or metal, shatterproof for handling, and multi-serve containers in distribution level. Table 2-8 indicates costs of 500 ml refillable and one-way glass and PET beverage containers in Europe.

Table 2-8. Costs of 500 ml refillable and one-way glass and PET beverage containers in Europe [41]

Type	Container Cost (Euros)	Trips/Life	Production Cost/Trip (Euros)
Refillable Glass Bottle	0.103	20	0.005
Refillable PET Bottle	0.133	20	0.007
One-Way Glass Bottle	0.047	1	0.047
One-Way PET Bottle	0.069	1	0.069
Aluminum Can	0.103	1	0.103

However, even though refilling system have many advantages, such as increasing cost benefit and decreasing environmental burden, the beer and soft drink industries in the U.S. have dismantled their refilling systems. "While American soft drink companies have replaced refillable glass bottles with single-use plastic bottles and aluminum cans in the U.S., they have been using state-of-the-art refillable containers in many European and Latin-American countries [41]." In many European countries and some Canadian provinces, policies to promote or require the use of refillable beverage containers have been enacted since the 1970s. Table 2-9 shows refilling rates and legislations for refilling system in some of European countries, and some Canadian provinces.

Table 2-9. Refillables as a portion of total beverage sales and policies in some countries [41]

	Soda	Beer	Policies
Prince Edward Island (Canada)	100%	100%	Bans non refillables
Ontario (Canada)	NA	81%	~9¢ tax on one-way beer container
Quebec (Canada)	NA	80%	No more than 37.5% of beer can be in one-ways
Finland	98%	73%	Levy on one-way containers
Denmark	90%	100%	Banned cans and required refillables for domestic soda/beer
The Netherlands	75-80%	100%	Cannot substitute one-way for refillables unless environmental impact is same or less
Germany	75%	75%	72% most be packaged in refillables or be subject to mandatory deposits
U.S.	<3%	<5%	

2.4.3 Recycling of PET packaging

Recycling has environmental benefits at every stage in the life cycle of PET packages [8]. Recycling reduces air, and water pollution and greenhouse gas emissions. In the U.S., 85 million tons of MSW were recycled, and 680 thousand tons of PET MSW were recycled [8]. Recycling 85 million tons of MSW provides an annual benefit of 193 million metric tons of CO_2 equivalent emission reduced, representing the emissions from 35 million passenger cars [8]. However, some barriers exist in increasing plastic recycling systems. Consumers', municipalities' and manufacturers' lack of understanding about the benefits provided by recycling systems is one of the obstacles. Many consumers, municipalities and manufacturers continue to be unaware of the significant benefits, demand, and value of recycled plastic. Another barrier to increased recycling is lack of sufficient access to recycling collection opportunities for post-consumer products.

2.5 Legislation of PET recycling for food use

Food-contact plastic packaging made from recycled plastic must ensure that recycled plastic has suitable purity and performance of virgin plastic. The 21 Code of Federal Regulation (CFR), Parts 174 through 179, shows the framework for testing and evaluation procedures for each type of recycled plastic and recycling system [42]. This guidance document recommends the maximum level of a chemical contaminant in the recycled material that would result in an estimated daily intake (EDI) that does not exceed 1.5 micrograms/person/day (0.5 ppb dietary concentration (DC)). This is the level that FDA would generally consider to be of negligible risk for a contaminant migrating from recycled plastic for food application. The guideline also recommends surrogate contaminants for use in evaluating a recycling process based on volatility and polarity (Table 2-10).

Table 2-10. Examples of recommended surrogates [42]

	Volatile	Non-volatile
Polar	Chloroform Chlorobenzene 1,1,1–Trichloroethane Diethyl ketone	Benzophenone Methyl salicylate
Non-polar	Toluene	Tetracosane Lindane Methyl stearate Phenylcyclohexane 1-Phenyldecane 2,4,6-Trichloroanisole

The FDA provided letters of non-objection for recycling process of PET if they could be shown to remove all surrogates to less than the 0.5 ppb dietary concentration level. Generally, letters of non-objection for PET can be categorized into 3 different groups (Table 2-11). By December 2008, 85 letters of non-objection for PET had been issued [43]. In case of chemically recycled PET, FDA letters of non-objection were issued to virgin PET producers for chemical processes as methanolysis and glycolysis. Physical recycling of PET is considered a better option than chemical recycling due to less controlled sources of recycled resin and less extreme recycling processes. Most non-objection letters for physical recycled PET for food contact were issued for processes with special cleaning steps, high temperature treatments and solid stating to optimize contaminant removal from the recycled polymer. In addition, in 1993, the FDA provided a letter of non-objection to Continental PET Technologies for the use of a trilayer PET container having recycled material as a middle polymer layer [44]. The internal food-contact layer serves as a functional barrier to contaminant migration from the bulk recycle layer in the center of the container wall [44].

Table 2-11. US FDA no objection letters, until December 2008 [43]

Subjects	No objection letters
Chemically recycled PET for food contact	18
Physically recycled PET for food contact	54
Multilayer technology	13

2.6 Recycled PET

The first recycling effort of PCR-PET (Post Consumer Recycled PET) bottles in the world was in 1977 [45]. As a result of environmental concerns, PET recycling industry started to improve PET waste management strategy. Another driving force for PET recycling industry is that PET products have a very slow rate of natural decomposition [46]. PET is a non-degradable plastic in normal conditions since no organism can consume its large molecules. Therefore, recycling processes are the best way to economically reduce PET waste [47]. Since the price of virgin PET remains and it should continuous to be high as explained in section 2.3.3, new and cheaper technologies for recycling PET can generate large value for the PET recycling industry. Recycled PET flakes must meet certain requirement to be used [13, 24]. Table 2-12 shows the minimum requirement for the PCR-PET flakes.

Table 2-12. Minimum requirements for PCR-PET flakes to be used for sheet applications [13, 24]

Property	Value
[η], dl/g	>0.7
Tm, °C	>240
Water content, wt.%	<0.02
Flake size, mm	0.4< D < 8
Dye content, ppm	<10
Yellowing index	<20
Metal content, ppm	<3
PVC content, ppm	<50
Polyolefin content, ppm	<10

2.6.1 Collection

Before recyclable materials are reprocessed to be new products, they must be collected. There are several types of residential collection systems, such as curbside recyclables collection, drop-off programs, buy-back operation, and container deposit systems. Collection of recyclables from commercial establishments is usually not counted as residential recyclables collection. In 2007, more than 8,600 curbside recyclables collection programs were reported in U.S., nearly 60 % of the U.S. population with access to curbside recyclables collection programs [8]. Table 2-13 indicates the number and population served by curbside recyclables collection programs. Table 2-13 also shows how residential curbside recycling programs are distributed to various regions, with the most extensive curbside collection occurring in the Northeast.

Table 2-13. Number and population served by curbside recyclables collection programs in the U.S. 2007 [8]

Region	Number of programs	Population	Population Served	
		(in thousands)	(in thousands)	%
NORTHEAST	3,299	50,557	42,592	84%
SOUTH	797	84,524	25,386	30%
MIDWEST	3,749	46,473	28,236	61%
WEST	814	63,985	48,702	76%
Total	8,659	245,539	144,916	59%
Total U.S. Population		301,621		

In case of drop off centers, located in grocery stores, sheltered workshops, charitable organizations, city-sponsored sites, and apartment complexes, can accept more materials than curbside collection programs. In the U.S., 12,694 programs were estimated in 1997 [8]. In 2007, it was estimated that over 20,000 communities have drop-off centers [48].

A buy-back center is operated commercially. Scrap metal dealers, aluminum can centers, waste haulers, or paper dealers pay individuals for recovered materials. Materials are collected by individuals, small businesses, and charitable organizations.

To date, eleven states have container deposit systems: California, Connecticut, Delaware, Hawaii, Iowa, Maine, Massachusetts, Michigan, New York, Oregon, and Vermont. In these programs consumer pays a deposit on beverage containers at the point of purchase, which is redeemed on return of the empty containers. Generally, deposit systems were planned for beverage containers, especially beer and soft drink, which account for less than 6 % of total MSW generation.

2.6.2 Recyclables processing of PET

After collecting recyclable materials containing PET, they must be sorted, washed and ground to remove label, aluminum, adhesive and other plastics before producing recycled PET products. These processes are performed at materials recovery facilities (MRFs) and mixed waste processing facilities [8]. Generally, reprocessing technologies are composed of sortation, granulation, air classification, washing, flotation, drying and electrostatic separation. At the sortation step, bales of unsorted PET bottles are screened by color and polymer type. The dirty, sorted PET bottles are first reduced to 0.125-0.375 inch flake by granulation [20]. After that, those flakes are delivered to air classification to remove labels. Basically, most labels are removed from PET flakes by granulation and air classification generally by using a hydrocyclone. The washing step removes the last traces of label material and disperses and dissolves the adhesives. Cleaned flake or chip moves into a flotation tank which separates the heavy PET and aluminum from light HDPE in a water medium [20]. After drying, the dried and cleaned PET and aluminum chips are fed into an electrostatic separator to remove aluminum chips.

2.6.2.1 Materials recovery facilities (MRFs)

Materials recovery facilities are distributed widely across the U.S. In 2007, 567 MRFs were operating in the U.S., with an estimated total daily throughput of over 91,000 tons per day (Table 2-14) [8]. The most extensive reclaiming process occurs in the Northeast and West.

Table 2-14. Material recovery facilities in U.S., 2007 [8]

Region	Number	Estimated Throughput (tons/daythroughput)
NORTHEAST	146	24,848
SOUTH	158	20,905
MIDWEST	138	20,455
WEST	125	25,242
U.S. Total	567	91,450

2.6.2.2 Mixed waste processing

The number of mixed waste processing facilities is smaller than conventional MRFs. Mixed solid waste (including recyclable and non-recyclable materials) is delivered to mixed waste processing facilities. Recyclable materials are removed by mechanical and manual sorting. In 2007, there were reported 34 mixed waste processing facilities in the U.S., handling about 43,000 tons of waste per day [8]. The largest number of these processing facilities is located in the Western region of the U.S., representing over 80 % of the daily per capita throughput [8].

2.6.3 Conventional recycling process

Once the PET bottles are collected and reprocessed, two major processes have been applied to PCR-PET flakes. These processes are chemical recycling (feedstock recycling) and mechanical recycling.

2.6.3.1 Chemical recycling

As shown in Figure 2-1, esterification and *trans*-esterification reactions are reversible (depolymerization). The chemicals used for depolymerization of PET include water (hydrolysis), methanol (methanolysis) and EG (glycolysis). For hydrolysis, PCR-PET flakes are treated with water in excess at an elevated temperature of 150-250 °C in the presence of sodium acetate as a catalyst to produce TPA and EG in four hours (Figure 2-13 (a))[20]. Acids or bases are used as catalyst to enhance the hydrolysis reaction [20]. An acid catalyst will promote the hydrolysis in 10-30 minutes at 60-95 °C [20]. In methanolysis, PCR-PET flakes are treated with an excess of methanol and 1:4 volume ratio (PET: methanol) to produce DMT and EG (Figure 2-13 (b)). A typical methanolysis process is performed with a catalyst at 160-240 °C under a pressure of 20-70 atm for less than an hour [20]. If PCR-PET flakes are recycled with an excess of a glycol, glycolysis process occurrs to produce BHET (bis-(hydroxyethyl)terephthalate) and EG (Figure 2-13 (c)). Typical catalysts are amines, alkoxides, or metal salts of acetic acid [20]. Glycolysis reactions are performed at 200 °C for over 8 hours with an EG/PET ratio of 1.5:1 [20]. The main disadvantage of chemical recycling is its higher cost than mechanical recycling.

$$\mathrm{PET} + \mathrm{H_2O} \xrightarrow[\text{High pressure}]{\text{High temp}} \mathrm{TPA} + \mathrm{EG}$$

(a)

$$\mathrm{PET} + \mathrm{CH_3OH_2} \xrightarrow[\text{High pressure}]{\text{High temp}} \mathrm{DMT} + \mathrm{EG}$$

(b)

$$\mathrm{PET} + \mathrm{EG} \xrightarrow[\text{High pressure}]{\text{High temp}} \mathrm{BHET} + \mathrm{EG}$$

(c)

Figure 2-13. Depolymerization of PET: (a) Hydrolysis (b) Methanolysis (c) Glycolysis [19, 22]

2.6.3.2 Mechanical recycling

PCR-PET flakes can be processed by normal extrusion systems. However, unlike chemical recycling, PCR-PET flakes for mechanical recycling may contain contaminants, which are not removed during reprocessing and cause degradation reactions. At the processing temperature (280 °C), PCR-PET flakes undergo thermal and hydrolytic degradations. Hydrolysis reactions occur between water and PET resulting in shorter chains with acid and hydroxyl-ester end groups (Figure 2-14 (a)). The thermal cleavage of the PET ester bond also results in shorter PET chains with acid and vinyl ester end groups (Figure 2-14(b)) [14, 25]. Therefore, the main disadvantage of mechanical recycling is the reduction of molecular weight and intrinsic viscosity during processing.

On the other hand, the main advantages of mechanical recycling are simple process, environmentally friendly and low investment.

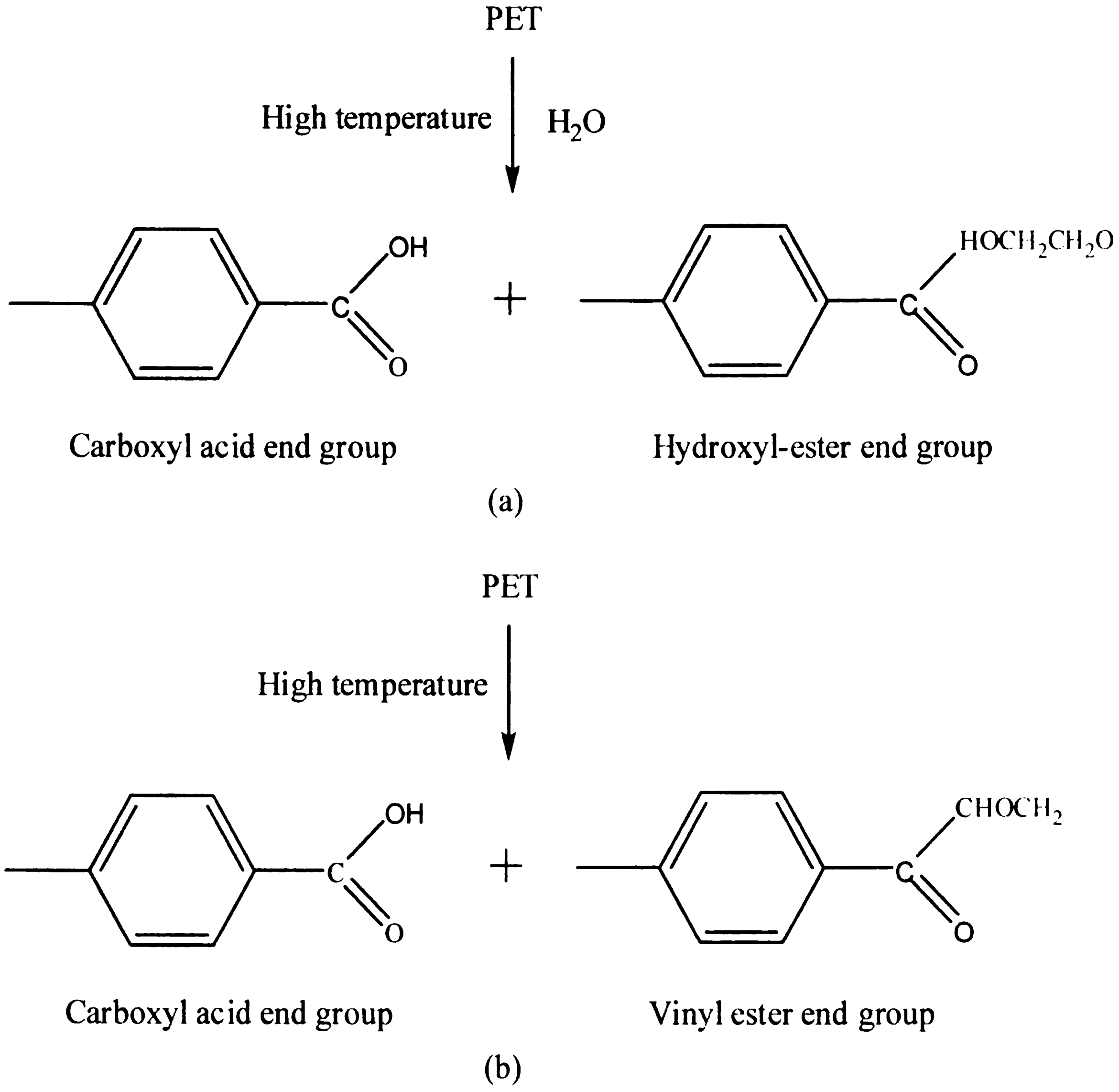

Figure 2-14. Degradation of PET: (a) hydrolysis (b) thermal degradation [14, 25]

2.6.4 Effects of contaminants on recycling of PET

Quality of recycled PET mostly depends on its intrinsic viscosity, aluminum content, and color. These properties are affected by contamination of PCR-PET flakes.

Minimizing the presence of these contaminants leads to better recycled PET quality [7]. Recycled PET can be contaminated with various substances, such as PVC, adhesives, labels, fragments of colored bottles, water and acetaldehyde.

2.6.4.1 Acid producing contaminants

The most troublesome contaminant in recycled PET is the adhesive [20]. Typically, adhesives produce acids, such as rosin producing abietic acid. Another acid producing contaminant is PVC which generates hydrochloric acid. Acetic acid is produced by poly (vinyl acetate) closure degradation [6, 17, 49]. These acids promote the chain scission reactions during melt processing of PCR-PET . Especially, the presence of small amounts of PVC increases PCR-PET flakes chain scission due to the catalytic effect of hydrogen chloride during degradation of PVC [16]. The presence of PVC also causes discoloration of PCR-PET during processing.

2.6.4.2 Water

As shown in Figure 2-14 (a), the presence of water causes a hydrolysis reaction to reduce molecular weight and intrinsic viscosity. In order to prevent hydrolysis reactions, moisture content must be below 0.02% [49]. Most of the water can be removed by proper drying during reprocessing of PCR-PET.

2.6.4.3 Coloring contaminants

Discoloration of PCR-PET can occur not only due to the presence of PVC, but also fragments of colored bottles and printed ink labels. By proper sorting and washing processes, discoloration due to fragments of colored bottles and printed ink labels can be reduced.

2.6.4.4 Acetaldehyde

Acetaldehyde is also a degradation product in recycled or virgin PET, and is a by-product of hydrolysis degradation reactions of PET. Due to the migration of acetaldehyde into food products, the presence of acetaldehyde can be a serious problem when recycled PET containers are made for food contact applications. However, acetaldehyde can be easily removed by processing under vacuum or by drying, due to its high volatility [49].

2.6.4.5 Other contaminants

Since PET containers are containing not only food and beverage but also other substances such as detergents, fuel and pesticides, the remains of these substances can cause health hazards if these substances remain after PCR-PET recycling.

2.6.5 End use applications of recycled PET

In 2007, a total 862 mm lbs were used for the primary conversion categories of recycled PET [1]. In addition, U.S. reclaimers sold 38 mm lbs to secondary markets, including exporters, for a total of 900 mml bs of recycled PET end use consumption (Table 2-15) [1]. Among 900 mm lbs, U.S. and Canadian reclaimers supplied about 744 mm lbs which was mainly produced from post consumer bottles [1]. The remaining 156 mm lbs was imported from reclaimers all over the world, including France, Italy, India, China, Mexico, Brazil, Peru and other Central and South American countries [1]. Figure

2-15 indicates that the sheet converters increased their purchasing of PET by 73% over 2006. The use of recycled PET in industrial strapping continued to grow by 9% compared to 2006 while recycled PET use in bottles also increased but at a much lower rate [1].

Table 2-15. U.S. consumption of recycled PET as different product categories [1]

	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Fiber	415	417	452	435	344	296	479	463	422	383
Sheet & Film	89	68	65	37	18	32	58	71	74	128
Strapping	67	80	101	82	83	77	116	131	132	144
Engineered Resin	30	26	27	24	10	10	12	8	9	11
Food & Beverage Bottles	52	68	54	77	86	106	126	115	139	136
Non-Food Bottles	47	50	40	44	43	24	63	63	49	60
Other	7	9	5	2	4	7	24	13	30	38
Total U.S. CONVERTER CONSUMPTION	707	718	744	701	588	552	878	864	855	900

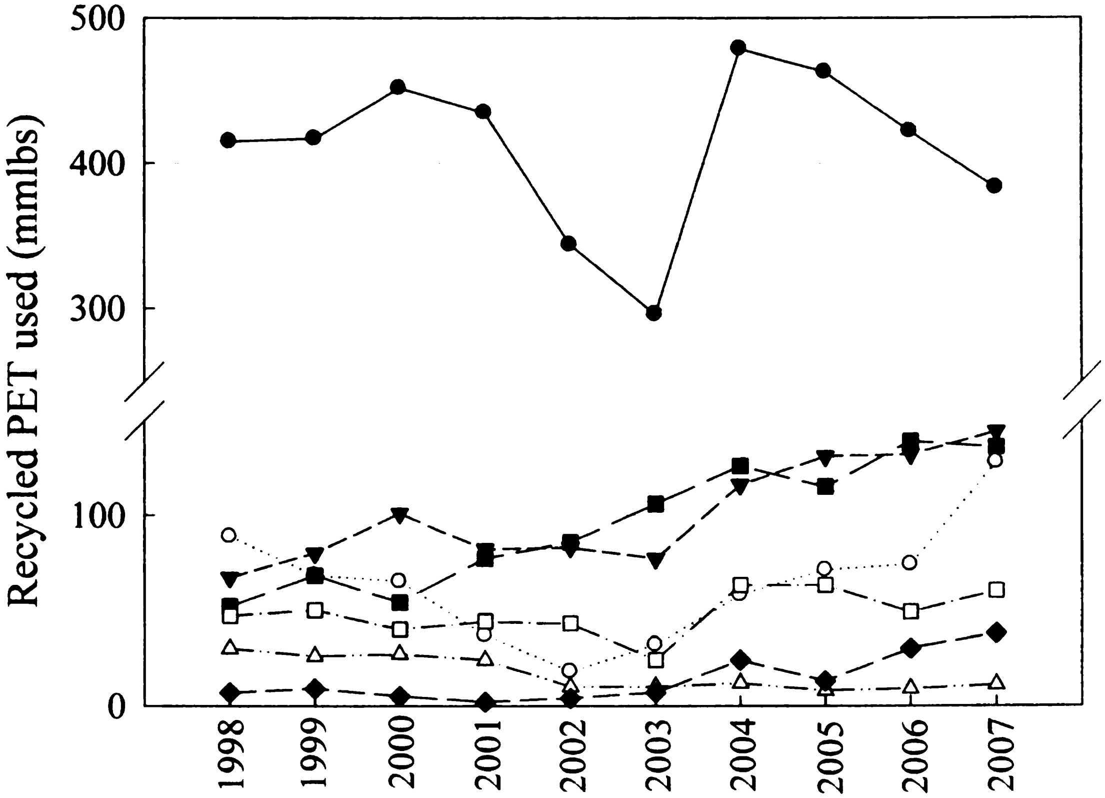

Figure 2-15. U.S. converter consumption of recycled PET as different product categories [1]; Fiber (•), Sheet & Film (o), Strapping (▼), Engineering resin (Δ), Food & Beverage bottles (■), Non-food Bottles (□), Other (♦)

3. METHODOLOGY

3.1 Materials

Feedstocks of 100% virgin PET (V) and 100% post-consumer recycled PET (R) (RPET were blended to create ratios of 0, 20, 40, 60, 80 and 100% RPET in a plant trial conducted at Peninsula Packaging Company (Exeter, CA, USA), Virgin PET resin was supplied by Eastman (Columbia, CA, USA) with an intrinsic viscosity of 0.80 ± 0.02 dl g^{-1}. Recycled PET, which is mostly collected by bottle deposit system, was provided by ECO2 (Modesto, CA, USA),PET sheets were tested after processing. A detailed description of manufacturing steps is shown in APPENDIX A.

3.2 Optical properties

UV-Visible spectroscopy was used to determine the light transmission of PET sheets with varying percent of virgin and recycled PET. UV analysis was performed using a Perkin-Elmer Lambda 25 (Waltham, MA, USA) with measurements carried out at 480 nm/min and a wavelength range of 190 to 800 nm in transmittance (%) mode. All results are presented as transmittance values. Five to ten samples were scanned for each PET sheet with varying percent of virgin and recycled PET contents.

Tristimulus color values of PET samples with varying percent of virgin and recycled PET contents were obtained using LabScan XE from HunterLab (Reston, VA, USA) and were converted by the instrument to Hunter L*, a*, b* values. 'L*' value indicates the level of light and dark, the 'a*' value redness or greenness, and the 'b*' value yellowness or blueness. The maximum 'L*' is 100, which would be a perfect reflecting diffuser. The minimum 'L*' would be zero, which would be black. A positive 'a*' is red, and negative 'a*' is green. Positive 'b*' is yellow, and negative 'b*' is blue. ΔE indicates the total color difference which takes into account the differences between the 'L*', 'a*' and 'b*' of the sample and standard. 100% virgin PET (V) was assumed to be the standard, and was compared with varying percent of virgin and recycled PET sheets for ΔE. ΔE was calculated with Equation (3.1) [50]. Five replicates were measured and averaged.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{3.1}$$

where $\Delta L = L_{\text{Sample}} - L_{\text{Standard}}$, $\Delta a = a_{\text{Sample}} - a_{\text{Standard}}$ and $\Delta b = b_{\text{Sample}} - b_{\text{Standard}}$

3.3 Mechanical properties

Dynamic mechanical analysis (DMA) was utilized to analyze the thermo-mechanical properties of PET sheets with varying percent of virgin and recycled PET contents. A DMA Q800 from TA Instruments (New Castle, DE, USA) was used. Samples with a width of 4.8 – 6.0 mm and a length of 17-20 mm were cut and tested with a tension mode clamp and 0.010 N preload force applied. The frequency was 1 Hz. These measurements were carried out at a heating rate of 5 °C /min and a temperature range of -80 to 150°C under the DMA-multi-frequency strain. The glass transition temperature was determined from the storage modulus, loss modulus and loss tan delta. Each treatment was replicated three times per sheet.

A Universal Material Testing Machine was used to analyze the tensile and break strength, break elongation, modulus of elasticity and energy to break by using a Universal Material Testing Machine 5560 series (Dual Column Models) from Instron (Norwood, MA, USA) in accordance with ASTM D 882 [51]. Samples with a width of 25.4 mm were cut and tested at 508 mm/sec with 50.8 mm of gauge length. Five samples were measured and averaged.

3.4 Thermal properties

A differential scanning calorimeter (DSC Q100, TA Instruments, (New Castle, DE, USA)) was used to determine the thermal properties of PET sheets with varying percent of virgin and recycled PET contents. Every sample was tested under a heat/cool/heat cycle between 40 to 300°C at a rate of 10 °C /min with a nitrogen atmosphere. The weight of the samples ranged between 12 - 17 mg. The glass transition temperature (T_g), onset of cold crystallization temperature ($T_{cc\ onset}$), cold crystallization temperature (T_{cc}), onset of melting temperature ($T_{m\ onset}$) and melting temperature (T_m) of the samples were recorded. T_{cc} onset and T_{cc} were taken from the first heating run, and T_g, $T_{m\ onset}$ and T_m were obtained from the second heating run. The percent of crystallinity, χ_c, for samples was calculated from the Equation (3.2).

$$\chi_c(wt.\%) = 100 \times \frac{\Delta H_m - |\Delta H_c|}{\Delta H_m^o} \tag{3.2}$$

where ΔH_m is the heat of melting, and ΔH_c is the heat of crystallization, and ΔH_m^o is the heat of fusion of 100% crystalline PET ($\Delta H_m^o = 140\ J/g$) [15].

3.5 Barrier properties

The water vapor transmission rate (WVTR) was measured with a Permatran^{TM} C3/31 (Modern Controls Inc., Minneapolis, MN,) according to ASTM F1249 [52]. The testing temperature was 37.8 °C with 100% RH. All measurements were performed in triplicate for all samples. The WVTR values were used to calculate the water vapor permeability from Equation (3.3).

$$\text{Water vapor permeability} = \frac{\text{Water vapor transmission rate (q)} \times \text{thickness (l)}}{\text{partial pressure } (\Delta p) \times \text{time (sec)} \times \text{area}(m^2)} \qquad (3.3)$$

The oxygen transmission rate (OTR) was measured using an Illinois 8001 system (Illinois Instruments Inc., Johnsburg, IL, USA). The test was performed in accordance with ASTM D 3985 [53]. The temperature and relative humidity were 23 °C and 50% RH. All PET sheet measurements were performed in triplicate. OTR values were used to calculate the oxygen permeability value from the Equation (3.4).

$$\text{Oxygen permeability} = \frac{\text{Oxygen transmission rate (q)} \times \text{thickness (l)}}{\text{partial pressure } (\Delta p) \times \text{time (sec)} \times \text{area}(m^2)} \qquad (3.4)$$

3.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectra were obtained on a Varian VXR-500 FT spectrometer (Chemistry Department, Michigan State University). ^1H spectra were at 500MHz. PET sheets with varying percent of virgin and recycled PET contents were dissolved in a ratio of 2 to 1 mixture of trifluoroacetic acid/chloroform solution by volume. These mixtures dissolve the high molecular weight polyesters to analyze the end group signal at ambient temperature [54]. Chemical shifts are reported in parts per million from tetramethylsilane. Samples were tested in triplicate.

3.7 Viscosimetry

Solution viscosity measurement were carried out using 1C Ubbelhode capillaries provided by Cannon instrument company (State College, PA,) (Appx.constant: 0.03 mm^2/s^2, Kinematic viscosity range: 6 to 30 mm^2/s) in a mixture of phenol and 1, 1, 2, 2-tetrachloroethane (60:40 by volume) provided by Sigma-Aldrich (St. Louis, MO) at 24 ± 0.5°C. This test was performed in accordance with ASTM D 445 and D 446 [55-56]. The intrinsic viscosity, [η] was determined by the Huggins equation (3.5). The viscosity molecular weight, $\overline{M_v}$, was determined by the Mark-Houwink Equation (3.6) ($K = 7.44 \times 10^{-4} dl/g$ and $\alpha = 0.648$ at 25°C) [7].

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \tag{3.5}$$

$$[\eta] = KM_v^{\alpha} \tag{3.6}$$

3.8 Statistic Analysis

One way ANOVA and Tukey's HSD (Honestly Significant Differences) test were performed to analyze the statistical significant differences of the data set from each experiment (α=0.05). This test was conducted using the SPSS software program, SPSS Inc. (Chicago, IL, USA).

A stepwise regression analysis was used to develop a model to predict the amount of RPET in the samples. The stepwise regression used a mixture of categorical and continuous variables to handle partially observed responses [57]. This regression can be carried out in three different ways: forward, backward and stepwise selection. Due to a relatively small data set, the power was too low to identify important predictors as statistically significant at the standard significant level (α=0.05). Therefore, backward selection was applied in this study with a high significant level (α=0.15) [58]. Backward elimination was performed to remove the weakest predictor variable, and to establish the optimal regression model. The SAS software program, SAS Inc. (Cary, NC, USA) was used. APPENDIX B explains the stepwise regression analysis and backward regression analysis with SAS code used for this study.

4. RESULTS AND DISCUSSION

4.1 Optical analysis

4.1.1 UV-Visible Spectroscopy

Figure 4-1 shows the constitutional unit of PET. The chromophorie groups in PET are the benzene ring and the ester group. The ester group (-COOR) absorbs at the 205 nm wave length through $\pi \rightarrow \pi^*$ transition and $\eta \rightarrow \pi^*$ transition, and benzene ring absorbs the UV-light source at 198 and 255 nm maximum wave length [59]. Therefore, the absorbance of PET mainly occurred in the ultraviolet region (200~400nm).

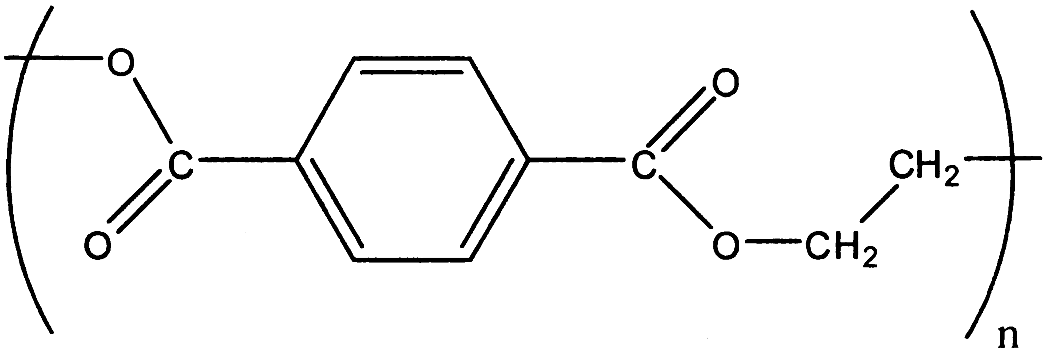

Figure 4-1. Constitutional unit of PET

Figure 4-2 indicates that most of the absorbance of PET occurred between 330 and 390 nm. Figure 4-3 shows that there is another peak arising between 675 and 678 nm where the red light region is located. This might be because of residual contaminants, especially fragments of green or blue colored bottles and printed ink labels.

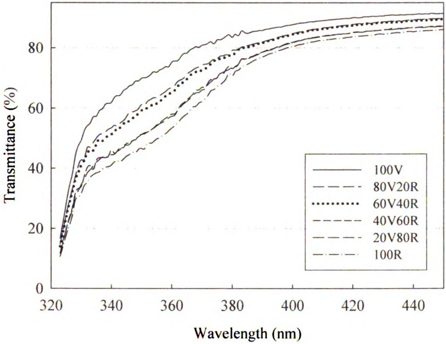

Figure 4-2. Light transmission of PET sheets with varying percent of virgin and recycled PET contents between 323 and 450nm

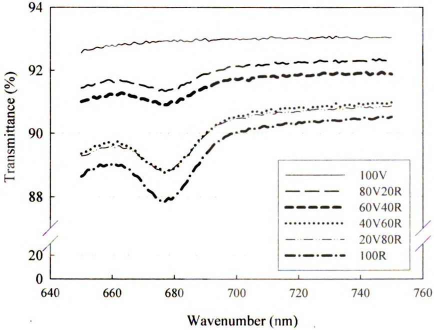

Figure 4-3. Light transmission of PET sheets with varying percent of virgin and recycled PET contents between 650 and 750nm

According to Tsai *et al.* [60], the number, the volume fraction and the size of the crystallites contribute to the scattering of the light. Namely, recycled PET contains lead to lower transmittance because of impurities acting as nucleating agents. However, in this study, % crystallinity values from DSC show no statistically significantly differences at $\alpha = 0.05$. Table 4-1 provides the light transmission values for PET and RPET at different wavelengths. At 350, 380, 676, 677 and 678 nm, there are statistically significant differences amongst the light absorption of PET sheets with varying percent of virgin and recycled PET content.

Table 4-1. Light transmission (%) for PET sheets with varying percent of virgin and recycled PET contents

λ (nm)	Transmittance (%)					
	100V	80V20R	60V40R	40V60R	20V80R	100R
250	1.26 ± 0.57^{a}	1.51 ± 0.28^{a}	1.26 ± 0.33^{a}	1.57 ± 0.34^{a}	1.59 ± 0.37^{a}	1.10 ± 0.19^{a}
300	1.08 ± 0.37^{a}	1.23 ± 0.43^{a}	1.18 ± 0.33^{a}	1.20 ± 0.31^{a}	1.06 ± 0.24^{a}	1.39 ± 0.34^{a}
350	69.90 ± 1.60^{a}	61.18 ± 1.14^{b}	59.25 ± 0.57^{b}	54.07 ± 0.97^{c}	51.22 ± 0.94^{d}	46.62 ± 0.42^{e}
380	83.53 ± 0.81^{a}	79.18 ± 1.13^{b}	$77.63\pm0.75^{b,c}$	75.84 ± 1.29^{c}	73.43 ± 1.13^{d}	70.64 ± 0.76^{e}
676	92.93 ± 0.25^{a}	91.40 ± 0.46^{b}	90.93 ± 0.17^{b}	88.70 ± 0.26^{c}	88.82 ± 0.54^{c}	87.88 ± 0.12^{d}
677	92.94 ± 0.21^{a}	91.35 ± 0.41^{b}	90.92 ± 0.16^{b}	88.69 ± 0.24^{c}	88.81 ± 0.51^{c}	87.86 ± 0.12^{d}
678	92.94 ± 0.22^{a}	91.38 ± 0.42^{b}	90.94 ± 0.16^{b}	88.68 ± 0.24^{c}	88.85 ± 0.50^{c}	87.95 ± 0.12^{d}
700	93.01 ± 0.21^{a}	92.13 ± 0.40^{b}	91.72 ± 0.12^{b}	90.72 ± 0.25^{c}	90.48 ± 0.55^{c}	90.03 ± 0.12^{c}
800	93.01 ± 0.21^{a}	92.30 ± 0.35^{b}	92.00 ± 0.14^{b}	91.31 ± 0.22^{c}	90.94 ± 0.55^{c}	90.63 ± 0.15^{c}

*Values in the same row with different superscripts are significantly different at $\alpha=0.05$.

4.1.2 Colorimeter

Results of color measurement for varying percents of virgin and recycled PET content as Hunter L, a, b scale are shown in Table 4-2. The data show that more recycled PET contents lead to grayer ('L*' decreases), greener ('a*' becomes more negative), and more yellow ('b*' increase) of PET sheets. The data also indicate that 'L*', 'a*' and 'b*' value of PET sheets with varying percent of recycled PET contents show statistically significantly differences (α=0.05), except 'L*' value between 40V60R and 20V80R, b value between 80V20R and 60V40R, and ΔE between 40V60R and 20V80R. Since recycled PET flake may contain fragments of green or blue colored bottles, this causes the 'a*' value to be more negative. Generally, PET yellowing is associated with thermal degradation [61]. During PET processing above its melting temperature, the thermal cleavage of the PET ester bond result in shorter chain with acid and vinyl ester end groups [6]. The carboxyl end group content generated by PET processing promotes the oxidation of PET [18]. Namely, repeated recycling processes generate more carboxyl end groups in PET, and cause more oxidation of PET. Therefore, more recycled PET contents in PET sheets leads to an increased 'b*' value.

Table 4-2. Results of color measurement for varying percent of virgin and recycled PET sheets

	L*	a*	b*	ΔE
100V	89.94 ± 0.022^{a}	-1.14 ± 0.015^{a}	1.10 ± 0.022^{a}	0^{a}
80V20R	89.18 ± 0.110^{b}	-1.29 ± 0.013^{b}	1.62 ± 0.047^{b}	0.93 ± 0.08^{b}
60V40R	88.76 ± 0.283^{c}	-1.36 ± 0.019^{c}	1.55 ± 0.015^{b}	1.28 ± 0.26^{c}
40V60R	87.69 ± 0.103^{d}	-1.58 ± 0.017^{d}	2.31 ± 0.034^{c}	2.59 ± 0.09^{d}
20V80R	87.60 ± 0.168^{d}	-1.65 ± 0.012^{e}	2.39 ± 0.061^{d}	2.72 ± 0.16^{d}
100R	86.90 ± 0.075^{e}	-1.68 ± 0.005^{f}	3.10 ± 0.022^{e}	3.68 ± 0.06^{e}

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$.

4.2 Mechanical analysis

4.2.1 Dynamic Mechanical Analysis (DMA)

The transition of polymeric materials from the glassy to the rubbery state has long been recognized as an important material and polymer property [62]. During this transition, Tg can be observed from storage, loss modulus and tan delta peak of the dynamic mechanical test. The storage modulus represents the stiffness of a viscoelastic material, and loss modulus is defined as being proportional to the energy dissipated during the loading cycle. Tan delta is composed of the storage and loss modulus and determines how well the material can disperse energy. As shown in table 4-3, it was found that PET sheets with varying percent of virgin and recycled PET content show no statistically significant differences at 95% confidence level.

Table 4-3. Maximum loss, tan delta curve and onset of rubbery plateau as temperature values

	Maximum loss modulus (°C)	Maximum Tan delta (°C)	Onset of rubbery plateau (°C)
100V	84.92 ± 0.96^{a}	92.52 ± 0.78^{a}	89.15 ± 0.61^{a}
80V20R	84.12 ± 1.10^{a}	92.20 ± 1.40^{a}	88.45 ± 1.18^{a}
60V40R	85.35 ± 0.01^{a}	92.83 ± 0.75^{a}	89.57 ± 0.16^{a}
40V60R	84.08 ± 1.05^{a}	91.59 ± 1.06^{a}	88.35 ± 1.15^{a}
20V80R	85.19 ± 0.72^{a}	92.31 ± 0.91^{a}	89.50 ± 0.43^{a}
100R	84.48 ± 0.99^{a}	92.27 ± 0.93^{a}	88.91 ± 0.93^{a}

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$.

4.2.2 Universal Material Testing

The percent crystallinity, the size of spherulites and the molecular weight of semi-crystalline polymers, such as PET, affect the mechanical properties of the materials [7]. Usually, crystallization produces a drastic mobility restriction that renders the material brittle [7]. Table 4-4 indicates that the mechanical properties of varying percent of virgin and recycled PET sheets show no linear trend; mechanical properties were not a function of recycled PET content.

Table 4-4. Mechanical properties for PET sheets with varying percent of virgin and recycled PET contents

		Tensile Strength (ksi)	Break Strength (ksi)	Break Elongation (%)	Modulus of Elasticity (ksi)	Energy to Break (in·lbf/in^3)
100V	MD	9.49±0.16 ^{a,b,c}	5.54±0.29 ^{a}	480.42±40.22 ^{a,b}	236.07±4.59 ^{a,b,c}	1842.32±190.19 ^{a,b,c}
	CD	9.52±0.17 ^{a,b,c}	5.24±0.99 ^{a,b}	459.05±79.16 ^{a,b}	167.18±10.30 ^{d}	1768.20±321.66 ^{a,b,c}
80V20R	MD	9.42±0.13 ^{a,b,c}	5.00±0.78 ^{a,b}	495.56±19.27 ^{a,b}	234.67±3.25 ^{a,b,c}	1901.87±84.00 ^{a,b,c}
	CD	9.67±0.12 ^{c}	5.21±0.35 ^{a,b}	455.34±41.96 ^{a,b}	238.91±2.11 ^{b,c}	1730.32±181.33 ^{a,b,c}
60V40R	MD	9.31±0.09 ^{a,b,c}	5.65±0.09 ^{a}	544.40±1.41 ^{a,b}	227.00±2.29 ^{a,b,e}	2196.89±38.96 ^{a}
	CD	9.26±0.29 ^{a}	4.63±0.86 ^{a,b}	432.36±41.22 ^{a,b,c}	223.02±6.64 ^{a,e}	1574.92±181.79 ^{b,c,d}
40V60R	MD	9.55±0.13 ^{a,b,c}	4.80±0.69 ^{a,b}	421.49±37.56 ^{b,c}	237.43±5.34 ^{a,b,c}	1549.13±144.46 ^{c,d}
	CD	9.54±0.10 ^{a,b,c}	4.52±1.11 ^{a,b}	424.05±56.43 ^{b,c}	237.42±4.43 ^{a,b,c}	1570.56±251.49 ^{c,d}
20V80R	MD	8.88±0.27 ^{d}	5.19±0.49 ^{a,b}	540.60±27.46 ^{a,b}	200.05±13.99 ^{f}	2069.06±177.56 ^{a,b}
	CD	9.27±0.07 ^{a,b}	4.07±1.21 ^{a,b}	449.85±58.20 ^{a,b}	216.37±6.74 ^{e}	1608.27±247.35 ^{b,c,d}
100R	MD	9.63±0.09 ^{b,c}	3.56±0.90 ^{b}	322.30±78.98 ^{c}	241.07±7.39 ^{b,c}	1172.94±270.49 ^{d}
	CD	9.58±0.27 ^{a,b,c}	4.23±1.39 ^{a,b}	329.67±130.32 ^{c}	243.73±10.28 ^{c}	1204.41±508.92 ^{d}

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$

4.3 Thermal analysis

During the first DSC heating run, the onset of cold crystallization temperature and the cold crystallization temperature were obtained. The cold crystallization temperature, T_{cc}, is the point where the amorphous area of polymer starts to reorganize itself and turn into crystalline area. PET sheets with 100% virgin show the highest onset of T_{cc} and T_{cc}. Generally, PET sheets containing more recycled PET contents show lower onset of T_{cc} and T_{cc}. This indicates that more recycled PET content leads to crystallization process at a lower temperature. During the second heating run, T_g, onset of T_m, T_m and χc were obtained. According to Torres *et al.* [7], impurities in recycled PET may play the role of nucleating agents, facilitating crystallization. However, it was found that the % crystallinity showed no statistically significantly differences among PET sheets with varying virgin and recycled PET content (α=0.05) (Table 4-5).

Table 4-5. DSC data for PET sheets with varying percent of virgin and recycled PET contents

	T_g (°C)	$T_{cc,\ onset}$ (°C)	T_{cc} (°C)	$T_{m,\ onset}$ (°C)	T_m (°C)	χc (wt. %)
100V	79.2 ± 0.2^{a}	130.5 ± 0.6^{a}	137.0 ± 0.5^{a}	231.3 ± 0.9^{a}	245.2 ± 0.1^{a}	6.9 ± 0.9^{a}
80V20R	77.1 ± 0.4^{b}	127.4 ± 0.7^{b}	134.4 ± 0.2^{b}	233.1 ± 0.8^{a}	245.6 ± 0.4^{a}	$8.6\pm1.5^{a,b}$
60V40R	77.7 ± 0.4^{b}	$125.3\pm1.2^{b,c}$	$133.3\pm0.4^{b,d}$	232.9 ± 0.7^{a}	$245.8\pm0.4^{a,b}$	$9.3\pm0.5^{a,b}$
40V60R	77.2 ± 0.4^{b}	124.0 ± 1.1^{c}	130.6 ± 0.8^{c}	234.2 ± 0.6^{a}	$246.7\pm0.7^{b,c}$	10.1 ± 0.9^{b}
20V80R	77.9 ± 0.5^{b}	124.6 ± 0.2^{c}	132.1 ± 0.6^{d}	233.4 ± 0.4^{a}	247.0 ± 0.2^{c}	$9.3\pm1.6^{a,b}$
100R	77.5 ± 0.5^{b}	124.2 ± 1.2^{c}	132.5 ± 0.2^{d}	233.4 ± 0.8^{a}	247.5 ± 0.1^{c}	$8.1\pm0.7^{a,b}$

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$

4.4 Intrinsic viscosity

In order to analyze the intrinsic viscosity of PET sheets with varying percent of recycled PET, solution viscosity measurement was carried out. Basically, the concentration and molecular weight of the dissolved polymer determine the viscosity of a polymer solution. In order to determine the intrinsic viscosity of a polymer solution, the Huggins equation was used. In addition, the viscosity molecular weight was calculated using the Mark-Houwink equation.

Table 4-6 indicates the intrinsic viscosity [η] and viscosity average molecular weight $\overline{M}_V$ of PET sheets with varying recycled PET content at 24 ± 0.5°C. All intrinsic viscosity values were between 0.53 and 0.72 dl/mol. Viscosity molecular weight ranged from 25,000 to 41,000 g/mol. There were significantly statistically differences in both intrinsic viscosity and viscosity molecular weight for 100V and 100R PET. It was also found that the higher the percent of recycled PET in PET sheets the lower the intrinsic viscosity and viscosity molecular weight. This reduction of the intrinsic viscosity may be due to the contaminants of recycled PET, such as retained moisture, adhesive and so on [63], which generate acid compounds during processing and catalyze the hydrolytic cleavage of the ester bond to yield carboxylic acid end group and hydroxyl-ester end group [7]. The impurities in recycled PET contents may induce chain scission processes that lead to lower intrinsic viscosity and viscosity molecular weight. In addition, additional heat history also played a role to change the [η] of PET.

Table 4-6. Intrinsic viscosity and viscosity molecular weight

	Intrinsic viscosity (dl/g)	Viscosity molecular weight (g/mol)
100V	0.722±0.029 ^{a}	40742 ± 2052 ^{a}
80V20R	0.696±0.022 ^{a}	38449 ± 1839 ^{a}
60V40R	0.630±0.006 ^{b}	32989 ± 449 ^{b}
40V60R	0.631±0.006 ^{b}	33038 ± 478 ^{b}
20V80R	0.607±0.009 ^{b}	31141 ± 695 ^{b}
100R	0.533±0.017 ^{c}	25479 ± 1275 ^{c}

*Values in the same column with different superscripts are significantly different at α=0.05

4.5 Barrier properties

Generally, permeability of water vapor and oxygen play a major role in deciding the protective properties of plastic films and containers. The water vapor transmission rate and oxygen transmission rate were analyzed for PET sheets with varying percent of recycled PET. Four replicates were measured and averaged. The last ten points of the water vapor transmission rate were collected from the machine and averaged for calculating water vapor permeability values. Table 4-7 show that water vapor permeability of 100V, 80V20R, 60V40R and 40V60R are statistically significantly different, and 80V20R and 60V40R, and 40V60R, 20V80R are statistically significantly different (α=0.05) with respect to 100R. In the case of oxygen permeability results, it was found that 100V and 60V40R are statistically significantly different, and 60V40R, 40V60R, 20V80R and 100R are not statistically significantly different (α=0.05) (Table 4-7).

Table 4-7. Water vapor permeability for PET sheets with varying percent of recycled PET as SI units

	Water vapor permeability $(\mathrm{kg}\times\mathrm{m}/\mathrm{m}^2\times\mathrm{Pa}\times\mathrm{sec})\ (\times10^{-15})$	Oxygen permeability $(\mathrm{kg}\times\mathrm{m}/\mathrm{m}^2\times\mathrm{Pa}\times\mathrm{sec})\ (\times10^{-19})$
100V	$2.73 \pm 8.31\times10^{-2}$ $^{\mathrm{a,\ d}}$	5.86 ± 0.13 $^{\mathrm{a}}$
80V20R	$2.52 \pm 2.88\times10^{-2}$ $^{\mathrm{b}}$	5.62 ± 0.06 $^{\mathrm{a,\ b}}$
60V40R	$2.58 \pm 9.85\times10^{-2}$ $^{\mathrm{b}}$	5.26 ± 0.08 $^{\mathrm{c}}$
40V60R	$2.65 \pm 5.54\times10^{-2}$ $^{\mathrm{c}}$	5.34 ± 0.24 $^{\mathrm{b,\ c}}$
20V80R	$2.72 \pm 1.97\times10^{-2}$ $^{\mathrm{a,\ c}}$	5.32 ± 0.06 $^{\mathrm{b,\ c}}$
100R	$2.76 \pm 2.21\times10^{-2}$ $^{\mathrm{d}}$	5.54 ± 0.15 $^{\mathrm{b,\ c}}$

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$

4.6 Nuclear Magnetic Resonance analysis (NMR)

Through the recycling processes, chemical or mechanical, PET can be degraded. Chemical recycling of PET utilizes depolymerization of PET, and may create bis-(hydroxyethyl) terephthalate, dimethylterephthalate and terephthalic acid. In mechanical recycling of PET, degradation reactions of PET occur including hydrolysis and thermal degradation. PET hydrolysis generally introduces carboxylic acid and hydroxyl-ester end groups, and thermal degradation generally produces carboxylic acid end group and vinyl ester end groups. The ^{1}H NMR spectrum of the 100V PET samples is illustrated in Figure 4-4. There are four peaks in the spectrum attributed to four kinds of ^{1}H protons. The most obvious peaks are a singlet at δ 8.2 arising from aromatic protons (a) of the PET repeat units. Since mixtures of TFA/$CDCl_3$ (2:1) were used as solvents for the PET samples, trifluoroacetic acid anhydride leads to a rapid esterification of the OH end-groups. As a consequence, the two CH_2 signals of the ethylene glycol (b) end-groups shift down field and coalesce with the main signal at δ 4.8 [64]. The diethylene glycol (c). (d) signals were remained without change. The small peaks between δ 1 and 2 ppm were analyzed as impurities of $CDCl_3$ and residual of moisture, respectively.

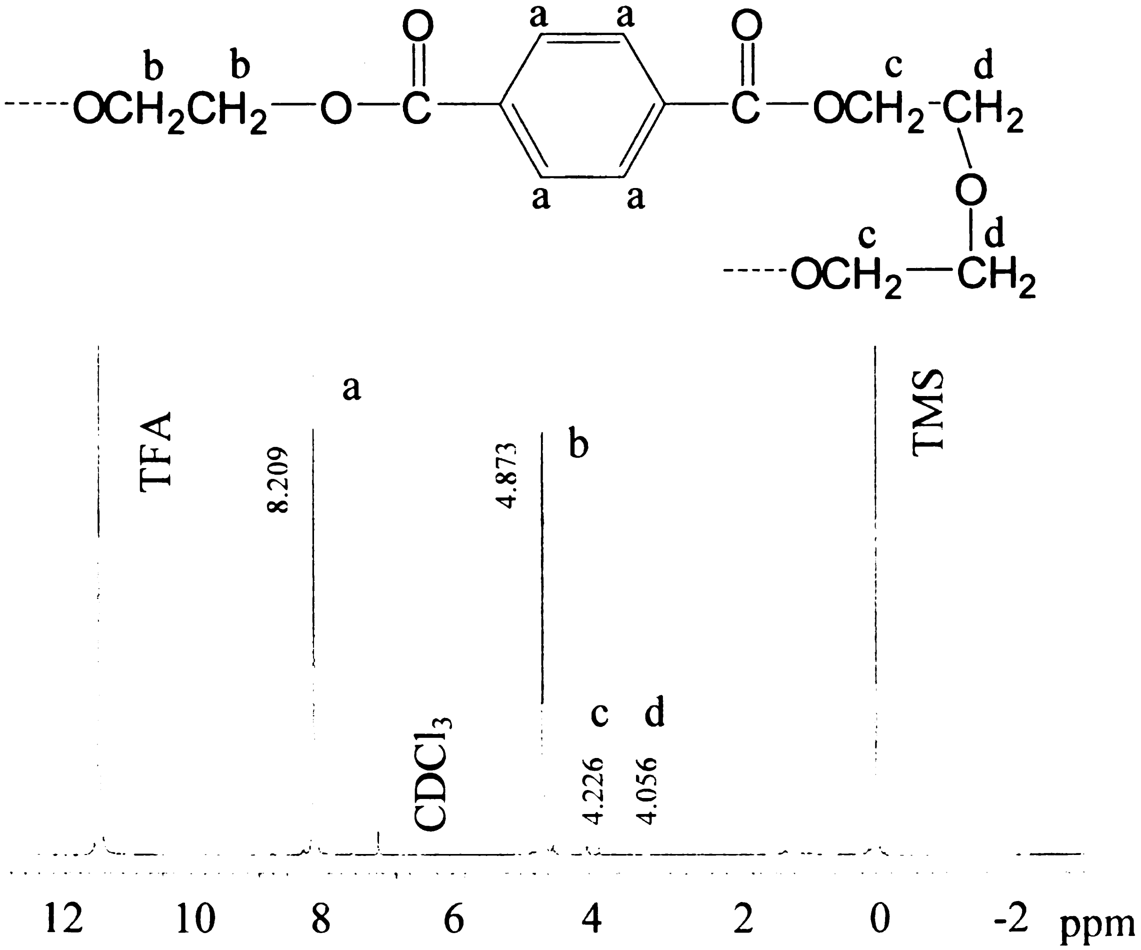

Figure 4-4. 500 MHz ^{1}H-NMR spectrum of 100V PET samples measured in TFA/$CDCl_3$

Table 4-8 indicates the composition ratio of aromatic protons (a), ethylene glycol protons (b) and diethylene glycol protons (c), (d) for PET sheets with varying recycled and virgin PET content. Due to the recycling process, protons of ethylene glycol (b) and diethylene glycol (c), (d) were considered as indicators for the difference among PET sheets with varying percent of virgin and recycled PET contents. It was found that protons of end groups in 60V40R, 40V60R and 20V80R PET were statistically significantly higher than 100V PET.

Table 4-8. Composition ratio of PET sheets with varying percent of recycled and virgin PET contents

	Composition ratio (mol ratio)				
	a	b	c	D	c + d
100V	1	$1.0307 \pm 0.0026^{a,b}$	0.0363 ± 0.0019^{a}	0.0189 ± 0.0006^{a}	0.0552 ± 0.0024^{a}
80V20R	1	1.0369 ± 0.0041^{c}	0.0390 ± 0.0019^{a}	$0.0210 \pm 0.0017^{a,b,c}$	$0.0599 \pm 0.0035^{a,b,c}$
60V40R	1	$1.0357 \pm 0.0003^{b,c}$	0.0346 ± 0.0065^{a}	$0.0221 \pm 0.0003^{b,c}$	$0.0567 \pm 0.0063^{b,c}$
40V60R	1	$1.0320 \pm 0.0016^{a,b,c}$	0.0416 ± 0.0012^{a}	$0.0219 \pm 0.0013^{b,c}$	$0.0636 \pm 0.0020^{b,c}$
20V80R	1	$1.0355 \pm 0.0020^{b,c}$	0.0408 ± 0.0005^{a}	0.0234 ± 0.0011^{c}	0.0642 ± 0.0017^{c}
100R	1	1.0293 ± 0.0004^{a}	0.0373 ± 0.0008^{a}	$0.0193 \pm 0.0006^{a,b}$	$0.0566 \pm 0.0014^{a,b}$

*Values in the same column with different superscripts are significantly different at $\alpha=0.05$

4.7 Stepwise regression analysis

Different kinds of PET sheets with varying percent of virgin and recycled PET were chosen as the criterion variables. DSC values (Tg, Tcc, Tm, χc), UV-Visible spectroscopy (UV350, 380, 678), WVTR, OTR, NMR, Intrinsic viscosity and colorimeter (L, a and b) results were included as predictor variables. DMA (Tg from storage, loss modulus, and tan delta peak) and universal material testing results were excluded since they were no statistically significant differences amongst PET sheets with varying percent of virgin and recycled PET contents at $\alpha=0.05$. In order to obtain a good prediction, the predictor variables should be correlated with the criterion variables. However, the predictor variables must not be correlated among themselves. Therefore, a Pearson correlation and a simple linear regression were used to exclude predictor variables, which were highly correlated with other ones. The upper top part of Table 4-9 indicates the Pearson correlation of predictor variables for PET sheets with varying percent of virgin and recycled PET. Predictor variables that were not highly correlated with another predictor variable ($r<0.5$), are highlighted. Initially, T_m, WVTR were chosen by Pearson correlation as valid predictor variables.

Table 4-9. Pearson correlation of predictor variables for PET sheets with varying percent of virgin and recycled PET contents

*Blank (-) represents the p-value which is below 0.0001
*Glass transition temperature (Tg), cold crystallization temperature (Tcc), melting temperature (Tm), Percent crystalinity (Xc), light transmission at 350 nm (UV350), light transmission at 380 nm (UV380), light transmission at 678 nm (UV678), intrinsic viscosity (IV), water vapor transmission rate (WVTR), oxygen transmission rate (OTR), intensity ratio of δ 4.2 combined with 4.0 peak (NMR424), L value for colorimeter (L), a value for colorimeter (a) and b value for colorimeter (b)

Table 4-9. Pearson correlation of predictor variables for PET sheets with varying percent of virgin and recycled PET contents

	T_g	T_{cc}	T_m	Xc	UV 350	UV 380	UV 678	IV	WVTR	OTR	NMR 424	L	a	b
							Pearson Correlation Coefficients (r)							
T_g		0.758	**-0.450**	-0.652	0.590	0.577	0.582	**0.489**	**0.499**	0.515	**-0.288**	-0.556	-0.526	-0.488
T_{cc}	0.000		-0.745	-0.798	0.821	0.795	0.858	0.690	**0.169**	0.782	-0.552	0.828	0.852	-0.713
T_m	0.070	0.001		**0.399**	-0.915	-0.918	-0.912	-0.828	**0.275**	**-0.346**	0.530	-0.900	-0.917	0.917
Xc	0.006	0.000	**0.126**		**-0.452**	**-0.463**	-0.528	**-0.358**	**-0.285**	-0.681	0.586	**-0.477**	-0.521	**0.332**
UV350	0.013	-	-	**0.079**		0.984	0.971	0.926	**-0.148**	**0.489**	**-0.374**	0.973	0.973	-0.958
UV380	0.015	0.000	-	**0.071**	-		0.965	0.942	**-0.175**	**0.490**	**-0.333**	0.956	0.955	-0.951
UV678	0.014	-	-	0.035	-	-		0.879	**-0.190**	**0.472**	**-0.434**	0.977	0.977	-0.960
IV	**0.055**	0.003	-	**0.173**	-	-	-		**-0.116**	0.568	**-0.140**	0.915	0.886	-0.909
WVTR	**0.049**	**0.532**	**0.303**	**0.285**	**0.531**	**0.460**	**0.421**	**0.668**		**0.388**	**-0.001**	**-0.175**	**-0.197**	**0.307**
OTR	0.034	0.003	**0.173**	0.004	**0.021**	**0.021**	**0.027**	0.023	**0.091**		**0.412**	**0.468**	0.513	**-0.308**
NMR 424	**0.279**	0.027	0.035	0.017	**0.154**	**0.207**	**0.093**	**0.606**	**0.998**	**0.113**		-0.999	0.947	-0.653
L	0.020	-	-	**0.062**	-	-	-	-	**0.461**	**0.028**	-		-0.944	0.581
a	0.030	-	-	0.039	-	-	-	-	**0.406**	0.015	-	-		-0.740
b	0.047	0.001	-	**0.209**	-	-	-	-	**0.189**	**0.163**	0.002	0.002	-	
							p-value							

In order to make sure that the highly correlated variables were not just excluded since they may be important predictor variables, and easy to determine experimentally, a simple linear regression analysis was performed with Tg, Tm, χc, UV380, IV, OTR, WVTR, intensity ratio of δ 4.2 combined with 4.0 peak (NMR424) and 'L', 'a' and 'b' values as a function of RPET contents. Good correlation between the predictor variables with the criterion variable must have p-value <0.05, moderate skewness, and the median value must be similar to the mean value to comply with the condition of residual normality.

Table 4-10. p-value, skewness, mean, median for the simple regression analysis for the predictor variables for PET sheets with varying percent of virgin and recycled PET content. (α and β values for the equation $y=\alpha*X+\beta$ and the normal distribution of the standard errors are shown in appendix C.)

	p-value	Skewness	Mean	Median
Tg	0.0504	-0.3450	0.0000	0.1212
Tm	<0.0001	0.7269	0.0000	-0.0374
χc	0.1062	-0.7702	0.0000	0.1556
UV380	<0.0001	0.3335	0.0000	0.0141
IV	<0.0001	-0.2682	0.0000	-0.0148
WVTR	0.2543	0.6301	0.0000	-0.0633
OTR	0.0255	-0.6791	0.0000	0.1476
NMR424	0.8292	-0.0034	0.0000	0.0606
L	0.9774	-0.075	0.0000	0.0915
a	0.7154	0.1656	0.0000	0.0649
b	0.0004	-1.5935	0.0000	0.0308

To sum up, Tm, OTR, UV380, IV, 'b' values were included since the residual are normally distributed (data not shown). APPENDIX C shows detailed descriptions for each linear regression. So, those predictor variables were used in the backward stepwise regression analysis (final predictor variables are highlighted in gray in Table 4-10). Table

4-11 shows the backward elimination steps with R-square and adjusted R-square as goodness of fit indicators. It was found that every model from step 0 to 1 accounts for at least over 95% of variance in each predictor. By using MANOVA, it was also confirmed that every model was statistically significant at $p < 0.0001$.

Table 4-11. Backward elimination sequence for PET sheets with varying percent of virgin and recycled PET as function of results from each different technique

	Step 0	Step 1
R^2	0.9812	0.9809
Adjusted R^2	0.9718	0.9740
F value	104.23 ($p<0.0001$)	141.38 ($p<0.0001$)
	IV ($p=0.2180$)	IV ($p=0.1047$)
	OTR ($p=0.0843$)	OTR ($p=0.0162$)
	Tm ($p=0.1479$)	Tm ($p=0.0563$)
	b ($p=0.0382$)	b ($p=0.0031$)
	UV380 ($p=0.7215$)	

Table 4-12 indicates the final simple proposed model for determining recycled PET contents from PET sheets. Figure 4-5 shows the experimental values of PET sheets with varying percent of virgin and recycled PET contents and the predicted ones, and the standard residual between these values. APPENDIX C shows the estimated parameters for each step.

Table 4-12. Proposed linear model ($PET = \alpha + \beta * IV + \chi * OTR + \delta * Tm + \eta * b + \varepsilon$)

Predictor variable	Parameter estimate	95% confidence interval		P value
		Lower bound	Upper bound	
α	20.317 ± 9.885	0.145	41.568	0.064
β	1.101 ± 0.623	0.196	2.558	0.105
χ	0.222 ± 0.078	0.040	0.349	0.016
δ	-0.086 ± 0.040	-0.173	-0.004	0.056
η	-0.267 ± 0.071	-0.387	-0.102	0.003

*Values are expressed as $\overline{X} \pm$ std

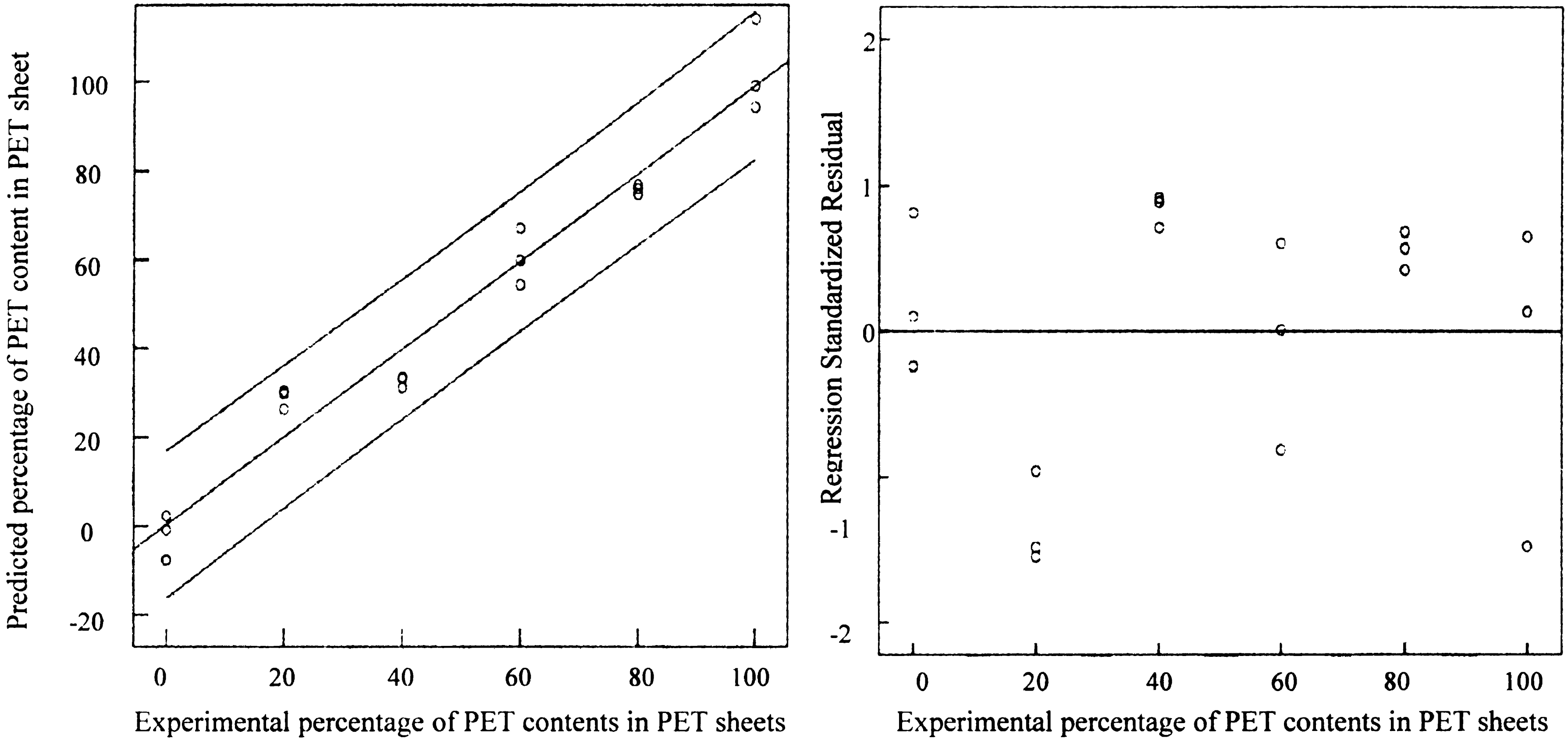

Figure 4-5. Predicted percentage of PET contents in PET sheets as function of experimental PET contents in PET sheets (left), Standardized residual vs percentage of PET contents in PET sheets (right)

4.8 Preliminary verification of the model

For the preliminary verification of the model, one unknown PET container from Pactiv (Lake Forest, IL) and 3 different kinds of unknown PET sheets from Clearlam (Elk Grove Village, IL) were requested and tested. Techniques selected in the backward stepwise regression analysis, intrinsic viscosity, UV-Visible spectroscopy, melting temperature, oxygen permeability, and 'b' value, were used to verify the model. In the case of intrinsic viscosity, there was no statistically significantly difference amongst the Pactiv container and the 3 different kinds of Clearlam PET sheets at $\alpha=0.05$. For the results of UV-Visible spectroscopy at 380 nm, it was found that only sample A of Clearlam PET sheets shows statistically significantly difference, compared to Pactiv container, sample B and sample C of Clearlam PET sheets ($\alpha=0.05$). The results of the 'b' value shows that the Pactiv container is statistically significantly different from samples A,B and C of Clearlam PET sheets ($\alpha=0.05$). The results of melting temperature indicate that sample A and B of Clearlam PET sheets have higher melting temperatures than the Pactiv container and sample C of the Clearlam PET sheets ($\alpha=0.05$). Sample A of the Clearlam PET sheets had lower water vapor permeability value than Sample B of Clearlam PET sheets. The results of oxygen permeability values indicated that sample B of Clearlam PET sheets is statistically significantly different with respect to Pactiv and samples A and C of Clearlam PET sheets ($\alpha=0.05$). The results of each predictor parameter for 4 different kinds of unknown PET samples are shown in Table 4-13. Based on these results, the percentage of PET was predicted using the stepwise regression model (Table 4-12). Table 4-14 indicates that actual PET contents of sample A of Clearlam PET sheets was difference with averaged predicted PET percentage of sample

A of Clearlam PET sheets, whereas the actual PET percentage of Pactiv was close to their averaged predicted PET percentage, and were located within the 95% confidence interval. The difference between the actual PET percentage of sample A of Clearlam PET sheets and averaged predicted PET percentage is due to the origin of its RPET flakes as reported by the company after the test was conducted. Namely, the current generated model was based on post-consumer recycled PET mostly collected by the bottle deposit system and recycled mechanically. However, as reported by Clearlam samples A, B and C of Clearlam PET sheets contained industrial recycled PET from bottle production (This information was reported after the test was conducted). Pre-consumer recycled PET is not expected to be contaminated by consumers so it has generally higher quality than post-consumer recycled PET. In consequence, sample A, B and C of Clearlam PET sheets' can not be used to verify the model. Further, new samples and analysis will be needed to verify and validate the model. At this stage, only one sample provide by Pactiv can be considered as tested to validate the model and the value was predicted betweent the 95% confidence interval. Further exhaustive testing are needed to determine if the model may possible predict the recycled PET content in PET sheets. At this time, the model was developed for a specific mechanical RPET stream provided by the ECO2 company (Modesto, CA, USA). Therefore, it may not be applicable for other recycled PET streams and products without new studies.

Table 4-13. Results of each predictor parameter for 4 different kinds of unknown PET samples

	Pactiv	Clearlam A	Clearlam B	Clearlam C
IV (dl/g)	0.699 ± 0.030^{a}	0.711 ± 0.004^{a}	0.710 ± 0.015^{a}	0.686 ± 0.012^{a}
UV380 (nm)	78.622 ± 2.579^{a}	92.264 ± 0.899^{b}	81.425 ± 1.469^{a}	81.082 ± 3.418^{a}
b	0.328 ± 0.101^{a}	1.194 ± 0.017^{b}	1.324 ± 0.022^{b}	1.430 ± 0.353^{b}
Tm (^{o}C)	245.173 ± 0.550^{a}	248.463 ± 0.221^{b}	248.963 ± 0.274^{b}	247.147 ± 0.506^{c}
OTR ($\times 10^{-19}$) (kg·m/m^{2}·Pa·sec)	$5.800 \pm 4.310 \times 10^{-1}$ ^{a}	$6.160 \pm 5.380 \times 10^{-2}$ ^{b}	$5.450 \pm 5.960 \times 10^{-2}$ ^{a}	$5.78 \pm 4.740 \times 10^{-2}$ ^{a}

*Values in the same low with different superscripts are significantly different at α=0.05

Table 4-14. Comparison between predicted fraction of virgin PET and company specification

Sample name	Predicted fraction of virgin PET	95% Confidence interval		Company Specification
Pactiv	0.756 ± 0.128	0.611	0.900	0.7~0.78
Clearlam A	0.777 ± 0.016	0.759	0.795	0.4
Clearlam B	0.544 ± 0.054	0.482	0.605	0.5
Clearlam C	0.761 ± 0.068	0.684	0.838	0.8

4.9 Limitation of the study and the model

As previously explained, the aim of this study was to explore the use of stepwise regression analysis to determine the amount of recycled PET content, which was previously recycled by mechanical recycling, in PET/RPET sheets. Therefore, few limitations should be stated about this study.

a- The model was developed only considering a single recycled PET stream obtained from the bottle deposited program and provided by the ECO2 company (Modesto, CA, USA) and one virgin PET stream supplied by Eastman (Columbia, CA, USA) with an intrinsic viscosity of 0.80 ± 0.02 dl g^{-1}.

b- The model was not properly validated between for different batch from the same company. This should be conducted to understate if the model can predict the amount of RPET for the same providers but a different industrial batch.

c- The model was not properly validated with unknown samples from the industry since only one unknown RPET samples could be tested with 20 to 30 % RPET. Therefore, further validation is needed.

d- The model does not consider postindustrial PET content as feedstock; therefore, it should not be tested outside the design domain of the model. At this stage, this model is not applicable for other recycled PET streams and products without new studies.

5. CONCLUSION

This study explored the use of stepwise regression analysis as a tentative tool to create a model to predict RPET content in PET sheets. A backward stepwise regression analysis was performed with a high significance level (α=0.15). By using backward elimination, a significant model emerged ($F_{4,15}$ = 141.38, p< 0.0001) with adjusted R square = 0.9740. Good prediction of the recycled content in PET samples between the designed domain of the model was obtained by measuring the melting temperature, intrinsic viscosity, oxygen permeability and 'b*' value. Since this model was developed for a specific mechanical RPET stream provided by the ECO2 company (Modesto, CA, USA), one virgin PET stream supplied by Eastman (Columbia, CA, USA), this model is not applicable for other recycled PET streams and products without further studies. Furthermore, verification of the model is needed inside and outside of the design domain of the model. At this time, only one sample with PCR-PET was obtained; therefore, the model needs further verification. Additiinal studies are needed for comparing post-industrial and post-consumer recycled PET.

Specifically, for the results of UV-Visible spectroscopy for PET sheets with varying percent of virgin and recycled PET contents, it was found that most of the absorption occurred from 200 to 400 nm due to their ester groups and benzene rings. The peak arising around 678 nm may be due to fragments of green or blue colored bottles and printed ink labels. These green or blue colored fragments also affect the color results. especially 'a*' value. The results of 'b*' value were affected by oxidation of PET (yellowing). It was found that more RPET content leads to greyer ('L*' decreases), greener ('a*' decrease) and more yellow color ('b*' increase). Dynamic mechanical analysis and universal material testing did not show differences between PET sheets with varying percent of virgin and recycled PET. The percent crystallinity measured by DSC showed no statistically significant differences except between 100V and 40V60R PET (α=0.05). Oxygen permeability results show that 100V and 60V40R PET show statistically significantly differences (α=0.05). It was also found that there was no a linear trend of oxygen permeability values as function of recycled PET contents. Water vapor permeability values indicate that there was no statistically significantly different between 100V and 100R PET. The NMR results do not show a trend as function of recycled PET contents. The results of intrinsic viscosity and viscosity molecular weight indicate that the reduction of molecular weight was occurred with chain scission through repeated recycling.

Future Work

After developing this exploratory stepwise regression model to tentatively determine RPET in PET samples, few points arise for further consideration and study.

- The criterion parameters used for this model should be further evaluated and verified. Also, it should be evaluated if better criterion parameters could be obtained to get better predictions. Models with different criterion parameters should be studied (e.g., including all the criterion parameters of this study and also a lower number than the current model.)

- This type of model should be verified with samples provided by the same manufacturer for different PET sample lots to understand if the model can predict inside its domain.
- Verification of the model should also be conducted with a number of unknown samples for a number of PET sheet producers that add post-consumer RPET in their samples.
- Studies should include a number of different PET samples suppliers with different type of PET and RPET streams.
- Limitations of the RPET predictions of this model should be better evaluated, and the effect of different RPET streams should be further understood.

6. APPENDICES

6.1 Appendix A- Description of sample production and processing conditions

In order to make PET sheets with varying percent of virgin and recycled PET contents, the resins of virgin PET and the flakes of recycled PET were delivered by train to Peninsula Packaging Company (Exeter, CA, USA). PET resins were stored at PET resin silos. RPET flakes were stored at RPET regrind storages. Amounts of RPET resins needed for making the expected concentration with PET were shifted to blender, AEC Whitlock blending system OS series blender (Wooddale, IL, USA). After passing through the blender, RPET was crystallizaed by crystallizers, Conair model CGT 700 (Franklin, PA, USA) during 45 min to 1 hour to increase crystalline areas of RPET. The temperature of air flowed in the crystallizer at 310 °F. The temperature of air flowed out from crystallizer was usually 100~150 °F. RPET was delivered to another blender, AEC Whitlock blending system OS series blender (Wooddale, IL, USA) to mix up with virgin PET. These subsequent blends experienced drying process using a Conair model CAG 2400 carousel drier (Franklin, PA, USA). After the drying process, the mixed resins were feed to two extruders and extruded on one die and turned to sheets. In order to analyze the difference between silicon coated PET sheet and uncoated PET sheet, two kinds of sheets were made as cutting half and half of origin sheets for making coated containers and uncoated containers. The silicon, Ivanhoe Industries Inc 35% silicone antifoam emulsion I-SIL 335 EFG (Zion, IL, USA), was used for coating materials. Cutting and coating process was carried out using a Montalvo system 3000 S-3100-CE (Gorham, MN.

USA). Figure 6-1 shows the flow chart of PET sheets processing. This study was only worked with the uncoated samples.

Table 6-1. Description of extruder zone

ZONE	Description	ZONE	Description	Zone	Description
0.1	Feed zone	2.1	Transition zone	3.4~3.8	Feed block
1.1	Transition zone	2.2	Pineapple mix	4.1	Eastside deckless
1.2	Pressure ring	2.3	Bullet zone	4.2~4.8	Die
1.3	Pressure ring	2.4	West side screen changer	4.9	Westside deckless
1.4	Pressure ring	2.5	East side screen changer	4.10	Die lip
1.5	Transition or melting zone	3.1	Flow choke	4.11	Die lip
T.1	Vacuum port	3.2	Gear pump		
T.2	Vacuum chamber	3.3	Crossover zone		

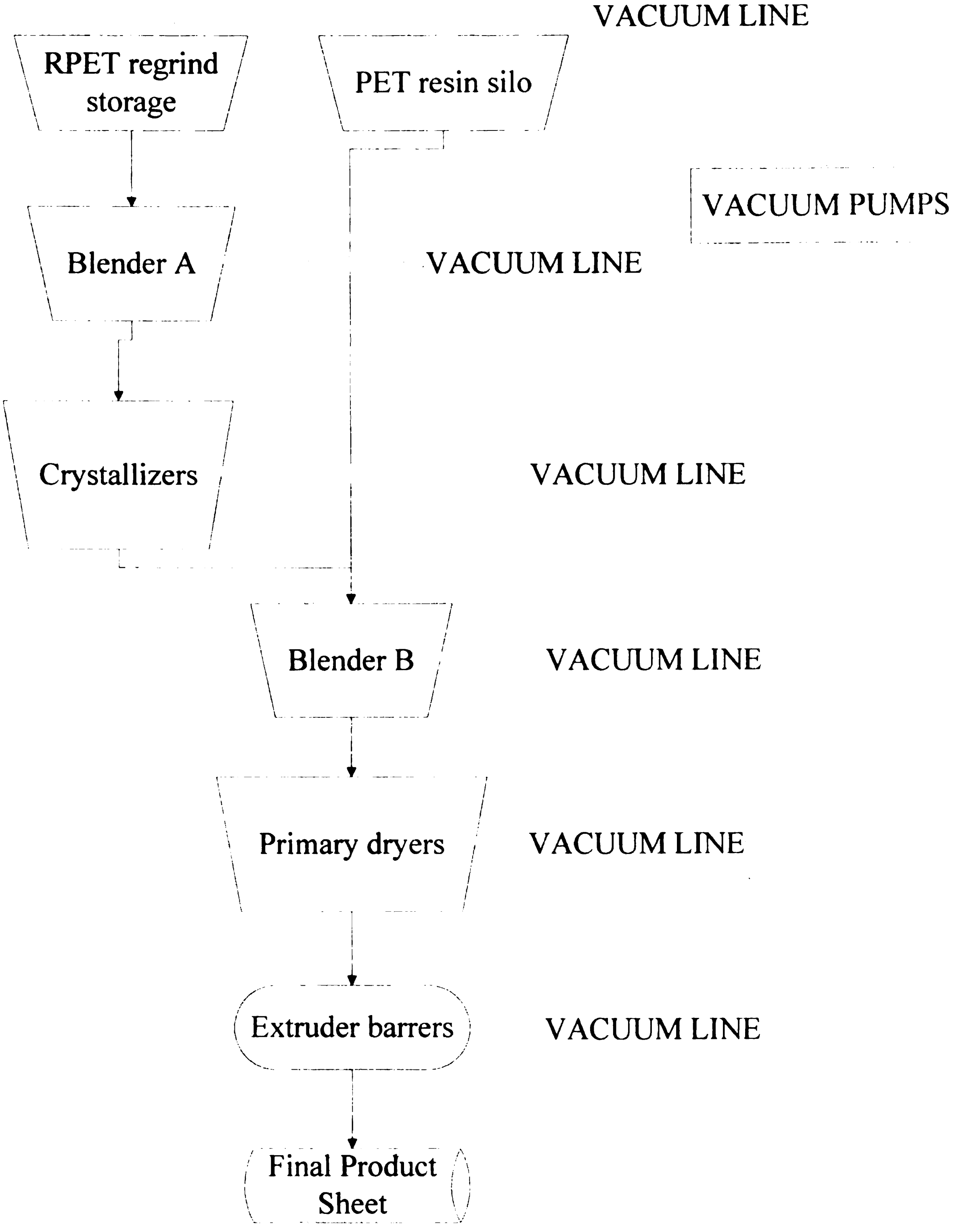

Figure 6-1. The flow chart of PET sheet processing

6.1.1 Processing condition of 80R20V PET sheet

Table 6-2, 6-3 and 6-4 describe the conditions of two extruders, roller and dryer used for making the sheets of 80R20V PET sheet

Table 6-2. The condition of two extruders for 80R20V PET sheet

	SPEED (1/min)	Current (%)	Pressure (psi)		M-Temp (°F)	Screen (psi)	Melting pressure control	Melt pressure behind dosing pump
Extruder A	86	64	916		564	930	450	60
Dosingpump A	36	41	732	44				
Extruder B	85	66	1025		549	950	600	1020
Dosingpump B	36	42	593	1523				
Die			1611				326	

Actual temperature (°F)

ZONE	Extruder A	Extruder B	ZONE	Die
0.1	522	520	3.4	495
1.1	513	513	3.5	495
1.2	506	505	3.6	495
1.3	505	499	3.7	495
1.4	504	501	3.8	495
1.5	507	499	4.1	495
2.1	511	505	4.2	495
2.3	503	515	4.3	495
2.4	528	540	4.4	495
2.5	536	534	4.5	495
3.1	502	497	4.6	495
3.2	533	537	4.7	495
3.3	505	500	4.8	498
T 1	135	104	4.9	498
T 2	999	999	4.10	554
2.2	505	504	4.11	534

Table 6-3. The temperature of dryer and plant for 80R20V PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	285 °F	285 °F
Dew point	-40 °F	-43 °F
Plant temperature at roller	108 °F	

Table 6-4. The condition of roller for 80R20V PET sheet

	Speed (m/min)	Current (%)	Temperature (°F)	Gap (mm)	
				left	right
Roll 1	23.63	38	63	0.06	0.05
Roll 2	23.63	38	70		
Roll 3	23.63	7	68	0.19	0.17
Haul-off	23.39	18			

6.1.2 Processing condition of 100R PET sheet

Table 6-5, 6-6 and 6-7 describes the conditions of two extruders, roller and dryer used for making the sheets of 100R PET sheet.

Table 6-5. The condition of two extruders for 100R PET sheet

<table>
<tr><th></th><th>SPEED (1/min)</th><th>Current (%)</th><th colspan="2">Pressure (psi)</th><th>M-Temp (°F)</th><th>Screen (psi)</th><th>Melting pressure control</th><th>Melt pressure behind dosing pump</th></tr>
<tr><td>Extruder A</td><td>82</td><td>66</td><td colspan="2">1249</td><td>558</td><td>1270</td><td>450</td><td>50</td></tr>
<tr><td>Dosingpump A</td><td>36</td><td>39</td><td>742</td><td>70</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Extruder B</td><td>88</td><td>65</td><td colspan="2">1003</td><td>547</td><td>1030</td><td>600</td><td>940</td></tr>
<tr><td>Dosingpump B</td><td>36</td><td>38</td><td>610</td><td>1410</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Die</td><td></td><td></td><td colspan="2">1476</td><td></td><td></td><td>295</td><td></td></tr>
<tr><td colspan="9">Actual temperature (°F)</td></tr>
<tr><td colspan="2">ZONE</td><td colspan="2">Extruder A</td><td colspan="2">Extruder B</td><td colspan="2">ZONE</td><td>Die</td></tr>
<tr><td colspan="2">0.1</td><td colspan="2">520</td><td colspan="2">520</td><td colspan="2">3.4</td><td>495</td></tr>
<tr><td colspan="2">1.1</td><td colspan="2">516</td><td colspan="2">515</td><td colspan="2">3.5</td><td>495</td></tr>
<tr><td colspan="2">1.2</td><td colspan="2">505</td><td colspan="2">505</td><td colspan="2">3.6</td><td>495</td></tr>
<tr><td colspan="2">1.3</td><td colspan="2">505</td><td colspan="2">500</td><td colspan="2">3.7</td><td>495</td></tr>
<tr><td colspan="2">1.4</td><td colspan="2">505</td><td colspan="2">501</td><td colspan="2">3.8</td><td>495</td></tr>
<tr><td colspan="2">1.5</td><td colspan="2">505</td><td colspan="2">499</td><td colspan="2">4.1</td><td>498</td></tr>
<tr><td colspan="2">2.1</td><td colspan="2">509</td><td colspan="2">508</td><td colspan="2">4.2</td><td>495</td></tr>
<tr><td colspan="2">2.3</td><td colspan="2">501</td><td colspan="2">515</td><td colspan="2">4.3</td><td>495</td></tr>
<tr><td colspan="2">2.4</td><td colspan="2">530</td><td colspan="2">528</td><td colspan="2">4.4</td><td>495</td></tr>
<tr><td colspan="2">2.5</td><td colspan="2">530</td><td colspan="2">530</td><td colspan="2">4.5</td><td>495</td></tr>
<tr><td colspan="2">3.1</td><td colspan="2">505</td><td colspan="2">503</td><td colspan="2">4.6</td><td>495</td></tr>
<tr><td colspan="2">3.2</td><td colspan="2">529</td><td colspan="2">533</td><td colspan="2">4.7</td><td>495</td></tr>
<tr><td colspan="2">3.3</td><td colspan="2">505</td><td colspan="2">500</td><td colspan="2">4.8</td><td>498</td></tr>
<tr><td colspan="2">T 1</td><td colspan="2">135</td><td colspan="2">112</td><td colspan="2">4.9</td><td>498</td></tr>
<tr><td colspan="2">T 2</td><td colspan="2">999</td><td colspan="2">999</td><td colspan="2">4.10</td><td>548</td></tr>
<tr><td colspan="2">2.2</td><td colspan="2">505</td><td colspan="2">504</td><td colspan="2">4.11</td><td>530</td></tr>
</table>

Table 6-6. The temperature of dryer and plant for 100R PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	285 °F	285 °F
Dew point	-40 °F	-40 °F
Plant temperature at roller	81 °F	

Table 6-7. The condition of roller for 100R PET sheet

	Speed (m/min)	Current (%)	Temperature (^{o}F)	Gap (mm)	
				left	right
Roll 1	23.62	38	63	0.06	0.05
Roll 2	23.62	38	70		
Roll 3	23.64	6	68	0.19	0.17
Haul-off	23.39	18			

6.1.3 Processing condition of 60R40V PET sheet

Table 6-8, 6-9 and 6-10 describe the conditions of two extruders, roller and dryer used for making the sheets of 60R40V PET sheet.

Table 6-8. The condition of two extruders for 60R40V PET sheet

	SPEED (1/min)	Current (%)	Pressure (psi)		M-Temp (°F)	Screen (psi)	Melting pressure control	Melt pressure behind dosing pump
Extruder A	80	62	1036		565	1030	460	150
Dosingpump A	36	45	734	150				
Extruder B	80	62	1047		554	980	590	1140
Dosingpump B	36	43	625	1710				
Die			1842				367	

Actual temperature (°F)

ZONE	Extruder A	Extruder B	ZONE	Die
0.1	507	518	3.4	494
1.1	536	537	3.5	495
1.2	527	523	3.6	493
1.3	522	520	3.7	485
1.4	511	513	3.8	490
1.5	524	516	4.1	495
2.1	515	516	4.2	495
2.3	500	517	4.3	495
2.4	533	533	4.4	495
2.5	529	529	4.5	493
3.1	513	510	4.6	490
3.2	534	542	4.7	487
3.3	511	510	4.8	494
T 1	135	109	4.9	485
T 2	999	999	4.10	552
2.2	503	502	4.11	529

Table 6-9. The temperature of dryer and plant for 60R40V PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	285 °F	285 °F
Dew point	-40 °F	-43 °F
Plant temperature at roller	78 °F	

Table 6-10. The condition of roller for 60R40V PET sheet

	Speed (m/min)	Current (%)	Temperature (^{o}F)	Gap (mm)	
				left	right
Roll 1	23.62	41	63	0.06	0.05
Roll 2	23.62	41	69		
Roll 3	23.59	6	68	0.19	0.17
Haul-off	23.37	18			

6.1.4 Processing condition of 40R60V PET sheet

Table 6-11, 6-12 and 6-13 describe the conditions of two extruders, roller and dryer used for making the sheets of 40R60V PET sheet.

Table 6-11. The condition of two extruders for 40R60V PET sheet

<table>
<tr><th></th><th>SPEED (1/min)</th><th>Current (%)</th><th colspan="2">Pressure (psi)</th><th>M-Temp (°F)</th><th>Screen (psi)</th><th>Melting pressure control</th><th>Melt pressure behind dosing pump</th></tr>
<tr><td>Extruder A</td><td>76</td><td>70</td><td colspan="2">996</td><td>565</td><td>1040</td><td>460</td><td>90</td></tr>
<tr><td>Dosingpump A</td><td>36</td><td>48</td><td>722</td><td>77</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Extruder B</td><td>78</td><td>72</td><td colspan="2">985</td><td>555</td><td>940</td><td>600</td><td>1180</td></tr>
<tr><td>Dosingpump B</td><td>36</td><td>47</td><td>610</td><td>1780</td><td></td><td></td><td></td><td></td></tr>
<tr><td>Die</td><td></td><td></td><td colspan="2">1945</td><td></td><td></td><td>384</td><td></td></tr>
</table>

Actual temperature (°F)				
ZONE	Extruder A	Extruder B	ZONE	Die
0.1	522	518	3.4	495
1.1	521	525	3.5	495
1.2	514	513	3.6	495
1.3	513	512	3.7	495
1.4	511	514	3.8	495
1.5	510	510	4.1	495
2.1	512	512	4.2	495
2.3	504	520	4.3	495
2.4	535	535	4.4	495
2.5	535	535	4.5	495
3.1	509	503	4.6	495
3.2	532	540	4.7	495
3.3	510	510	4.8	498
T 1	135	104	4.9	498
T 2	999	999	4.10	554
2.2	505	506	4.11	533

Table 6-12. The temperature of dryer and plant for 40R60V PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	295 °F	293 °F
Dew point	-40 °F	-47 °F
Plant temperature at roller	77 °F	

Table 6-13. The condition of roller for 40R60V PET sheet

	Speed (m/min)	Current (%)	Temperature (^oF)	Gap (mm)	
				left	right
Roll 1	23.66	41	63	0.06	0.05
Roll 2	23.66	41	70		
Roll 3	23.64	6	68	0.19	0.17
Haul-off	23.40	17			

6.1.5 Processing condition of 20R80V PET sheet

Table 6-14, 6-15 and 6-16 describe the conditions of two extruders, roller and dryer used for making the sheets of 20R80V PET sheet.

Table 6-14. The condition of two extruders for 20R80V PET sheet

	SPEED (1/min)	Current (%)	Pressure (psi)		M-Temp (°F)	Screen (psi)	Melting pressure control	Melt pressure behind dosing pump
Extruder A	76	73	1267		572	1250	450	190
Dosingpump A	36	53	732	179				
Extruder B	74	70	1223		561	1230	600	1340
Dosingpump B	36	51	612	2007				
Die			2205				442	

Actual temperature (°F)

ZONE	Extruder A	Extruder B	ZONE	Die
0.1	531	531	3.4	500
1.1	515	520	3.5	500
1.2	511	510	3.6	500
1.3	510	510	3.7	500
1.4	511	511	3.8	500
1.5	511	511	4.1	500
2.1	512	514	4.2	500
2.3	506	520	4.3	500
2.4	535	535	4.4	500
2.5	535	535	4.5	500
3.1	511	507	4.6	500
3.2	539	548	4.7	500
3.3	510	510	4.8	500
T 1	135	112	4.9	500
T 2	999	999	4.10	561
2.2	505	505	4.11	539

Table 6-15. The temperature of dryer and plant for 20R80V PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	295 °F	290 °F
Dew point	-40 °F	-47 °F
Plant temperature at roller	79 °F	

Table 6-16. The condition of roller for 20R80V PET sheet

	Speed (m/min)	Current (%)	Temperature (^{o}F)	Gap (mm)	
				left	right
Roll 1	23.65	34	63	0.06	0.05
Roll 2	23.65	34	72		
Roll 3	23.65	7	68	0.19	0.17
Haul-off	23.41	15			

6.1.6 Processing condition of 100V PET sheet

Table 6-17, 6-18 and 6-19 describe the conditions of two extruders, roller and dryer used for making the sheets of 100V PET sheet.

Table 6-17. The condition of two extruders for 100V PET sheet

	SPEED (1/min)	Current (%)	Pressure (psi)		M-Temp (°F)	Screen (psi)	Melting pressure control	Melt pressure behind dosing pump
Extruder A	74	69	1157		576	1170	450	530
Dosingpump A	36	56	766	513				
Extruder B	73	71	1205		564	1210	600	1400
Dosingpump B	36	55	600	2091				
Die			2329				469	

Actual temperature (°F)

ZONE	Extruder A	Extruder B	ZONE	Die
0.1	564	548	3.4	500
1.1	515	519	3.5	500
1.2	509	510	3.6	500
1.3	510	510	3.7	500
1.4	511	511	3.8	500
1.5	510	509	4.1	500
2.1	513	519	4.2	500
2.3	509	520	4.3	500
2.4	535	535	4.4	500
2.5	535	535	4.5	500
3.1	510	507	4.6	500
3.2	548	552	4.7	501
3.3	510	510	4.8	500
T 1	135	110	4.9	501
T 2	999	999	4.10	564
2.2	505	505	4.11	544

Table 6-18. The temperature of dryer and plant for 100V PET sheet

Dryer	Setting point (°F)	Actual temperature (°F)
Delivery Air	295 °F	290 °F
Dew point	-40 °F	-50 °F
Plant temperature at roller	81 °F	

Table 6-19. The condition of roller for 100V PET sheet

	Speed (m/min)	Current (%)	Temperature (^oF)	Gap (mm)	
				left	right
Roll 1	23.63	35	63	0.06	0.05
Roll 2	23.63	35	72		
Roll 3	23.64	6	68	0.19	0.17
Haul-off	23.43	15			

6.2 Appendix B – Description of stepwise regression analysis and SAS code

6.2.1 Multiple linear regression analysis

Basically, regression analysis is a statistical method for analyzing a relationship between two or more variables in such a manner that one variable can be predicted or explained by using information on the others [65]. In simple linear regression, the relationship is focused on only one factor variable and the relationship can be described by a straight line. Namely, simple linear regression relates observed values of the dependent or response variable y to values of a single independent variable x (Equation (6.1)).

$$y=\beta_0 + \beta_1 x + \varepsilon \tag{6.1}$$

Multiple linear regression is the extension of simple linear regression to allow a number of independent variables and it can be written as Equation (6.2)

$$y=\beta_0 + \beta_1 x_1 + \beta_2 x_2 + \cdots + \beta_m x_m + \varepsilon \tag{6.2}$$

In the Equation (6.2), y is the dependent variable, and the x_i, i = 1, 2, ..., m, are the m independent variables. The β_i are the (m) parameters or regression coefficients and β_0 is the intercept.

6.2.2 Pearson correlation coefficient

In statistics, correlation coefficient provides a convenient index of the strength of the linear relationship between two variables. There are several different coefficients used for different situations. Pearson correlation coefficient is one of the correlation coefficient, which is obtained by dividing the covariance of the two variables by their standard deviation (Equation (6.3)) [65].

$$\text{Pearson correlation coefficient (r)} = \frac{\sum_{i=1}^{n}(X_i-\overline{X})(Y_i-\overline{Y})}{\sqrt{\sum_{i=1}^{n}(X_i-\overline{X})^2}\sqrt{\sum_{i=1}^{n}(Y_i-\overline{Y})^2}} \tag{6.3}$$

In the Equation (6.3), X_i and Y_i is sample of paired data. $\overline{X}$ is sample mean of independent variables and $\overline{Y}$ is sample mean of dependent variables. Pearson correlation coefficient is reported from -1 to +1, with a value of 0 indicating no relationship and values of -1 and +1 indicating a perfect linear relationship.

6.2.3 R, R Square and adjusted R Square

Correlation and regression analysis can be related in number of ways. R is a measure of the correlation between the observed value and the predicted value of the dependent variables. R Square (R^2) is the square of this measure of correlation and indicates the proportion of the variance in the dependent variable (Equation (6.4)) [66].

$$R^2 = \frac{\mathrm{var}(Y')}{\mathrm{var}(Y)} \tag{6.4}$$

In the Equation (6.4), Y' is predicted value by only using independent variables (X_i). Y is dependent variables. Therefore, by knowing R Square (R^2), it can be measured how good a prediction of the dependent variables when only X_i are observed. However, R Square tends to somewhat over-estimate the success of the model when applied to the actual case. Adjusted R Square is the solution of this problem, and it is calculated which takes into account the number of variables in the model and the number of observations [66]. For example, Adjusted R Square is 0.90, indicating this model has accounted for 90% of the variance in the dependent variables.

6.2.4 Stepwise regression

Stepwise model-building technique is one of the techniques for designing regression model. The basic procedures consists of (1) identifying an initial model, (2) repeatedly altering the model at the previous step by adding or removing a predictor variable in accordance with critical value, and (3) terminating the search when adding or removing predictor variable is no longer possible given the critical value, or when a specified maximum number of steps has been reached [67].

6.2.4.1 Forward selection

In forward selection, predictor variables are into the model one at a time in an order determined by the strength of their correlation with the dependent variable. The effect of adding each is assessed as it is entered, and variables that do not significantly add to the success of the model are excluded [66].

6.2.4.2 Backward selection

In backward selection, all the predictor variables are into the model. The weakest predictor variable is than removed and the regression recalculated. This procedure is then repeated until only useful predictor variables remain in the model. It is generally agreed upon that backward selection is preferable to forward selection [68]. The stopping rule for adding or removing predictor variables usually applies the standard significance level (α=0.05). However, this significance level is too small to identify important predictor variables. Therefore, if stepwise regression analysis is used, backward manner with a high significance (α=0.15 or 0.20) level must be used.

6.2.4.3 Stepwise selection

Stepwise selection is the most sophisticated methods among stepwise regression analysis. Each predictor variables is entered in sequence and its value assessed. If adding the variable contributes to the model then it is remained, but all other variables in the model are then re-tested to assure that they are still contributing to the success of the model. If they have no effect they are removed. Therefore, this method produces smallest possible set of predictor variables included in model.

6.2.5 SAS code for this study

For raw data input,

```
data PET;
input PET TG TCC TC TM DH LM MT ORP UV350 UV380 UV678 IV VM
WVTR OTR NMR424 L a b E;
cards;
```

observation data input here

```
;
run;
proc print data=PET;
run;
```

For Pearson correlation test

```
proc corr data=PET;
var PET TG TCC TM Xc UV350 UV380 UV678 IV VM WVTR OTR
NMR424 L a b;
run;
```

For simple linear regression analysis with residual plot and normality test

```
*TG;
proc reg data=PET ;
model PET=TG/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;

*TM;
proc reg data=PET ;
model PET=TM/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;
```

```
*UV380;
proc reg data=PET ;
model PET=UV380/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;
proc univariate data=myout plot normal;
var resid;
run;

*IV;
proc reg data=PET ;
model PET=IV/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;

*WVTR;
proc reg data=PET ;
model PET=WVTR/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;
```

```
*OTR;
proc reg data=PET ;
model PET=OTR/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;


*NMR424;
proc reg data=PET ;
model PET=NMR424/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;

*L;
proc reg data=PET ;
model PET=L/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;
```

```
*a;
proc reg data=PET ;
model PET=a/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;

*b;
proc reg data=PET ;
model PET=b/cli clm ;
output out=myout r=resid p=pred;
run;

proc plot data=myout;
plot resid*pred;
run;

proc univariate data=myout plot normal;
var resid;
run;
```

For stepwise regression analysis (Backward manner)

```
proc reg data=PET;
model PET=TM UV380 IV OTR b/adjrsq selection=backward
sls=0.15;
run;
```

6.3 Appendix C – Description for each linear regression and estimated parameter for each step

6.3.1 Description for simple linear regression between TG and dependant variables

```
                         Analysis of Variance

                              Sum of       Mean
Source             DF        Squares      Square    F Value    Pr > F

Model               1        0.46559      0.46559     4.52     0.0504
Error              15        1.54382      0.10292
Corrected Total    16        2.00941


          Root MSE           0.32081   R-Square    0.2317
          Dependent Mean     0.49412   Adj R-Sq    0.1805
          Coeff Var         64.92654

                         Parameter Estimates

                     Parameter      Standard
Variable     DF      Estimate       Error        t Value    Pr > |t|

Intercept     1     -16.57983       8.02794       -2.07      0.0566
TG            1       0.21940       0.10315        2.13      0.0504

                      Basic Statistical Measures

          Location                        Variability

      Mean     0.000000         Std Deviation          0.31063
      Median   0.121152         Variance               0.09649
      Mode      .               Range                  1.03256
                                Interquartile Range    0.54365
```

```
                         Tests for Normality

Test                    --Statistic---        -----p Value------

Shapiro-Wilk            W     0.918466        Pr < W      0.1391
Kolmogorov-Smirnov      D     0.207068        Pr > D      0.0504
Cramer-von Mises        W-Sq  0.126398        Pr > W-Sq   0.0453
Anderson-Darling        A-Sq  0.676624        Pr > A-Sq   0.0666

                       The UNIVARIATE Procedure
                      Variable:  resid  (Residual)

                        Normal Probability Plot

  0.5+                       +++++*+
     |                   +*+*++*
     |              * ***+*+**
     |            +*++++
     |         ++++*+*
 -0.5+      +*++++* *
      +----+----+----+----+----+----+----+----+----+----+
          -2   -1    0   +1   +2
```

6.3.2 Description for simple linear regression between TM and dependant variables

```
                        Analysis of Variance

                              Sum of          Mean
Source              DF       Squares        Square    F Value    Pr > F

Model                1       1.71533       1.71533      87.49    <.0001
Error               15       0.29408       0.01961
Corrected Total     16       2.00941


        Root MSE              0.14002    R-Square     0.8536
        Dependent Mean        0.49412    Adj R-Sq     0.8439
        Coeff Var            28.33735
```

```
                         Parameter Estimates

                    Parameter     Standard
Variable    DF      Estimate      Error       t Value    Pr > |t|

Intercept    1      88.52697      9.41160      9.41      <.0001
TM           1      -0.35745      0.03821     -9.35      <.0001

                     Basic Statistical Measures

          Location                    Variability

          Mean      0.00000           Std Deviation          0.13557
          Median   -0.03739           Variance               0.01838
          Mode       .                Range                  0.53992
                                      Interquartile Range    0.21004

                        Tests for Normality

     Test                   --Statistic---         -----p Value------

     Shapiro-Wilk           W      0.933711        Pr < W       0.2509
     Kolmogorov-Smirnov     D      0.165698        Pr > D      >0.1500
     Cramer-von Mises       W-Sq   0.093171        Pr > W-Sq    0.1311
     Anderson-Darling       A-Sq   0.531804        Pr > A-Sq    0.1518

                      The UNIVARIATE Procedure
                     Variable:  resid  (Residual)

                       Normal Probability Plot

     0.35+                             *   +++
         |                         ++++++++
         |                     * *+*++*+
     0.05+                    +++*+*++
         |              +**+*+***
         |          +*++*+*
    -0.25+  ++++*+++
          +----+----+----+----+----+----+----+----+----+----+
              -2        -1         0        +1        +2
```

6.3.3 Description for simple linear regression between χc and dependant variables

```
                          Analysis of Variance

                                Sum of        Mean
Source              DF         Squares       Square   F Value    Pr > F

Model                1         0.35077      0.35077     2.98     0.1062
Error               14         1.64673      0.11762
Corrected Total     15         1.99750


        Root MSE             0.34296    R-Square     0.1756
        Dependent Mean       0.48750    Adj R-Sq     0.1167
        Coeff Var           70.35136

                          Parameter Estimates

                        Parameter      Standard
Variable       DF        Estimate         Error    t Value    Pr > |t|

Intercept       1         1.42648       0.55046       2.59      0.0213
Xc              1        -0.10986       0.06361      -1.73      0.1062

                       Basic Statistical Measures

            Location                       Variability

        Mean     0.000000           Std Deviation            0.33133
        Median   0.155594           Variance                 0.10978
        Mode      .                 Range                    1.04186
                                    Interquartile Range      0.50959

                          Tests for Normality

        Test                  --Statistic---          -----p Value------

        Shapiro-Wilk          W     0.870606          Pr < W       0.0278
        Kolmogorov-Smirnov    D     0.258146          Pr > D      <0.0100
        Cramer-von Mises      W-Sq  0.184956          Pr > W-Sq    0.0072
        Anderson-Darling      A-Sq  0.965296          Pr > A-Sq    0.0115
```

```
                         The UNIVARIATE Procedure
                       Variable:  resid  (Residual)

                          Normal Probability Plot

        0.5+                      +++++*
           |                  +*+*++*
           |              **+**+*+*
       -0.1+              ++*+++
           |          ++++*+*
           |     +++++*  *
       -0.7+ ++++++*
             +----+----+----+----+----+----+----+----+----+----+
                -2    -1     0    +1    +2
```

6.3.4 Description for simple linear regression between UV380 and dependant variables

```
                            Analysis of Variance

                                 Sum of         Mean
Source               DF         Squares       Square   F Value   Pr > F

Model                 1         2.54680      2.54680    336.48   <.0001
Error                20         0.15138      0.00757
Corrected Total      21         2.69818


          Root MSE            0.08700   R-Square    0.9439
          Dependent Mean      0.49091   Adj R-Sq    0.9411
          Coeff Var          17.72224


                            Parameter Estimates

                      Parameter      Standard
Variable      DF       Estimate         Error    t Value    Pr > |t|

Intercept      1       -5.51895       0.32816     -16.82      <.0001
UV380          1        0.07847       0.00428      18.34      <.0001



                       Basic Statistical Measures
```

```
          Location                  Variability

          Mean     0.000000         Std Deviation           0.08490
          Median   0.014113         Variance                0.00721
          Mode      .               Range                   0.39426
                                    Interquartile Range     0.07267

                           Tests for Normality

     Test                     --Statistic---          -----p Value------

     Shapiro-Wilk             W     0.931772          Pr < W      0.1336
     Kolmogorov-Smirnov       D     0.151982          Pr > D     >0.1500
     Cramer-von Mises         W-Sq  0.103095          Pr > W-Sq   0.0967
     Anderson-Darling         A-Sq  0.628273          Pr > A-Sq   0.0911

                         The UNIVARIATE Procedure
                        Variable:  resid  (Residual)

                         Normal Probability Plot

    0.225+                                  *   ++
         |                              ++++++
         |                          ++++++
         |                      ++++*+*  *
    0.025+                     *+***** **
         |             ** ****+
         |           ++++++
         |       ++*++* *
   -0.175+       ++++*+
          +----+----+----+----+----+----+----+----+----+----+
             -2   -1    0   +1   +2
```

6.3.5 Description for simple linear regression between IV and dependant variables

```
                          Analysis of Variance

                              Sum of        Mean
Source              DF       Squares       Square      F Value    Pr > F

Model                1       1.76878       1.76878     108.27     <.0001
Error               14       0.22872       0.01634
Corrected Total     15       1.99750


        Root MSE            0.12782    R-Square    0.8855
        Dependent Mean      0.48750    Adj R-Sq    0.8773
        Coeff Var          26.21902


                          Parameter Estimates

                      Parameter      Standard
Variable     DF       Estimate       Error        t Value    Pr > |t|

Intercept     1       -2.80581       0.31812       -8.82     <.0001
IV            1        5.20692       0.50042       10.41     <.0001

                       Basic Statistical Measures

            Location                       Variability

            Mean     0.00000               Std Deviation          0.12348
            Median  -0.01478               Variance               0.01525
            Mode      .                    Range                  0.38397
                                           Interquartile Range    0.21655
                          Tests for Normality

    Test                      --Statistic---          -----p Value------

    Shapiro-Wilk              W      0.9318           Pr < W       0.2603
    Kolmogorov-Smirnov        D    0.182203           Pr > D      >0.1500
    Cramer-von Mises          W-Sq 0.080368           Pr > W-Sq    0.1978
    Anderson-Darling          A-Sq 0.459591           Pr > A-Sq    0.2333
```

```
                    The UNIVARIATE Procedure
                    Variable:  resid  (Residual)

                     Normal Probability Plot

   0.225+                              +*++
        |                          *+++
        |                       * *+*++
        |                      *++++
   0.025+                      +**++
        |                  ++++
        |                ++*+* **
        |              ++*+*
  -0.175+              * +++*
         +----+----+----+----+----+----+----+----+----+----+
           -2        -1         0        +1        +2
```

6.3.6 *Description for simple linear regression between OTR and dependant variables*

```
                         Analysis of Variance

                              Sum of          Mean
Source               DF      Squares        Square    F Value    Pr > F

Model                 1      0.60903       0.60903       5.83    0.0255
Error                20      2.08915       0.10446
Corrected Total      21      2.69818


        Root MSE             0.32320    R-Square     0.2257
        Dependent Mean       0.49091    Adj R-Sq     0.1870
        Coeff Var           65.83683


                        Parameter Estimates

                       Parameter       Standard
   Variable     DF      Estimate          Error    t Value    Pr > |t|

   Intercept     1      -3.43158        1.62593      -2.11      0.0476
   OTR           1       0.71277        0.29519       2.41      0.0255
```

```
                     Basic Statistical Measures

     Location                       Variability

    Mean     0.000000              Std Deviation            0.31541
    Median   0.147601              Variance                 0.09948
    Mode      .                    Range                    1.00191
                                   Interquartile Range      0.44258

                        Tests for Normality

  Test                    --Statistic---          -----p Value------

  Shapiro-Wilk            W     0.876023          Pr < W       0.0102
  Kolmogorov-Smirnov      D     0.214006          Pr > D      <0.0100
  Cramer-von Mises        W-Sq  0.189236          Pr > W-Sq    0.0066
  Anderson-Darling        A-Sq  1.090584          Pr > A-Sq    0.0061

                     The UNIVARIATE Procedure
                     Variable:  resid  (Residual)

                      Normal Probability Plot

   0.3+                 **** **+*+*  *   *
      |               *+*+++++
      |            *+*****+
      |         ++++*+
      |     ++++*++* *
  -0.7+++++++*
       +----+----+----+----+----+----+----+----+----+----+
          -2   -1    0    +1   +2
```

6.3.7 Description for simple linear regression between WVTR and dependant variables

```
                          Analysis of Variance

                            Sum of        Mean
Source            DF       Squares       Square   F Value   Pr > F

Model              1       0.19151      0.19151      1.39   0.2543
Error             18       2.48649      0.13814
Corrected Total     19       2.67800


       Root MSE            0.37167     R-Square    0.0715
       Dependent Mean      0.49000     Adj R-Sq    0.0199
       Coeff Var          75.85089


                          Parameter Estimates

                    Parameter     Standard
  Variable    DF    Estimate       Error     t Value   Pr > |t|

  Intercept    1    2.85714       2.01211       1.42     0.1727
  WVTR         1   -0.88319       0.75008      -1.18     0.2543

                       Basic Statistical Measures

              Location                    Variability

              Mean     0.00000            Std Deviation           0.36176
              Median  -0.06326             Variance               0.13087
              Mode      .                  Range                  1.09613
                                          Interquartile Range     0.47153

                          Tests for Normality

    Test                    --Statistic---          -----p Value------

    Shapiro-Wilk            W     0.903731           Pr < W       0.0485
    Kolmogorov-Smirnov      D     0.145487          Pr > D      >0.1500
    Cramer-von Mises         W-Sq 0.085857          Pr > W-Sq   0.1676
    Anderson-Darling         A-Sq 0.628571          Pr > A-Sq   0.0898
```

```
                 The UNIVARIATE Procedure
               Variable:  resid  (Residual)

                  Normal Probability Plot

    0.7+                  *  ++*+++
       |               * *+++++
       |             ++++++
    0.1+            ++***+**
       |         +++** *
       |       *+*+** **
   -0.5+     *  ++*++
         +----+----+----+----+----+----+----+----+----+----+
            -2      -1       0      +1      +2
```

6.3.8 Description for simple linear regression between NMR424 and dependant variables

```
                      Analysis of Variance

                            Sum of        Mean
Source             DF      Squares      Square   F Value   Pr > F

Model               1      0.00707     0.00707      0.05   0.8292
Error              17      2.50241     0.14720
Corrected Total    18      2.50947


        Root MSE            0.38367    R-Square    0.0028
        Dependent Mean      0.49474    Adj R-Sq   -0.0558
        Coeff Var          77.54970


                      Parameter Estimates

                       Parameter      Standard
   Variable     DF      Estimate         Error   t Value   Pr > |t|

   Intercept     1       0.48635       0.09598      5.07     <.0001
   NMR424        1    0.00059792       0.00273      0.22     0.8292
```

```
                    Basic Statistical Measures

        Location                    Variability

     Mean     0.000000          Std Deviation          0.37286
     Median   0.060554          Variance               0.13902
     Mode      .                 Range                 1.05187
                                Interquartile Range    0.60001

                    The UNIVARIATE Procedure
                   Variable:  resid  (Residual)

                     Normal Probability Plot

      0.5+                   * *++*++ *
         |                *+*+++
         |             **+**+
         |          ++*+*
         |       +++*+**
     -0.5+     * ++*++* *
          +----+----+----+----+----+----+----+----+----+----+
              -2   -1    0   +1   +2
```

6.3.9 Description for simple linear regression between 'L' and dependant variables*

```
                        Analysis of Variance

                              Sum of        Mean
Source              DF       Squares       Square      F Value   Pr > F

Model                1    0.00011269   0.00011269     0.00      0.9774
Error               24     3.29835      0.13743
Corrected Total     25     3.29846


        Root MSE            0.37072   R-Square    0.0000
        Dependent Mean      0.50769   Adj R-Sq   -0.0416
        Coeff Var          73.02004
```

```
                           Parameter Estimates

                         Parameter      Standard
Variable     DF          Estimate          Error      t Value     Pr > |t|

Intercept     1          0.50203         0.21062       2.38       0.0254
L             1          0.00007255      0.00253       0.03       0.9774

                       Basic Statistical Measures

         Location                         Variability

     Mean      0.000000         Std Deviation            0.36323
     Median    0.091514         Variance                 0.13193
     Mode      0.491441         Range                    1.00639
                                Interquartile Range      0.59990

                          Tests for Normality

     Test                       --Statistic---          -----p Value------

     Shapiro-Wilk               W      0.897894         Pr < W        0.0141
     Kolmogorov-Smirnov         D      0.148208         Pr > D        0.1455
     Cramer-von Mises           W-Sq   0.109424         Pr > W-Sq     0.0829
     Anderson-Darling           A-Sq   0.804914         Pr > A-Sq     0.0337

                        The UNIVARIATE Procedure
                       Variable:  resid  (Residual)

                        Normal Probability Plot

  0.55+                            +++
      |                      * *+* *   *
      |                      +++
      |                   * ***
      |                  +++
      |                ****
      |              ++
      |             ++***
      |           +++
      |         +++*** *
      |       ++
 -0.55+      *  +*+* * *
       +----+----+----+----+----+----+----+----+----+----+
          -2     -1      0       +1      +2
```

6.3.10 Description for simple linear regression between 'a' and dependant variables*

```
                         Analysis of Variance

                              Sum of         Mean
Source               DF      Squares       Square    F Value    Pr > F

Model                 1      0.01860      0.01860       0.14    0.7154
Error                24      3.27986      0.13666
Corrected Total      25      3.29846


          Root MSE              0.36968      R-Square     0.0056
          Dependent Mean        0.50769      Adj R-Sq    -0.0358
          Coeff Var            72.81512


                         Parameter Estimates

                     Parameter       Standard
Variable     DF       Estimate          Error    t Value    Pr > |t|

Intercept     1        0.53266        0.09918       5.37      <.0001
a             1        0.02358        0.06392       0.37      0.7154

                      Basic Statistical Measures

        Location                       Variability

     Mean      0.00000           Std Deviation            0.36221
     Median    0.06486           Variance                 0.13119
     Mode     -0.49305           Range                    1.10140
                                 Interquartile Range      0.59175

                          Tests for Normality

    Test                  --Statistic---         -----p Value------

    Shapiro-Wilk          W      0.920065        Pr < W       0.0451
    Kolmogorov-Smirnov    D      0.140449        Pr > D      >0.1500
    Cramer-von Mises      W-Sq   0.088835        Pr > W-Sq    0.1527
    Anderson-Darling      A-Sq   0.644568        Pr > A-Sq    0.0858
```

```
                 The UNIVARIATE Procedure
                Variable:  resid  (Residual)

                  Normal Probability Plot

   0.45+                   * *+* *   *
       |                  +++
       |               * *+*
       |              *++
       |             **+
       |            ***
       |           +++
       |          **+ *
       |        +++
       |      * *+*
       |     +++
  -0.65+     *+++
        +----+----+----+----+----+----+----+----+----+----+
            -2   -1    0   +1   +2
```

6.3.11 Description for simple linear regression between 'b' and dependant variables*

```
                          Analysis of Variance

                               Sum of          Mean
Source              DF        Squares        Square    F Value    Pr > F

Model                1        1.32665       1.32665      16.75    0.0004
Error               25        1.98002       0.07920
Corrected Total     26        3.30667


        Root MSE              0.28143    R-Square     0.4012
        Dependent Mean        0.51111    Adj R-Sq     0.3773
        Coeff Var            55.06167


                         Parameter Estimates

                     Parameter       Standard
    Variable   DF     Estimate          Error    t Value    Pr > |t|

    Intercept   1      0.98081        0.12690       7.73      <.0001
    b           1     -0.26592        0.06497      -4.09      0.0004
```

```
                    Basic Statistical Measures

     Location                      Variability

   Mean      0.00000          Std Deviation          0.27596
   Median    0.03081          Variance              0.07615
   Mode     -0.15911          Range                1.30049
                              Interquartile Range    0.39846

                       Tests for Normality

  Test                    --Statistic---        -----p Value------

  Shapiro-Wilk             W     0.827949       Pr < W      0.0004
  Kolmogorov-Smirnov       D    0.165207        Pr > D     0.0574
  Cramer-von Mises        W-Sq  0.153676        Pr > W-Sq   0.0207
  Anderson-Darling        A-Sq  1.14039         Pr > A-Sq  <0.0050

                     The UNIVARIATE Procedure
                    Variable:  resid  (Residual)

                      Normal Probability Plot

   0.3+                    ****+**+++ *   *
      |                 **+*+**+++
      |             **  ***+*++
  -0.3+            * +*+++++
      |   ++++++++
      |++++
  -0.9+     *
       +----+----+----+----+----+----+----+----+----+----+
         -2   -1    0    +1    +2
```

6.3.12 Description of the estimated parameter for each step

Table 6-20 indicate the description of the estimated parameter, P value and 95% confidence interval for step 0. At the step 0, F value is 104.23 (<0.0001) with adjusted R-square of 0.9718.

Table 6-20. Estimated parameter, P value and 95% confidence interval for step 0

Predictor variable	Parameter estimate	95% confidence interval		P value
		Lower bound	Upper bound	
Intercept	17.551 ± 12.767	-6.580	46.567	0.1992
IV	0.971 ± 0.739	-0.011	2.702	0.2180
OTR	0.198 ± 0.103	-0.024	0.397	0.0843
TM	-0.077 ± 0.049	-0.188	0.017	0.1479
b	-0.241 ± 0.101	-0.449	-0.023	0.0382
UV380	0.009 ± 0.023	-0.044	0.050	0.7215

Table 6-21 indicate the description of estimated parameter, P value and 95% confidence interval for step 1. At the step 1, F value is increased to 141.38 (<0.0001) with adjusted R-square of 0.9740 by excluding UV380 variable.

Table 6-21. Estimated parameter, P value and 95% confidence interval for step 1

Predictor variable	Parameter estimate	95% confidence interval		P value
		Lower bound	Upper bound	
Intercept	20.317 ± 9.885	0.145	41.568	0.064
IV	1.101 ± 0.623	0.196	2.558	0.105
OTR	0.222 ± 0.078	0.040	0.349	0.084
TM	-0.086 ± 0.040	-0.173	-0.004	0.056
b	-0.267 ± 0.071	-0.387	-0.102	0.003

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