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Kinetics and Chemical Reactions of Acetaldehyde Stripping and 2-methyl-
1,3-dioxolane Generation in Poly (ethylene terephthalate)

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements
for the Master of Science in Chemical Engineering

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An Abstract of
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Poly (ethylene terephthalate) otherwise called PET has gained importance over the years in making beverage bottles and containers. The amount of residual acetaldehyde present in this material is crucial because of its ability to diffuse from the inner walls of the plastic and affect the flavor and odor of the product present inside the packaging. It is therefore, necessary to reduce the residual acetaldehyde concentration in the PET resin to a low amount of less than 1ppm before it can be used to make preform and later container. For this purpose, the rate of change of residual acetaldehyde concentration during air stripping of poly (ethylene terephthalate) has been studied simultaneously with determination of the residual concentrations of other less volatile compounds such as 2-methyl-1,3-dioxolane and ethylene glycol.

Two PET resins with different initial intrinsic viscosities have been air stripped at temperatures from 160°C to 190°C in a solid state polymerization reactor for 12 hours. Samples collected during the air stripping process were

analyzed in terms of their residual concentrations of acetaldehyde and 2-methyl-1,3-dioxolane, using gas chromatography with a column temperature of 120°C. It has been observed that the residual concentration of acetaldehyde decreases and reaches a minimum value with time during air stripping of poly (ethylene terephthalate). The rate constants for polymerization and acetaldehyde diffusivity coefficients have been determined at different temperatures of air stripping of PET. The residual 2-methyl-1,3-dioxolane concentration change with time is less straightforward and does not follow the behavior of residual acetaldehyde concentration change. The trend it follows at different temperatures of air stripping the poly (ethylene terephthalate) resins has; however, been explained. In an attempt to elucidate the mechanism of 2MD formation, the free ethylene glycol concentrations in PET have been measured using techniques such as thermal desorption and nuclear magnetic resonance spectroscopy. The changes in other properties of PET such as the intrinsic viscosity, density, percentage crystallinity and color have also been monitored as an aid to studying the kinetics of acetaldehyde removal from poly (ethylene terephthalate).

Dedicated to my advisor Dr. Saleh A Jabarin, my family and my friends...

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Contents

Abstract	iii
Acknowledgements	v
Contents	vi
List of Tables	ix
List of Figures	xi

Chapter

1. Introduction	1
1.1 Poly(ethylene terephthalate).....	2
1.2 History of Poly(ethylene terephthalate).....	3
1.3 Properties of Poly(ethylene terephthalate).....	3
1.4 Drying Characteristics of Poly(ethylene terephthalate).....	4
1.5 Preparation of PET in Melt Phase.....	5
1.6 Solid State Polymerization of PET.....	7
1.7 Advancements in PET Manufacturing and its Hurdle.....	8
1.8 Research Objective.....	9

2. Experimental	11
2.1 Materials.....	11
2.2 Air Stripping of PET Resins.....	13
2.3 Rheology Measurements.....	15
2.4 Density Measurements.....	17
2.5 Percentage Crystallinity Measurements.....	20
2.6 Color Measurements.....	21
2.7 Chemical Analysis.....	22
2.7.1 Determination of Residual Acetaldehyde and Residual 2-methyl-1,3-dioxolane Concentrations in PET.....	22
2.7.2 Determination of Free Ethylene Glycol Content in PET using Thermal Desorption and Gas Chromatography.....	29
2.7.3 Determination of Free Ethylene Glycol Concentration in PET using Nuclear Magnetic Resonance (^1H NMR) Technique.....	32
3. Results and Discussion	35
3.1 Intrinsic Viscosity and Molecular Weight.....	35
3.1.1 Calculation of Rate Constants for Polymerization during Air Stripping.....	40
3.2 Density and Percentage Crystallinity.....	48
3.3 Color.....	55
3.4 Residual Acetaldehyde Concentration.....	58

3.5	Residual 2-methyl-1,3-dioxolane Concentration.....	74
3.6	Free Ethylene Glycol Concentration by Automatic Thermal Desorption (ATD) and Gas Chromatography (GC).....	84
3.7	Free Ethylene Glycol Concentration by Nuclear Magnetic Resonance (NMR) Spectroscopy.....	89
3.7.1	Determination of Free Ethylene Glycol Concentration in PET Resins.....	95
3.7.2	Determination of Free Ethylene Glycol with 30/70 (wt/wt) Deuterated Trifluoroacetic Acid/Chloroform Mixture as the Solvent.....	103
3.7.3	Kinetic Study of the Generation and Diffusion of Ethylene Glycol during Solid State Polymerization from Literature.....	105
4.	Conclusion	118
5.	Future Recommendation	122
	References.....	124

List of Tables

Table 3.1	Rate constants for polymerization of poly(ethylene terephthalate) resins A and B at different temperatures of air stripping.....	44
Table 3.2	Activation energy values for polymerization during air stripping and solid state polymerization of PET at temperatures from 160°C – 190°C.....	45
Table 3.3	Change in the lightness value 'L' and degree of yellowness value 'b' for PET resins A and B during air stripping at different temperatures.....	56
Table 3.4	Diffusivities of acetaldehyde in PET without the crystallinity correction during air stripping at different temperatures.....	67
Table 3.5	Diffusivities of acetaldehyde in PET with crystallinity correction at different air stripping temperature.....	72
Table 3.6	Intrinsic viscosity data for the vacuum oven experiment.....	88
Table 3.7	Initial and final ethylene glycol concentrations for air stripped resin B pellets at different temperatures.....	100

Table 3.8	Ethylene glycol concentrations for commercially solid stated resins.....	101
Table 3.9	Ethylene glycol concentrations in amorphous PET resins of different molecular weights.....	102
Table 3.10	Comparison of the concentrations of ethylene glycol in TCE and TFA/chloroform solvents.....	105
Table 3.11	(a) Rate constant values for the polycondensation and esterification reaction in powdered PET and pressed PET chips at different temperatures.....	108
Table 3.11	(b) Rate constant values for the polycondensation and esterification reaction in PET pellets at different temperature.....	109
Table 3.12	Comparison of the diffusivities of ethylene glycol, water and acetaldehyde from literature.....	115

List of Figures

Figure 1.1	Structure of poly(ethylene terephthalate) or PET.....	2
Figure 1.2	Hydrolytic degradation of poly(ethylene terephthalate).....	4
Figure 1.3	Melt phase polymerization of poly(ethylene terephthalate).....	6
Figure 2.1	Schematic diagram of Buhler solid state polymerization reactor.....	14
Figure 2.2	Rheometric Scientific RDA III viscoelastic tester.....	16
Figure 2.3	Density gradient column.....	17
Figure 2.4	Preparation of density gradient column.....	18
Figure 2.5	Calibration of GC column to determine the calibration factor for residual acetaldehyde in PET.....	24
Figure 2.6	Calibration of GC to determine the calibration factor for residual 2MD in PET.....	26
Figure 2.7	Chromatograph showing the peaks for residual acetaldehyde and residual 2-methyl-1,3-dioxolane in a PET sample and their corresponding retention times.....	28
Figure 2.8	Calibration of GC column to determine the calibration factor for free ethylene glycol content in PET.....	31

Figure 3.1	IV as a function of time at different temperatures of air stripping for resin A pellets.....	37
Figure 3.2	IV as a function of time at different temperatures of air stripping for resin B pellets.....	38
Figure 3.3	Polymerization reactions inside the PET pellets during air stripping.....	39
Figure 3.4	Number average molecular weight (M_n) plotted as a function of the square root of time at different temperatures of air stripping for resin A.....	42
Figure 3.5	Number average molecular weight (M_n) plotted as a function of the square root of time at different temperatures of air stripping for resin B.....	43
Figure 3.6	$\ln(k)$ plotted as a function of $1/T$ for resin A.....	46
Figure 3.7	$\ln(k)$ plotted as a function of $1/T$ for resin B.....	47
Figure 3.8	Density plotted as a function of time at different temperatures of air stripping for resin A.....	51
Figure 3.9	Density plotted as a function of time at different temperatures of air stripping for resin B.....	52
Figure 3.10	Percentage crystallinity plotted as a function of time at different temperatures of air stripping for resin A.....	53
Figure 3.11	Percentage crystallinity plotted as a function of time at different temperatures of air stripping for resin B.....	54

Figure 3.12	Change in color of resin B PET pellets (a) before air stripping, (b) after 12 hrs of air stripping at 180°C and (c) after 12 hrs of air stripping at 190°C.....	57
Figure 3.13	Residual acetaldehyde concentrations plotted as a function of time at different temperatures of air stripping for resin A PET pellets.....	61
Figure 3.14	Residual acetaldehyde concentrations plotted as a function of time at different temperatures of air stripping for resin B PET pellets.....	62
Figure 3.15	Length distribution among resin B pellets.....	64
Figure 3.16	Minor diameter distribution among resin B pellets.....	65
Figure 3.17	Major diameter distribution among resin B pellets.....	66
Figure 3.18	A model of a cylindrical pellet.....	67
Figure 3.19	logarithm of diffusion coefficient without crystallinity correction plotted as a function of the inverse of air stripping temperatures.....	70
Figure 3.20	logarithm of diffusion coefficient with crystallinity correction plotted as a function of the inverse of air stripping temperatures.....	72
Figure 3.21	Structure of 2-methyl-1,3-dioxolane and its formation from residual acetaldehyde and free ethylene glycol in poly(ethylene terephthalate).....	75

Figure 3.22	Residual 2MD concentrations plotted as a function of time at different temperatures of air stripping for resin A.....	76
Figure 3.23	Residual 2MD concentrations plotted as a function of time at different temperatures of air stripping for resin B.....	77
Figure 3.24	Change of 2MD concentration with intrinsic viscosity of resin A at different temperatures of air stripping.....	81
Figure 3.25	Change of 2MD concentration with intrinsic viscosity of resin B at different temperatures of air stripping.....	82
Figure 3.26	Representation of the various physical and chemical processes taking place simultaneously inside the cylindrical pellet of PET.....	83
Figure 3.27	Ethylene glycol concentrations plotted as a function of time at different temperatures of air stripping for resin B.....	85
Figure 3.28	NMR spectrum for pure deuterated 1,1,2,2-tetrachloroethane solvent.....	90
Figure 3.29	(a) Structure of ethylene glycol molecule, (b) NMR spectrum for pure deuterated 1,1,2,2-tetrachloroethane and pure ethylene glycol.....	91
Figure 3.30	a) NMR Spectrum for PET in deuterated 1,1,2,2-tetrachloroethane solvent b) Expanded view of the NMR Spectrum for PET in deuterated 1,1,2,2-tetrachloroethane.....	94

Figure 3.31 NMR Spectrum for PET in deuterated 1,1,2,2-tetrachloroethane solvent on addition of pure ethylene glycol.....	95
Figure 3.32 Free ethylene glycol concentrations as a function of air stripping time for PET pellets of resin B at 170°C and 180°C.....	99
Figure 3.33 The two main reactions that occur during solid state polymerization of PET.....	107
Figure 3.34 Diffusion coefficients of ethylene glycol and water for PET at different temperatures, according to Mallon and Ray, Kang, Gao et al. and Ravindranath and Mashelkar.....	113

Chapter 1

Introduction

Poly(ethylene terephthalate) (PET), is extensively used in the form of fibers, bottles, films and in many other applications. Conventionally, the polymerization of this material for use as containers and beverage bottles has been a two step process, during which it is initially prepared in the melt to a low intrinsic viscosity (IV) of 0.5 – 0.6 dl/g and then solid stated to higher IV of 0.8 dl/g or above in the next step ^(8,22). Solid stating has been a key part in preparing higher IV resins of the PET polymer and achieving the desired mechanical, processing and end use properties. Recent advancements in the manufacture of PET show a substitution process or an innovative method, instead of the two-step procedure, by which the PET resin can be prepared to an acceptable IV in the melt phase; thereby excluding the solid state polymerization (SSP) step ⁽³²⁻³⁷⁾. In this new process; however, the residual acetaldehyde concentration at the end of melt phase polymerization is higher than in the case of solid stated resins. In order to reduce this concentration to a tolerable lower value, a stripping process has been employed on the

polymer as an additional step after completion of polymerization in the melt. The stripping process is usually performed with pelletized resin in air environment at temperatures between 150°C – 190°C. It is anticipated that at these temperature other changes and reactions may occur in addition to residual acetaldehyde removal. The objective of this research was; therefore, to study the kinetics of removal of residual acetaldehyde during air stripping and its influences on the physical and chemical properties of the PET polymer.

1.1 Poly(ethylene terephthalate)

Poly (ethylene) terephthalate, commonly abbreviated as PET, polyester, is a well known thermoplastic polymer used in many applications. It is a long chain linear polymer made of ethylene and terephthalate groups. The chemical structure of PET is shown in Figure 1.1. It is made with a polycondensation reaction between ethylene glycol and terephthalic acid, which are derived from petroleum, and has ethylene terephthalate as its repeat unit. PET has a glass transition temperature T_g of 80°C and its melting temperature T_m is around 260°C.

Figure 1.1: Structure of Poly (ethylene) Terephthalate (PET).

1.2 History of Poly(ethylene terephthalate)

The first polyester fiber of PET was invented by the British chemists John R. Whinfield and James T. Dickson along with some other inventors under the trade name “ Terylene” which was patented in 1941. The second polyester fiber was made by DuPont Corporation and was called “ Dacron”. Further advanced research on polyesters led to the creation of various trademarked products of PET like Mylar, Melinex, Teijin, Tetoron, Arnite and others⁽¹⁻⁴⁾.

1.3 Properties of Poly(ethylene terephthalate)

PET can exist either as a glassy amorphous material or a semi crystalline material. Depending on the size of the crystals, the semi crystalline material can be transparent or opaque. It is lightweight, dimensionally stable material and has excellent barrier properties against carbon dioxide and oxygen which enables its use for carbonated soft drinks, mineral water and bottled beverages. Because of its high mechanical properties such as creep resistance and impact strength, it is also used in fabrication processes, tape applications etc. Its ability to be highly oriented under strain further increases its barrier properties, mechanical strength and clarity by inducing the formation of many crystal nuclei. One main advantage of using PET is its recyclability, through which the PET bottles and products are reused to make products again. PET is capable of being molded easily into different shapes and has very good chemical resistance against acids, greases and oils. It also has

excellent electrical and thermal resistance. PET incinerates to carbon dioxide and water on burning which makes it environment friendly ⁽⁵⁻⁸⁾.

1.4 Drying Characteristics of Poly(ethylene terephthalate)

Poly (ethylene terephthalate) is hygroscopic in nature. It absorbs moisture from its surroundings and the amount absorbed depends on the humidity of the environment, temperature and time. Amorphous PET absorbs more moisture compared to the crystalline form of PET at specified conditions. When PET is heated to higher temperatures; the absorbed moisture can react with it resulting in the breakage of the polymer chain, causing a drop in the molecular weight and increase in the number of hydroxyl and carboxyl end groups ^(8, 11-13), which further results in a change in the physical properties of the polymer, as shown in Figure 1.2. This is called hydrolytic degradation.

Figure 1.2: Hydrolytic degradation of Poly (ethylene terephthalate)

It is important; therefore, to dry PET before extrusion, injection molding or any other process which involves heating the resin to elevated temperatures. The drying is done by exposing PET to extremely dry conditions either by applying vacuum or by blowing dry air or nitrogen and heating to high temperatures to accelerate the process. During drying the water molecules diffuse out from the centre of the pellet to the surface and are carried away by the bulk gas flow. Temperature, time and environment play a key role in achieving low moisture content during drying. PET should not be dried too long in air to avoid oxidative degradation especially at temperatures above 150°C which can result in a yellow tint to the resin ^(8,10). For all purposes, the maximum limit for the moisture content in the PET is 50 ppm ^(8,9). It is also important that PET once dried should be properly stored to prevent it from absorbing moisture.

1.5 Preparation of PET in Melt Phase

PET is commercially prepared in the melt phase from purified ethylene glycol (EG) and either terephthalic acid (TPA) or dimethyl terephthalate (DMT) by a two step process ^(8,14-18). Initially ethylene glycol and terephthalic acid or dimethyl terephthalate are reacted to give bis-(2-hydroxyethyl) terephthalate (BHET) by giving out water or methanol as the side product respectively. A catalyst such as acetate of lithium, calcium or magnesium is required when DMT is used. This is called the esterification or transesterification reaction

respectively which takes place at 190-220°C in nitrogen atmosphere. The BHET monomer thus obtained is further treated at temperature of 280°C in the presence of catalyst and high vacuum to obtain PET. Common catalysts used are acetates or oxides of antimony, germanium or lead. The purpose of applying high vacuum during this polycondensation reaction is to drive the reaction forward by removing ethylene glycol side product. The chemistry for the melt phase polymerization of poly (ethylene terephthalate) is shown in Figure 1.3 (8,14,17).

Figure 1.3: Melt phase polymerization of poly (ethylene terephthalate)

1.6 Solid State Polymerization of PET

For some applications of PET such as packaging and high tenacity fiber, high molecular weight is required to obtain the desired properties for the product. It is difficult to prepare PET in the melt phase when the molecular weight is high because the melt viscosity of the polymer increases as the molecular weight increases. One way to prepare high molecular weight PET is to prepare it to a lower IV of 0.4-0.6 dl/g in the melt phase and then solid state polymerize it to a higher IV ^(8,22). Before solid stating, the PET resin prepared in the melt phase is pelletized and precrystallized to avoid sticking of the pellets during SSP. Solid state polymerization is carried out by heating the polymer pellets to a temperature well above the glass transition temperature and below the melting temperature generally of the range 200°C-240°C under vacuum or with an inert gas flow through the resin ^(8,21,22,25). The advantage of using this SSP process to obtain higher molecular weight PET is that it takes place well below the melting point of PET, therefore, there is less degradation of the polymer ^(8,24) and also there is diffusion of the unwanted volatile components such as acetaldehyde, ethylene glycol and water outward from the inside of the pellet to its surface and then into the inert gas stream where they are carried away ^(19-23,25).

1.7 Advancements in PET Manufacturing and its Hurdle

Researchers have tried to find various ways to produce high IV PET while eliminating the solid state polymerization step. Recent developments have shown that PET can be prepared to a high IV in the melt phase ⁽³³⁻³⁶⁾. For example, Lurgi Zimmer developed an integrated process that produces high IV PET in the melt from which the chips are fed to the preform unit directly without the need for solid state polymerization ^(37,38). Sometimes during this later process of preparing high IV PET, it is possible that the polymer can contain high concentrations of undesired components such as acetaldehyde⁽³²⁾ compared to resins prepared using the previous method of preparing PET with the SSP stage. Removing acetaldehyde from the polyesters is of particular interest and importance because acetaldehyde can migrate from the PET bottle wall into the food that is present inside the container. This could affect the taste and odor by bringing a fruity flavor which is not desired ⁽²⁶⁻³²⁾. Acetaldehyde is detectable in low concentrations. A concentration of 10 – 20 ppm can alter the taste of water. It is thus important to remove acetaldehyde from the PET before making beverage bottles or containers out of it.

1.8 Research Objective

One way to achieve low concentrations of acetaldehyde in PET is by air stripping. Stripping is the process of removing volatiles from the poly (ethylene terephthalate) by blowing dry gas through the resin for few hours at high temperatures during which the volatile components diffuse out from the PET pellets or flakes and are carried away in the gas stream. Gases such as dry air, CO₂, N₂ or other inert gases can be used for stripping. Since dry air is used in the current process, it is referred to as air stripping. A United States Patent 7790840 (Crystallizing Conveyor) employed a crystallizing conveyor system that carries pellets from the die cutter to the stripper, during which a hot conveying gas is used at temperatures between 150°C and 200°C to crystallize as well as strip the acetaldehyde from PET pellets. Over the past few years, very little research has been reported on studying the kinetics of air stripping and the accompanied chemical reactions. The objectives of this research are therefore:

1. To study the kinetics of air stripping of removal of residual acetaldehyde from PET at different temperatures and simultaneously monitor the changes in the concentration of other by-products such as 2-methyl-1,3-dioxolane and ethylene glycol during the process.
2. Study the kinetics of PET molecular weight changes resulting from polymerization during the air stripping.

3. Determine the mechanism of 2-methyl-1,3-dioxolane formation by inter-relating changes in its concentration with diffusion of acetaldehyde and production of other by-products.
4. Develop a technique to accurately measure the concentrations of free ethylene glycol in PET.

Chapter 2

Experimental

2.1 Materials

In order to study the kinetics of changes in concentrations of acetaldehyde and other low molecular weight compounds such as 2-methyl-1,3-dioxolane and ethylene glycol in PET during air stripping at different temperatures, two different kinds of PET resins were taken as the starting materials.

Resin A: In the case of resin A, recycled deposit PET flakes provided by Amcor Rigid Plastics, USA, were dried for 48 hours in an air drier and extruded into amorphous cylindrical pellets at the Polymer Institute, using a lab scale twin screw extruder. During extrusion, the melt temperature was maintained at 270°C and the screw speed at 300 rpm. The extruded material at the die is in the amorphous phase and the strands were drawn out of it under cold water to be chopped into pellets.

It was then precrystallized in an air oven at 120°C for one hour to prevent sticking of the PET pellets during air stripping. During this process,

crystallization of the pellet took place from the outside of the pellet to the inside since the temperature is higher at the surface of the pellet than at the inside.

Resin B: This is an underwater cut crystalline resin prepared from recycled PET by Amcor Rigid Plastics Company, USA, using a commercial process. The pellets were made cylindrical by cutting molten polymer from the extruder at the die under warm water. As a result the inside of the pellet has a higher temperature than the outside and the pellets were crystallized with the latent heat from the inside to the outside. This resin was not precrystallized or dried before air stripping but used as provided by Amcor because the pellets were already crystallized.

2.2 Air Stripping of PET Resins

The PET resins A and B were air stripped in a Buhler Solid State Polymerization Reactor. A schematic diagram of the SSP reactor is shown in Figure 2.1. The reactor has an oven or a heating chamber inside of which there is cylindrical stainless steel reactor housing capable of holding 1 kg of the material. The bottom of the reactor has small holes in order that the heated gas can flow through the material from the bottom and be vented out at the top. The gas flow rate and the pressure are controlled by the flow meter and gas pressure manometer respectively. There is an electrical heater to heat the gas entering the reactor. A seal block covers the reactor housing from which three thermocouples are projected downward at different lengths into the reactor housing to track the temperature of the material at the bottom, center and top. A sampler or a suction tube is used to collect sample material from the reactor at any time during the process. The seal block has a ball valve that can be opened to take the material through and is controlled by the electrical control box. This electrical control box also controls the time and temperature of the process. The temperature on the gas temperature display of the electrical control box is the temperature of the material at the centre of the container. The top and bottom temperatures along with the oven temperatures at the top and bottom are monitored by the data acquisition and control software on the computer.

Figure 2.1: Schematic diagram of Buhler Solid State Polymerization Reactor.

Resin A and resin B were each air stripped for 12 hours in the Buhler Solid State Polymerization reactor at temperatures of 160°C, 170°C, 180°C and 190°C. The resins took between 1 hr 30 min to 2 hrs to reach the selected air stripping temperatures and were maintained at those temperatures for 12 hrs. The unsampled material remained in the reactor during air stripping. The air flow rate was maintained at 1500 liters/hr and the pressure at 0.3 bars. The temperatures of the material at the bottom, at the center and at the top were monitored. At fixed time intervals, small quantities of each resin were collected from the reactor for analysis. Portions of each sample were immediately put in the refrigerator at 5°C to prevent the residual acetaldehyde from escaping as it boils at 21°C. A separate portion was used

immediately to measure its melt viscosity in order to monitor any changes in molecular weight.

2.3 Rheology Measurements

The melt viscosity of the air stripped PET samples was measured using the Rheometric Scientific RDA III viscoelastic tester with parallel plate geometry as shown in Figure 2.2. It has two circular parallel plates of 25mm diameter in an oven compartment. The bottom plate is movable while the top plate is fixed. The top plate can only move vertically to maintain the desired distance between the plates. The sample whose IV is to be determined is placed between the plates and torque is applied by the bottom plate at varying frequency. The instrument was previously calibrated by measuring the melt complex viscosity η for pure PET samples of known Intrinsic Viscosity. A linear equation was obtained as shown in equation (2.1).

$$IV = m (\eta) + b \quad (2.1)$$

‘m’ and ‘b’ are constants whose values are 0.14616 and -0.18562 respectively.

For the melt viscosity determinations, each of the resin sample collected from the reactor during air stripping was placed between the parallel plates after heating them to 280°C. The experiment was done by maintaining 1 mm distance between the plates and by applying torque at varying frequency or shear rate from 1 rad/sec to 100 rad/sec. A nitrogen purge was used during the experiment to prevent degradation of the polymer in the melt. A plot of torque frequency as a function of melt viscosity was monitored on the computer. Under these conditions, the PET polymer in the melt phase follows

the Newtonian behavior up to 10 rad/sec frequency i.e. the melt viscosity remains constant with increased torque frequency and the value at 10 rad/sec frequency was taken as the melt viscosity. The IV of the sample was calculated from the melt viscosity thus obtained from the experiment. The sample should be devoid of moisture before doing the experiment to prevent hydrolytic degradation. In order to measure the initial IV, resin A and resin B were dried in a vacuum oven at 130°C and 30 mm of mercury pressure overnight to ensure that the moisture content was low. The air stripped samples were dried by the conditions of air stripping in the reactor and were not further dried before the IV measurement.

Figure 2.2: Rheometric Scientific RDA III viscoelastic tester.

2.4 Density Measurements

The densities of the PET pellets were measured using a density gradient column as shown in Figure 2.3. The column is made of an aqueous calcium nitrate tetra hydrate solution and the temperature of the column is maintained at 25°C by circulating water around the column. The density of the solution in the column varies increasing from top to bottom. It has colored glass beads of standard density in the range of study floating at heights where their density matches that of the surrounding liquid in the column.

Figure 2.3: Density Gradient Column

To establish the gradient density column, the procedure by ASTM Designation: 1505, Standard test methods for density, was followed in which a high dense liquid solution (D) and a low dense liquid solution (L) are connected to each other as shown in Figure 2.4. A tube extends from L to the bottom of the column. As the liquid from L was deposited to the bottom of the column, equal amount of solution from D was drawn into L making the solution in L denser with time. In this manner as the solution from L goes to the bottom of the column, it settles below the previously present less dense solution. In this manner, the gradient density column was established.

Figure 2.4: Preparation of density gradient column.

The column was calibrated every time before doing the experiment by measuring the heights of the standard beads using the cathetometer and plotting their heights against their corresponding densities which gives a line. Therefore, to determine the density of the resin A and resin B samples collected during air stripping at different temperatures, pellets were coated with less dense solution of calcium nitrate tetra hydrate to prevent sticking of the air bubbles and were placed in the gradient column. The samples take some time to settle. They were allowed to come to an equilibrium height in 60 minutes and their heights were measured using the cathetometer. Their density was calculated either from the calibration chart directly or by the interpolation formula given by equation 2.2. Measurements were done in triplicate to ensure accuracy.

$$\text{Density at height } x = a + \frac{(x-y)*(b-a)}{(z-y)} \quad (2.2)$$

Where a, b are the densities of the two standard floats between which the unknown sample lies in the column and x, y, z are the heights of unknown and the two floats a and b respectively.

2.5 Percentage Crystallinity Measurements

Density is a convenient measure of the degree of crystallinity defined by equation 2.3. The crystallinity level attained during air stripping of resin A and resin B was determined by calculating the percentage crystallinity.

Volume fraction of crystallinity or the volume degree of crystallinity ⁽³⁹⁻⁴⁴⁾ of a PET sample is given by,

$$x_c = \frac{\rho_a - \rho_s}{\rho_a - \rho_c} \quad (2.3)$$

Where ρ_s = density of the sample

ρ_a = density of the amorphous phase (1.333 g/cc).

ρ_c = density of the crystalline phase (1.455 g/cc).

Percentage crystallinity = $x_c * 100$.

2.6 Color Measurements

Color measurements were done on air stripped PET pellets with the Hunter lab Digital Color and color difference meter. It has an optical unit and a measurement unit. The optical unit is responsible for analyzing the sample while the measuring unit converts the signal from the optical unit and is displayed as color specifications on the digital readout display panel. The PET pellets were poured in the cylindrical cell and it was placed on the reference standard of the optical unit. The instrument analyzed the PET pellets at room temperature to give L and b values by which we could measure the lightness and yellowness respectively.

L = measures lightness and varies from 100, for perfect white, to 0, for black; approximately as the eye would evaluate it.

b = measures yellowness when positive, gray when 0, and blueness when negative.

2.7 Chemical Analysis

2.7.1 Determination of Residual Acetaldehyde and 2-methyl-1,3-dioxolane concentrations in PET

A Perkin-Elmer TurboMatrix 40 Headspace Sampler and a Perkin-Elmer AutoSystem XL Gas Chromatograph (GC) were used to determine the residual acetaldehyde and residual 2-methyl-1,3-dioxolane concentrations present in the PET samples. The gas chromatograph contains a Stabilwax ®-DA column which is 30 meter in length with a 0.32 mm Inner Diameter (ID). The detector is a flame ionization detector (FID) with helium as the carrier gas. Air and hydrogen gases were used for combustion.

The Perkin-Elmer TurboMatrix 40 Headspace Sampler (HS-40) is an automatic sampler for headspace analysis. Headspace is the gas space in the chromatography vial above the sample. Headspace analysis is therefore the analysis of the components present in that gas. The HS-40 has a magazine capable of holding 40 vials or samples and an oven compartment where the sample was heated to the specified temperature for specified time. The volatiles collected in the headspace were then injected through a transfer line to the column of the GC for analysis.

The GC column was calibrated for acetaldehyde and 2-methyl-1,3-dioxolane before conducting the headspace experiments on PET samples to calculate the concentration of components in PET. For this purpose, a calibration

experiment was performed to determine the calibration factor for acetaldehyde, making use of 1 mg/1ml in water of acetaldehyde from AccuStandard Inc. About 2, 4, 6, 8 and 10 μ l of this solution was injected into each vial, sealed with a rubber septum and was placed in the TurboMatrix 40 Headspace Sampler magazine. Headspace analysis was done by heating the sample for 1 hr in the oven at 150°C and with the column temperature at 120°C. The column temperature was chosen as 120°C though acetaldehyde boils at around 21°C to facilitate measuring the residual acetaldehyde concentration simultaneously with the measurement of residual 2-methyl-1,3-dioxolane concentration for which the column temperature has to be 120°C. As presented in Figure 2.5, the calibration factor (microvolt*sec/micrograms) was determined by finding the slope of the line plotted between the concentration of acetaldehyde (micrograms) taken and the instrument response (microvolt*sec) which is the area under the peak for acetaldehyde in the chromatograph.

Calculation of acetaldehyde concentration for calibration:

Acetaldehyde solution concentration = 1mg/1ml

Volume of acetaldehyde solution taken = 2 μ l

Mass of acetaldehyde = (2 μ l) * (1 mg)/1 ml = 2 μ g.

Figure 2.5: Calibration of GC column to find the calibration factor for residual acetaldehyde in PET.

Similarly to calibrate the column for 2MD, 98% 2-methyl-1,3-dioxolane from Acros Organics is taken and diluted with water to a concentration of 0.001 ppm. Then 2, 4, 6, 8 and 10 μ l of the solution was injected into each vial and the headspace analysis was done with 120°C as the column temperature such that the temperature was atleast 40°C above the boiling point of 2MD which

is 82°C. As shown in Figure 2.6, the calibration factor (microvolt*sec/micrograms) was determined by finding the slope of the line plotted between concentration of 2MD (micrograms) and the instrument response (microvolt*sec).

Calculation of 2MD concentration for calibration:

The density of 98% pure 2MD solution is 0.99 g/ml.

Mass = (Volume) * (density)

$$= (2 \mu\text{l}) * (0.99 \text{ g/ml}) = 2 * 0.99 * 10^{-3} \text{ g.}$$

But it is 98% pure and was diluted 1000 times. So,

Mass of 2MD in 2 μl solution = $(2 * 0.99 * 10^{-3} \text{ g}) * (0.98) / (10^3)$

$$= 1.9404 * 10^{-6} \text{ g} = 1.9404 \mu\text{g.}$$

Figure 2.6: Calibration of GC column to find the calibration factor for residual 2MD in PET.

To determine the concentrations of residual acetaldehyde and residual 2MD in the air stripped PET samples, the samples collected during air stripping of PET resins A and B were ground to fine powder in the presence of liquid nitrogen. This was done to enhance the diffusion rate of acetaldehyde and

2MD from the PET samples during headspace analysis. A small quantity of powdered PET in the range of 0.4 – 0.5 grams was put into a glass vial, sealed with a rubber septum and was placed in the TurboMatrix 40 Headspace Sampler magazine. The experiment was started with settings listed below and the chromatograph was obtained on the computer. A chromatograph showing peaks for residual acetaldehyde and residual 2-methyl-1,3-dioxolane in poly (ethylene terephthalate) is presented in Figure 2.7 along with their retention times. The retention time is the time taken by a component to travel through the gas chromatography column. The areas under the peaks for acetaldehyde and 2-methyl-1,3-dioxolane at retention times in the range of 2.096 – 2.199 and 2.528 – 2.779 minutes respectively were measured as the instrument response and their size depends on the amount of sample taken. Measurements were done in triplicate to ensure accuracy and the concentration of the residual 2MD or residual acetaldehyde in the PET sample is calculated using equation 2.4. Thus, a method to determine the residual 2-methyl-1,3-dioxolane concentration simultaneously with the residual acetaldehyde concentration in PET has been developed using headspace analysis and gas chromatography

Oven temperature = 150°C.

Time of heating in the oven = 60 min.

Column temperature = 120°C.

Calculation of the concentration of a component in the PET samples:

Concentration of a component in PET =

$$\frac{\text{Instrument response for PET sample}(\text{microvolt} \cdot \text{sec})}{\text{Weight of PET sample}(\text{g}) * \text{Calibration Factor}(\text{microvolt} \cdot \frac{\text{sec}}{\text{microgram}})}, \frac{\mu\text{g}}{\text{g}} \text{ or ppm} \quad (2.4)$$

Figure 2.7: Chromatograph showing the peaks for acetaldehyde and residual 2-methyl-1,3-dioxolane and their corresponding retention times in a PET sample.

2.7.2 Determination of Free Ethylene Glycol content in PET using thermal desorption and gas chromatography

A Perkin–Elmer Automatic Thermal Desorption System (ATD 400) and a Perkin–Elmer AutoSystem XL Gas Chromatograph have been used to determine the amount of ethylene glycol volatilized from ground PET samples at 220°C. Nitrogen gas is used to control the pneumatics of ATD 400. Thermal desorption is a technique that extracts volatile components from a non-volatile matrix by heating the sample or the matrix in an inert atmosphere. The ATD 400 has a carousel on which 50 samples can be loaded. Once the experiment is started, one sample at a time is taken inside the ATD 400, uncapped and a leak test was performed to ensure that the tube is sealed properly. It was purged with helium, the carrier gas, for some time at room temperature to remove oxygen. The sample was then heated to the selected temperature during which the volatiles from the sample are desorbed into the gas stream and sent to the cold trap. The cold trap was a straight packed tube that can be cooled electrically from -30°C to 300°C and is used to concentrate the volatiles before they are transferred through a heated line to the gas chromatographic column for analysis.

Prior to doing any experiment, the column was calibrated for free ethylene glycol. For this purpose, 5 ml of water and 100 µl of 99.9% pure ethylene glycol from EDC Industries Inc. are mixed to give a 50 times diluted solution of EG. Small quantities such as 0.2, 0.5 and 1.0 µl of the solution are placed

in a Teflon tube bounded by glass wool on both ends, placed in a metal tube of 90 mm length and 6.35 mm outer diameter and capped. The metal tube was placed on the carousel and the thermal desorption experiment was done with the settings listed below. As shown in Figure 2.8, the calibration factor (microvolt*sec/microgram) is determined by finding the slope of the line plotted between concentration of EG (microgram) taken and the instrument response (microvolt*sec) which is the area under the peak for EG in the chromatograph.

Oven temperature = 220°C.

Purge time = 1 min.

Desorption = 10 min.

Trap low temperature = -30°C.

Trap high temperature = 300°C.

Trap hold = 5 min.

Line temperature = 145°C.

GC column temperature = 230°C.

Calculation of ethylene glycol concentration for calibration:

The density of 99.9% pure ethylene glycol is 1.1132 g/ml.

Mass = (Volume) * (density)

$$= (0.2 \text{ }\mu\text{l}) * (1.1132 \text{ g/ml}) = 0.2 * 1.1132 * 10^{-3} \text{ g.}$$

But it is 99.9% pure and diluted 50 times. So,

$$\text{Mass of EG in } 0.2 \text{ }\mu\text{l solution} = (0.2 * 1.1132 * 10^{-3} * 0.999) / 50$$

$$= 4.44 * 10^{-6} = 4.44 \text{ }\mu\text{g.}$$

Figure 2.8: Calibration of GC column to find the calibration factor for free ethylene glycol in PET.

In order to determine the free ethylene glycol content in air stripped PET samples, a small quantity of the powdered PET of 0.05 – 0.07 g is taken in the Teflon tube, bounded by cotton wool and placed in the metal tube. The settings for the experiment are the same as those used for calibrating the GC column. The chromatograph is obtained on the computer to determine the concentrations of the ethylene glycol, by measuring the area under the peak at retention time of 3.10 – 3.28 minutes. Measurements are done in triplicate for accuracy and the concentration of the free ethylene glycol in the PET sample is calculated according to equation 2.4.

2.7.3 Determination of free Ethylene Glycol Concentration in PET using Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance is a phenomenon that is observed when nuclei of certain atoms, which possess the spinning property, are immersed in a static magnetic field of particular frequency. NMR spectroscopy uses this phenomenon to study the chemical, physical and biological properties of matter. A high resolution INOVA- 600 MHz spectrometer manufactured by Varian Association Inc. was used to evaluate the concentration of free ethylene glycol in PET by Proton NMR (^1H NMR) analysis. The solvent used to dissolve the samples of PET is deuterated 1, 1, 2, 2-tetrachloroethane (TCE), (D-99.6%) purchased from Cambridge Isotope Laboratories Inc., USA and has a boiling point of 147°C.

The PET samples for ^1H NMR analysis is prepared by dissolving 10-12 mg of PET in the deuterated TCE solvent in a small glass vial at 140°C , which is below the boiling point of the solvent. The sample is maintained at this temperature for approximately 45 - 60 minutes until the entire PET sample is dissolved and a clear solution is obtained. The solution is transferred to the NMR tube and cooled before the experimental analysis. The experimental settings for ^1H NMR analysis of PET samples on the INOVA-600 MHz spectrometer are as shown below.

Solvent	=	CD_2Cl_2
Recycle delay	=	8 sec
Transients	=	100
Linear Prediction Parameters	=	4,3,3 or 5,4,4
Gaussian Parameter	=	0.4

Another solvent used for analysis of ethylene glycol concentration by ^1H NMR is 30/70 (wt/wt) deuterated trifluoroacetic acid/ chloroform mixture. Deuterated trifluoroacetic acid (D, 99.5%) and deuterated chloroform (D, 99.8%) were purchased from Cambridge Isotope Laboratories Inc., USA. The PET sample for ^1H NMR analysis is prepared by adding a small amount of PET material to the deuterated TFA/chloroform mixture in the NMR tube. Trifluoroacetic acid is an aggressive solvent and dissolves the PET material

in 30 – 45 minutes at room temperature if the material is taken in powdered form. It takes a longer time if the PET is taken in the form of pellets, depending on the size of the pellet. The experimental settings during ^1H NMR analysis used in the case of 30/70 deuterated TFA/chloroform solvent are as follows.

Solvent	=	CDCl_3
Recycle delay	=	8 sec
Transients	=	100
Linear Prediction Parameters	=	4,3,3 or 5,4,4
Gaussian Parameter	=	0.4

Chapter 3

Results and Discussion

3.1 Intrinsic Viscosity and Molecular Weight

In order to study the kinetics of acetaldehyde removal by air stripping, the A and B PET resins were air stripped in the Buhler Solid State Polymerization reactor for 12 hours at four different temperatures - 160°C, 170°C, 180°C and 190°C. The material was kept undisturbed in the reactor during this period. Though these temperatures are below the solid stating temperatures, while air stripping PET, it was anticipated that polymerization reactions could take place thereby increasing the molecular weight of PET. In order to determine the change in molecular weight with time of air stripping at any temperature, sample pellets of these resins were collected at regular intervals of time and their corresponding intrinsic viscosity was immediately measured by the Rheometric Scientific RDA III viscoelastic tester.

The initial intrinsic viscosity (IV) was measured as 0.65 dl/g for resin A which corresponds to a number average molecular weight of 20,809 g/mol and 0.78 dl/g for resin B with a corresponding number average molecular weight of

27,462 g/mol. As expected, the IV was observed to be increasing with time and the higher the air stripping temperature, the higher was the final IV attained after 12 hours. The changes in IV for resin A and resin B with time and temperature are shown in Figures 3.1 and 3.2 respectively. For resin A and B, at 160°C, there is very little change in the IV, but at 170°C, 180°C and 190°C, there are significant changes in IV. The final IV level attained after 12 hours for each resin at any temperature depends on the initial IV level as can be seen from Figures 3.1 and 3.2.

The molecular weight of the polymer increases by the chemical reactions that take place inside the pellets as shown in Figure 3.3. In addition to these reactions, there is diffusion of the reaction products and other less volatile components from the pellet during the air stripping process ^(8,22,45-47). The main reactions responsible for the increase in molecular weight are the polycondensation and the esterification reactions, since the carboxyl and hydroxyl end group concentrations are usually much higher compared to the vinyl ester end group concentrations in PET. The vinyl end group reaction depends on the number of vinyl ester end groups present in the polymer. Since it is established that the polymer molecular weight increases during air stripping, the rate at which the polymerization reactions take place and the activation energy can be determined from the intrinsic viscosity data with time at different temperatures.

Figure 3.1: IV plotted as a function of time at different temperatures of air stripping for Resin A pellets.

**zero time value is the IV value before the beginning of the air stripping process*

Figure 3.2: IV plotted as a function of time at different temperatures of air stripping for Resin B pellets.

**zero time value is the IV value before the beginning of the air stripping process*

a. Polycondensation reaction

b. Esterification reaction

c. Vinyl Ester end group reaction

Figure 3.3: Polymerization reactions inside the PET pellets during air stripping.

3.1.1 Calculation of Rate Constants for Polymerization during Air Stripping

The intrinsic viscosity of the polymer is related to the weight average molecular weight M_w by the Mark Houwink equation given by equation 3.1

$$IV = [\eta] = k M_w^a \quad (3.1)$$

'k' and 'a' are constants which had been determined by Gel Permeation Chromatography as 4.68×10^{-4} and 0.68 in (60/40) phenol/ tetrachloro ethane at 25°C ⁽⁴⁸⁻⁵⁰⁾. They depend on the nature of the polymer, solvent and on the temperature. The IV can be related to M_w by equation 3.2.

$$IV = 4.68 \times 10^{-4} \times M_w^{0.68} \quad (3.2)$$

For PET, $M_w = 2M_n$.

Therefore, IV in terms of M_n is given by equation 3.3.

$$IV = 7.5 \times 10^{-4} \times M_n^{0.68} \quad (3.3)$$

The number average molecular weight of PET at any time during air stripping can be given by the empirical relationship ^(51,52) shown in equation 3.4.

$$M_n = M_{no} + k^*(t)^{0.5} \quad (3.4)$$

Where k = equilibrium rate constant.

M_{no} = Initial number average molecular weight of the polymer.

M_n = number average molecular weight of the polymer at time t.

In order to determine the rate constants for polymerization, number average molecular weight was plotted against the square root of time for resin A and resin B as shown in Figures 3.4 and 3.5 respectively. The plot is a straight line whose intercept gives the initial number average molecular weight and the slope gives the rate constant. The higher slope at 190°C indicates higher rate of polymerization inside the PET pellets. The rate constants for air stripping resins A and B at different temperatures are compared in Table 3.1.

Figure 3.4: M_n plotted as a function of the square root of time at different temperatures of air stripping for resin A.

Figure 3.5: M_n plotted as a function of the square root of time at different temperatures of air stripping for resin B.

Table 3.1: Rate constants for polymerization of poly (ethylene terephthalate) resins A and B at different temperatures of air stripping

Temperature (°C)	Resin A (g/mol/min^{0.5})	Resin B (g/mol/min^{0.5})
160	33	47
170	68	73
180	112	92
190	152	143

The rate constants are a function of temperature and can be expressed by the Arrhenius Equation as

$$k = A e^{-E_a/RT}$$

where k = Rate Constant for polymerization during air stripping,

E_a = Activation Energy required for the polymerization to take place,

T = Polymerization temperature,

A = Pre exponential factor,

R = Universal gas constant, 8.314 kJ/mol °K.

By taking the natural logarithms on either side of the Arrhenius equation and plotting $\ln(k)$ vs. $1/T$ for resin A and resin B as shown in Figures 3.6 and 3.7 respectively, the activation energy for the polymerization of PET during air stripping of each resin is determined from the slope of the linear line obtained.

$$\ln(k) = \ln A - E_a/R(1/T)$$

The activation energy values obtained for resins A and B are compared to the solid stating activation energies from literature at these temperatures in Table 3.2. Though direct comparison of the rate constants might not be quite reliable because of the dependence of the rate constants on different reaction schemes considered and the amount of catalysts present in the prepolymer initially ⁽⁵³⁾, comparable values were obtained for the activation energy during air stripping and solid stating for a polymer resin of IV 0.65.

Table 3.2: Activation Energy for polymerization during air stripping and solid stating PET at temperatures from 160°C – 190°C

PET resins	Activation Energy during air stripping (160°C – 190°C)	Activation Energy during Solid Stating (160°C – 190°C)
Resin A (IV = 0.65)	20.2 kcal/mol	
Resin B (IV = 0.78)	14.1 kcal/mol	
IV = 0.64		19 Kcal/mol ⁽²²⁾

Figure 3.6: $\ln(k)$ plotted as a function of $1/T$ for resin A

Figure 3.7: $\ln(k)$ plotted as a function of $1/T$ for resin B

3.2 Density and Percentage Crystallinity

Another physical phenomenon which was expected to take place during air stripping is the change in crystallinity levels of the polymer over time at the temperatures of air stripping. The crystallinity level of a polymer can be measured from the density changes during air stripping by equation 2.3. The densities of resin A and resin B pellets, collected at different times during air stripping at different temperatures, were determined with a gradient density column. The calibration was done every time the density column was used and the values were obtained by the interpolation formula given in equation 2.2.

The initial density of resin A was found to be 1.339 g/cc. After pre-crystallization in an air oven at 120°C for an hour, the density increased to approximately 1.373 g/cc. Resin B had a starting density of 1.366 g/cc. The densities of resins A and B increased with increasing time of air stripping after few hours as shown in Figures 3.8 and 3.9 respectively. The increase in density is higher with increased temperature of air stripping. It is evident that the density increases drastically initially and reaches a plateau after a certain time.

The morphology of a polymer determines its properties. The physical, chemical and mechanical properties of the amorphous and the crystalline phases of the polymer are different. Depending on the relative amounts of the

phases the bulk properties of the polymer can vary, particularly the mechanical properties. The degree of crystallinity is zero for completely amorphous polymer and one for theoretically 100% crystalline polymer. The level of crystallinity also determines the optical properties because amorphous phase is transparent and semi crystalline polymer can be translucent or opaque depending on whether they have low or high crystallinity level respectively and also on the size of the crystals. The process of crystallization takes place at the cost of amorphous (non crystalline) material present in the polymer where the disordered polymer chains fold back and forth between two parallel planes to eventually form a thin platelet called lamellae and which further contributes to the formation of crystallites under suitable conditions of temperature and time. These crystallites aggregate into bigger molecular structures called spherulites, which are responsible for the crystalline nature of the polymer as well as the other properties of the polymer ⁽⁵⁴⁻⁵⁸⁾.

The increase in density for resin A and resin B with time, at different temperatures of air stripping, implies that the amount of crystalline material that has higher density than the amorphous material in the pellets was increasing, thereby increasing the overall density of the material. The percentage crystallinity level calculated from the corresponding density by equation 2.3 show an increase with time of air stripping at different temperatures for resin A and resin B as shown in Figures 3.10 and 3.11

respectively. The initial level of crystallinity for resin A is calculated as 5% which corresponds to 1.339 g/cc density and after pre-crystallization in the air oven for one hour, it increased to 33%. During pre-crystallization, the crystallization of each pellet takes place from outside to the inside, since the temperature of the outer surface increases first, gradually increasing the temperature at the inside of the pellet. With air stripping, the crystallinity level increases over a period of time and reaches a plateau. Resin B is more crystalline on the inside than on the outside of the pellet and has a starting crystallinity level at 27.6% from where it increases with time during air stripping. The final level of crystallinity attained after 12 hours, increases with increase of air stripping temperature for both resins A and B.

Figure 3.8: Density plotted as a function of time at different temperatures of air stripping for resin A.

Figure 3.9: Density plotted as a function of time at different temperatures of air stripping for Resin B.

Figure 3.10: Percentage Crystallinity plotted as a function of time at different temperatures of air stripping for Resin A

Figure 3.11: Percentage Crystallinity plotted as a function of time at different temperatures of air stripping for Resin B.

3.3 Color

During air stripping of the PET resins at different temperatures, particularly at 180°C and 190°C, it was observed that the pellets turned yellow by the end of 12 hours in the reactor. This implies that oxidative degradation had taken place at these temperatures, which were above 150°C, as the gas used for air stripping is air and contains oxygen. It is important to study the color changes in PET during this process because the color of the product is of significant importance to ensure customer satisfaction and cost reduction. The color, whiteness or yellowness of plastic pellets is measured before they are molded into preform or the final product. Therefore, the two PET resins A and B which were air stripped at different temperatures have been analyzed to determine their color by making use of the Hunter Lab Digital Color and Color Difference Meter.

The lightness value L and yellowness index b were measured for pellets of resin B at 6 hours and 12 hours of air stripping and at 12 hours for resin A which are compared in Table 3.3. The lightness values increased with temperature at any time during air stripping for resin A and resin B. The yellowness values also increased with temperature at any time during air stripping which indicates that the pellets turned more yellow at higher temperature of air stripping for resin A and resin B. It was also observed from the 'b' values of resin B at 6 hours and 12 hours that the longer the time of air stripping at a particular temperature the yellower the pellets turned.

The noticeable difference in color of resin B pellets before air stripping and after air stripping at 180°C and 190°C is shown in Figure 3.12.

Table 3.3: Change in lightness value 'L' and degree of yellowness value 'b' for PET resins A and B during air stripping at different temperatures

Air stripping temperature	Resin B ; IV = 0.78				Resin A ; IV = 0.65	
	6 hrs		12 hrs		12 hrs	
	L	b	L	b	L	b
160 C	61.0	0.3	61.7	0.7	61.5	2.5
170 C	68.1	0.7	68.7	1.5	62.3	2.7
180 C	68.8	1.4	69	3.0	63.5	3.5
190 C	68.9	3.1	68.2	5.3	64.5	5.0

This color change is due to the formation of ethyne compound during oxidative degradation of PET at temperatures above 150°C. The oxygen present in dry air that is used for air stripping PET can react with vinyl ester end groups in PET by a free radical mechanism to form ethyne gas which cause the pellets to turn yellow ^(59,60).

The inside of the pellets of resin A and resin B after air stripping for 12 hours at 190°C also show a change in color distinguishable by the naked eye when the pellets are cut through their centers. This indicates that the oxygen that is present in air is responsible for color change diffused into the pellets

during air stripping, causing oxidative degradation throughout the pellet. It should be noted that the surface of the pellet is yellower compared to the inside of the pellet as the surface was exposed to abundant oxygen from the flowing air, whereas the inside was exposed only to the diffused amount of oxygen.

Figure 3.12: Change in color of resin B PET pellets a) before air stripping (left), b) after 12 hours of air stripping at 180°C (center), c) after 12 hours of air stripping at 190°C (right).

3.4 Residual Acetaldehyde Concentration

The major objective of this research has been to study the changes in the residual acetaldehyde concentration during air stripping at different temperatures. The residual acetaldehyde (AA) is the amount of acetaldehyde that is present in PET. In order to determine this concentration in PET, samples were collected at regular intervals of time during air stripping. These collected pellets were ground in the presence of liquid nitrogen and were maintained at 5°C in a refrigerator to prevent volatilization of acetaldehyde. As previously discussed, the powdered form of these samples was then analyzed for its residual acetaldehyde concentration using headspace analysis on a Perkin-Elmer TurboMatrix 40 Headspace Sampler at 150°C for 60 minutes and a Perkin-Elmer AutoSystem XL Gas Chromatograph (GC) at 120°C. Along with the residual acetaldehyde concentration, residual 2-methyl-1,3-dioxolane concentration were measured simultaneously. A chromatograph showing peaks for residual acetaldehyde and residual 2-methyl-1,3-dioxolane in poly (ethylene terephthalate) is presented in Figure 2.7 along with their retention times. The retention time is different for different compounds and is based on the polarity and molecular weight of the compound. The areas for the acetaldehyde peak in the chromatographs thus obtained for different samples of each PET resin were converted to concentrations and plotted against time at different temperatures of air stripping. Figures 3.13 and 3.14 demonstrates the

changes in concentration of the residual acetaldehyde during 12 hours of air stripping at different temperature for resin A and resin B respectively.

It has been observed that both the resins show similar behavior as the concentration decreases over time during air stripping at any temperature. Resin A has an average initial residual acetaldehyde concentration of 6.2 ppm. After pre-crystallization for an hour in an air oven, it drops to an average value of 5.8 ppm which infers that acetaldehyde molecules have diffused out during this process at 120°C which is much higher than its boiling point. Moreover, the diffusion of acetaldehyde is faster at low levels of crystallinity. For the resins in the reactor to reach the required air stripping temperatures, it takes between 1.5 hrs to 2 hours. Even during this period, there is diffusion of acetaldehyde and therefore by the time it reached the air stripping temperatures, the concentration of the residual acetaldehyde had decreased. This is represented as the zero time concentration in Figures 3.13 and 3.14. The higher the air stripping temperature, the greater is the time taken to reach that temperature and therefore, lower is the residual acetaldehyde concentration at zero time. From the zero time concentrations; the acetaldehyde concentration decreases gradually with time of air stripping at any temperature. It is observed that the higher the temperature during stripping, the higher is the rate at which the concentration decreases in the initial stages of air stripping as the curve becomes steeper with increase in temperature. The concentration reaches a low value of 0.7 ppm on an average

and remains unchanged over time at each temperature. Resin B has an initial residual acetaldehyde concentration of 4 ppm and it decreases to a lower level by the time it reaches the air stripping temperatures as in the case of resin A. From this zero time concentration, it gradually decreases with continued air stripping at any temperature. A trend similar to that of resin A is followed and the concentration reaches to a final value of 0.5 ppm on an average after 12 hours of air stripping at any temperature.

As the polymerization reaction takes place during air stripping by the various reactions inside the PET pellet as shown in Figure 3.3, the vinyl ester end group reaction is responsible for the formation of acetaldehyde. This free acetaldehyde diffuses through the pellet to the surface of the pellet, crosses the boundary layer and then diffuses into the air stream to be carried away. At any time inside the pellet, there is generation and diffusion of acetaldehyde taking place. At low temperatures, it is diffusion controlled and at high temperatures, it is reaction controlled ⁽⁵³⁾. After a certain time, the generation and the diffusion of acetaldehyde come to equilibrium at any temperature as the end group concentration decreases. This means that the rate of the reaction will be the same as the rate of diffusion of acetaldehyde from inside the PET pellet. The concentration of the residual acetaldehyde therefore, remains unchanged with further time of air stripping at that temperature.

Figure 3.13: Residual AA Concentration plotted as a function of time at different temperatures of air stripping for Resin A PET pellets.

**zero time is the time when the resin reached the air stripping temperature.*

Figure 3.14: Residual AA concentration plotted as a function of time at different temperatures of air stripping for Resin B PET pellets.

**zero time is the time when the resin reached the air stripping temperature.*

Having determined the concentration change of residual acetaldehyde with time and temperature during air stripping for resins A and B, the diffusivity of residual acetaldehyde and the activation energy for diffusion can be determined from the concentration data. According to Fick's second law, the diffusion of a component whose concentration 'c' changes with time 't' along the radius 'r', length 'z' and in the angular direction 'θ' about the length is given by equation 3.5⁽⁵⁹⁾. It is a second order partial differential equation in a cylindrical co-ordinate system. Diffusivity 'D' is assumed to be independent of concentration and is a constant.

$$\frac{\partial C}{\partial t} = \frac{D}{r} \left(\frac{\partial}{\partial r} \frac{\partial C}{\partial r} + \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial C}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(r \frac{\partial C}{\partial z} \right) \right) \quad (3.5)$$

To determine the diffusion coefficient or the diffusivity of acetaldehyde, the dimensions of 20 pellets each of resins A and B were measured. Their lengths were measured and because the pellets are somewhat compressed to give an elliptical cross-sectional area, the minor and the major diameters were measured with a vernier calipers. The length and radii distributions among the resin B pellets are shown in Figures 3.15 - 3.17. The range of distribution is not large, therefore, the average dimensions were considered for calculations. The geometric mean of the average major diameter and minor average diameter was taken as the average diameter of the cross section of the pellet.

Figure 3.15: Length distribution among resin B pellets

Figure 3.16: Minor diameter distribution among resin B pellets.

Figure 3.17: Major diameter distribution among resin B pellets.

A model of a cylindrical pellet is presented in Figure 3.18.

Average length of the resin A pellet = 2.68 mm.

Average radius of the resin A pellet = 1.14 mm.

Average length of the resin B pellet = 2.74 mm.

Average radius of the resin B pellet = 1.517 mm.

Equation 3.5 can be reduced to equation 3.6 assuming that the concentration does not vary in the angular direction, 'θ',

$$\frac{1}{D} \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2} \quad (3.6)$$

c = Concentration of acetaldehyde at time t

r = Radius of the pellet

z = Half length of the pellet

D = Diffusivity of acetaldehyde at temperature T .

The differential equation 3.6 is solved by using the separation of variables technique and by using the following conditions.

- (1) Initial condition: $t = 0$; $C = C_0$; the initial concentration of acetaldehyde in the PET pellet.

(2) Boundary conditions:

(a) $r = a$; $C = \text{Constant}$;

(b) $z = +L$ or $-L$; $C = \text{Constant}$

(3) At the centre:

(a) $\left(\frac{\partial C}{\partial r}\right)_{r=0} = 0$; the change in concentration at the centre is zero.

(b) $\left(\frac{\partial C}{\partial z}\right)_{z=0} = 0$; the change in concentration at the centre is zero.

The final solution is of the form given in equation 3.7 as below. ⁽⁶¹⁾

$$C = 1 - \frac{8}{\pi a} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^n J_0(r\alpha_m)}{(2n+1)\alpha_m J_1(a\alpha_m)} \cos \frac{(2n+1)\pi x}{2l} e^{-kt(\alpha_m^2 + (2n+1)^2 \pi^2 / 4l^2)} \quad (3.7)$$

By using the acetaldehyde concentration data at different times, the average radius and length of the pellets, numerical simulations were performed with the help of a computer program developed by Dr. Michael Cameron, of the Polymer Institute at the University of Toledo, to determine the diffusivities of acetaldehyde at different temperatures of air stripping which are tabulated in Table 3.4.

The diffusivity values for Resin A and B were a function of temperature and increase with the air stripping temperature. The diffusivity value in the case of Resin A at 190°C is lower than expected because most of the diffusion has already taken place by the time it reached 190°C. It can also be due to the sensitivity of the program to 0.1 ppm deviation to the concentration of

residual AA at any time during air stripping. The diffusivity values for Resin B, however are higher compared to the values for Resin A because resin B is crystallized with its latent heat from inside to the outside whereas resin A is crystallized from outside to the inside during precrystallization. Since Resin B has high crystalline regions in the centre compared to at the outer edge, the diffusion of AA is easier. In the case of Resin A, the outer edge is higher in crystallinity level compared to that at the centre and therefore the diffusivity values for AA are lowered compared to those of Resin B at the corresponding air stripping temperatures.

Table 3.4: Diffusivities of acetaldehyde in PET at different temperatures of air stripping.

Air stripping temperature	Acetaldehyde Diffusivity, cm²/sec Resin A	Acetaldehyde Diffusivity, cm²/sec Resin B
160 °C	0.0835 * 10 ⁻⁶	0.095 * 10 ⁻⁶
170 °C	0.12 * 10 ⁻⁶	0.147 * 10 ⁻⁶
180 °C	0.136 * 10 ⁻⁶	0.161 * 10 ⁻⁶
190 °C	0.133 * 10 ⁻⁶	0.196 * 10 ⁻⁶

In order to determine the activation energy for the diffusion of acetaldehyde to take place through the pellet, the diffusivity is related to temperature by the Arrhenius equation which is given by

$$D = Ae^{-E_a/RT}$$

Taking the natural logarithm would give us

$$\ln (D) = \ln A - (E_a/R)(1/T)$$

Where D = Diffusivity of acetaldehyde from the PET pellet.

E_a = Activation energy for the diffusion of Acetaldehyde.

T = Temperature of air stripping.

R = Universal gas constant, 8.314 J/mol/ $^{\circ}$ K.

A = Pre-exponential factor.

This equation is linear; the slope gives E_a/R and $\ln (A)$ from the intercept. Therefore $\ln (D)$ is plotted against the inverse of temperature ($^{\circ}$ K) as shown in Figure 3.19 in the case of Resin B to determine the activation energy from the slope as 37.9 KJ/mol. Similarly for Resin A, the activation energy was determined as 39.9 KJ/mol ignoring the diffusivity value at 190 $^{\circ}$ C.

Figure 3.19: $\ln(D)$ vs. $1/T$ without the correction for crystallinity for Resin B.

The diffusivities of Resins A and B were calculated without considering the crystallinity effects during diffusion. The diffusivities at different temperatures cannot be compared because the crystallinity level is different at each temperature of air stripping and the rate of diffusion depends on the crystallinity level of the polymer as the crystals obstruct the transport of acetaldehyde from the pellet during diffusion. So the diffusivity of resin A and B, if it were completely amorphous, was calculated by using the Maxwell's (Dilute Spheres) equation 3.8⁽⁶²⁾ given below and the data is shown

in Table 3.5 where the corresponding activation energy is 40.9 KJ/mol from the plot of $\ln(D_a)$ as a function of $1/T$ as shown in Figure 3.20 in the case of Resin B. The diffusivity D_a for Resin A at 160°C was not calculated due to the lack of crystallinity data at that temperature during air stripping.

$$\frac{D}{D_a} = 1 - \frac{3V_c}{2+V_c} \quad (3.8)$$

Where D_a = Diffusivity of Acetaldehyde in PET if it were completely amorphous.

D = Diffusivity of acetaldehyde in PET with some volume fraction crystallinity V_c .

Table 3.5: Diffusivities of acetaldehyde in PET with crystallinity correction at different air stripping temperatures.

Air stripping temperature	Acetaldehyde Diffusivity, D_a , cm ² /sec	Acetaldehyde Diffusivity, D_a , cm ² /sec
	Resin A	Resin B
160 °C		0.165 * 10 ⁻⁶
170 °C	0.239 * 10 ⁻⁶	0.226 * 10 ⁻⁶
180 °C	0.267 * 10 ⁻⁶	0.268 * 10 ⁻⁶
190 °C	0.250 * 10 ⁻⁶	0.355 * 10 ⁻⁶

Figure 3.20: $\ln(D_a)$ plotted as a function of $1/T$ with correction for crystallinity for Resin B.

Comparing Figures 3.19 and 3.20, it is observed that with crystallinity correction, the line fits the data better. As seen from Tables 3.4 and 3.5 the diffusivities of acetaldehyde increased at each temperature, which is obvious because in the absence of crystals in the polymer, there is no obstruction to the diffusion of acetaldehyde and hence the increase in the diffusivity coefficients.

3.5 Residual 2-methyl-1,3-dioxolane (2MD) Concentration

The structure of 2-methyl-1,3-dioxolane is shown in Figure 3.21a. According to the US Patent 6864345 (Process and apparatus for producing polyethylene terephthalate), 2MD is formed by the reaction of residual acetaldehyde and free ethylene glycol present in PET giving out a water molecule. The reaction is illustrated in Figure 3.21b. Therefore, the residual 2MD concentration is that amount present in the unreacted state in PET. Similar to the residual AA concentration, residual 2MD concentration is also studied as a function of time and temperature making use of Perkin-Elmer TurboMatrix 40 Headspace Sampler and a Perkin-Elmer AutoSystem XL Gas Chromatograph (GC). The temperature is maintained at 150°C for headspace analysis for 1 hr followed by 120°C during gas chromatography. The results obtained from the chromatograph are converted to residual 2MD concentrations and plotted against time of air stripping. The change in concentration of 2MD during air stripping at different temperatures is shown in Figures 3.22 and 3.23 for resin A and resin B respectively.

(a)

(b)

Figure 3.21: a) Structure of 2-methyl-1,3-dioxolane. b) Formation of 2-methyl-1,3-dioxolane from residual acetaldehyde and free ethylene glycol in Poly(ethylene terephthalate).

Figure 3.22: Residual 2MD concentration plotted as a function of time at different temperatures of air stripping for Resin A.

Figure 3.23: Residual 2MD concentration plotted as a function of time at different temperatures of air stripping for Resin B.

At any temperature, the zero time concentration is the concentration of 2MD when the resin reached the air stripping temperature. Depending on the temperature required, it took 1.5 hrs to 2 hours to reach the air stripping temperature. It is found from Figure 3.22 that at 160°C, the concentration decreases from zero time concentration of 9.9 ppm with time reaching a value of 6.9 ppm after 12 hours. At 170°C, the concentration decreases from the zero time concentration of 7 ppm to 5.2 ppm after 2 hours and then increases to 7 ppm after 12 hours. At 180°C, the concentration decreases to 5.9 ppm from 7.3 ppm by the time resin A reaches 180°C and further drops to 4.8 ppm in just 30 minutes and increases to 8.4 ppm after 6 hours of air stripping and again tends to decrease to 7.4 ppm after 12 hours. Finally at 190°C, the concentration drops to 4.9 ppm at zero time and increases to 8.9 ppm after 2 hours and decreases with time to a low value of 3.6 ppm.

Resin B exhibits behavior similar to that of resin A. The average initial concentration of residual 2MD in resin B is 3 ppm. It drops to a certain value at zero time depending on the temperature of air stripping as shown in Figure 3.23. Exposure for less than 2 hours at 160°C and 170°C shows a decrease in the concentration value. Added time of exposure at these temperatures increases the 2MD concentration for up to 12 hours. At 180°C, it drops to a low value of 1.9 ppm in 30 minutes and with additional exposure at this temperature increases the concentration to 4.5 ppm for up to 9 hours. It then slightly decreases after 12 hours. At 190°C, the 2MD concentration

drops at zero time to a value of 1.5 ppm. As the air stripping is continued at 190°C, the concentration increases to 4.5 ppm after 4 hours and starts to decrease up to 12 hours to a value of 2.8 ppm.

In both the resins the concentration of 2MD does not follow the behavior of acetaldehyde and rather shows fluctuations in concentration with time and temperature of air stripping. On the whole, at any temperature, it tends to decrease initially, then it increases and later it decreases with time. This trend occurs at a faster rate with increase in temperature as the peak shifts towards the left at higher temperatures.

The fluctuations in 2MD concentration could be explained from the concentration changes of acetaldehyde. It can be interpreted that there is diffusion of the 2-methyl-1,3-dioxolane that is present in the PET before air stripping which results in the decrease of its concentration initially from the decline of the curve. It can be observed that the diffusion is faster with increase in air stripping temperature. Then with time, there is dominance of the 2-methyl-1,3-dioxolane formation reaction over its diffusion which means that the reaction has started to take place at a faster rate, which involves the utilization of acetaldehyde as a result of which the 2MD concentration increases again, while the acetaldehyde concentration decreases. After some hours, this reaction cannot continue longer at the same rate because of the low levels of acetaldehyde attained by its outward diffusion through the pellet and also by reacting with ethylene glycol to form 2MD. Therefore,

eventually there is a decrease of 2MD concentration as the 2-methyl-1,3-dioxolane formed is diffusing out.

The concentration of 2MD is plotted against the intrinsic viscosity for resin A and B to see if there can be any correlation between them as shown in Figures 3.24 and 3.25 respectively. It was found that the concentration of 2MD follows a similar trend like that followed with time of air stripping. The concentration of 2MD decreases initially, then increases and again decreases as the molecular weight of PET increases at any temperature. The 1st two points for resin A in Figure 3.24 at 180°C and 190°C are not joined directly and rather a dip in the curve is shown by the dotted line because from the concentration of 2MD data for resin A, it is observed that the concentration decreased approximately to 5ppm and 4.5 ppm at 180°C and 190°C respectively before it reached the concentration at 1 hr of air stripping. Thus, the concentrations of 2MD in both the resins follow the same trend with increase in molecular weight at the air stripping temperatures.

Figure 3.24: Change of 2MD concentration with intrinsic viscosity of resin A at different temperatures of air stripping

Figure 3.25: Change of 2MD concentration with intrinsic viscosity of resin B at different temperatures of air stripping

In brief, the process of air stripping can be visualized as a system in which there is diffusion, reaction and generation of the three components of interest; namely, acetaldehyde, 2MD and ethylene glycol. Acetaldehyde and ethylene glycol are generated by the vinyl ester end group and polycondensation reactions respectively, that are responsible for the buildup

of IV as shown in Figure 3.3. So at any point of time during air stripping at a given temperature, there is generation and diffusion of acetaldehyde and ethylene glycol along with the reaction with each other to form 2MD as presented in Figure 3.26 while there is generation and diffusion of 2MD; all these events are happening simultaneously, along with various other physical phenomenon and chemical reactions.

Figure 3.26: Representation of the physical and chemical processes taking place simultaneously inside the cylindrical pellet of PET.

3.6 Free ethylene glycol concentration by Automatic Thermal Desorption (ATD) and Gas Chromatography (GC)

Since the residual concentrations of acetaldehyde and 2MD were obtained, knowledge of the free ethylene glycol concentration changes with time and temperature of air stripping might be helpful in understanding the mechanism of 2MD formation. Therefore, along with the concentrations of residual acetaldehyde and residual 2-methyl-1,3-dioxolane, the changes in levels of free ethylene glycol were monitored to further evaluate the changes in concentrations of 2MD, since EG is involved in its formation. A thermal desorption technique was used to determine the free ethylene glycol concentrations of resin B during air stripping. As described previously in section 2.7, a Perkin–Elmer Automatic Thermal Desorption System (ATD 400) and a Perkin–Elmer AutoSystem XL Gas Chromatograph were used to determine the free or residual ethylene glycol concentration in resin B. The powdered samples of resin B that were collected at different times during air stripping were maintained at 220°C for 10 minutes in the ATD 400 to volatilize the free ethylene glycol molecules from PET that were then analyzed by gas chromatography at 230°C. The concentrations calculated for these samples from the chromatographs are plotted as a function of time and temperature as shown in Figure 3.27.

Figure 3.27: Ethylene Glycol Concentration plotted as a function of time at different temperatures of air stripping for Resin B.

The initial free ethylene glycol concentration in resin B was found to be 130 ppm on an average. It decreased continuously with time of air stripping at 170°C, 180°C and 190°C. The higher the temperature of air stripping, the greater is the decrease in the free ethylene glycol concentration and the lower is the value attained after 12 hours of air stripping. These quantitative values of free ethylene glycol concentrations; however, are of the orders of hundreds which are higher than expected to be considered as the residual concentration. Even after 12 hours of air stripping, the concentration is in the range on 60 – 110 ppm depending on the temperature. Therefore, there was an ambiguity on the method used to determine the free ethylene glycol concentration in PET samples.

Upon careful examination, it could be mentioned that this quantity of ethylene glycol obtained actually is the free ethylene glycol along with the EG that might have been generated during the measurement process in the Perkin Elmer ATD 400 because the temperature in the oven is 220°C which is the solid stating temperature of poly (ethylene terephthalate) with helium providing the inert atmosphere. It is possible that the PET sample undergoes solid state polymerization thereby generating free ethylene glycol by the reaction shown in Figure 3.3a. Since the PET sample is taken in the powder form, the rate of this reaction is very high because of the small particle size of PET taken.

In order to determine if the ethylene glycol was being generated during the automatic thermal desorption experiment, a similar experiment was conducted by making use of a vacuum oven. The PET in the form of pellets and powder were dried overnight at 125°C and the intrinsic viscosities were measured. The powder form of PET was placed in the oven for 1 hr at 220°C and the IV was measured. The data are tabulated in Table 3.6 for two different resins E and S and a rise in IV is noticed within one hour. This explains that solid state polymerization is taking place during the experiment and ethylene glycol is being generated when the sample is set to 10 min desorption time at 220°C. Moreover, it has also been observed that the amount of ethylene glycol being measured with increased times of desorption increased sharply confirming the generation of ethylene glycol during this process. For example, a PET resin showed a concentration of 130 ppm, 260 ppm and 320 ppm at 10 min, 20 min and 30 min of desorption times respectively. If the concentration of free ethylene glycol measured during the desorption experiment was just the free ethylene glycol concentration and not due to the ethylene glycol generation then the measured amounts would be expected to remain constant.

Table 3.6: Intrinsic Viscosity data for the vacuum oven experiment.

PET Resin	Intrinsic Viscosity		
	Pellets dried overnight for 18 hrs at 125 °C	Powder dried overnight for 18 hrs at 125 °C	Powder at 220 °C for 1 hr
E (IV 0.8)	0.82	0.83	0.94
S (IV 0.8)	0.79	0.82	0.95

3.7 Free Ethylene Glycol Concentration by Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) has been used for analysis of free ethylene glycol concentration in PET. The purpose of choosing this technique was that it does not involve the use of high temperatures such as in the case of thermal desorption technique where the PET sample had to be heated to 220°C for ethylene glycol analysis. In addition, NMR can be used to estimate the total concentration of ethylene glycol in the sample, whereas in the case of desorption technique, only the amount of ethylene glycol that diffused out during the measurement could be measured. The method used for determination of carboxyl and hydroxyl end groups in PET ⁽⁶³⁻⁶⁵⁾ was used as the basis for development of a method for the measurement of ethylene glycol concentration with several modifications. An INOVA – 600 MHz ¹H NMR spectrometer has been used to determine the chemical shift for the ethylene glycol protons in deuterated TCE solvent. Initially, the NMR spectrum for pure TCE solvent was obtained as shown in Figure 3.28. Figure 3.29(b) shows the NMR spectrum for small amount ($\approx 1\mu\text{l}$) of pure ethylene glycol in TCE solvent. Comparing Figures 3.28 and 3.29(b), two new peaks were observed at chemical shifts of 3.62 ppm and 1.71 ppm, which should belong to the protons of ethylene glycol. The ethylene glycol molecule has two kinds of protons, namely, four protons bonded to the carbon atom and two protons which are bonded to the oxygen atom as shown in Figure 3.29(a).

Since these two kinds of protons have different environments, they are expected to show different chemical shifts from each other. The two new peaks which appear in Figure 3.29(b) are identified as the peaks from these two kinds of protons showing different chemical shifts. The ratio of the areas under the peak for the carbon bonded protons and oxygen bonded protons is approximately two, which further confirms the identity of the peaks because the ratio of the number of carbon bonded protons to the number of oxygen bonded protons is two in an ethylene glycol molecule.

Figure 3.28: NMR spectrum for pure TCE solvent

(a)

(b)

Figure 3.29: (a) Structure of ethylene glycol Molecule, (b) NMR spectrum for pure TCE and pure ethylene glycol.

Since the peaks for protons of pure ethylene glycol have been determined in TCE solvent, the peaks for protons of ethylene glycol molecules in the PET sample must also be determined. In order to accomplish this, about 12mg of resin B PET was dissolved in TCE solvent at 140°C for 45 min and the solution was transferred to the NMR tube for analysis. Figure 3.30 (a) shows the NMR spectrum obtained for the PET sample in the solvent. A tiny peak observed at a chemical shift of 3.59 ppm was thought to be the peak belonging to the carbon bonded protons of the ethylene glycol molecule in PET. The peak for the oxygen bonded protons was not clear, perhaps because of interference with water molecules. An expanded spectrum of these peaks is shown in Figure 3.30 (b). In order to confirm that the peak for carbon bonded protons of EG is at 3.59 ppm chemical shift; a small amount of pure ethylene glycol was added to the same sample of PET in the NMR tube and analyzed by the spectrometer. Figure 3.31 shows the NMR spectrum thus obtained. An increase in the size of the peak for carbon bonded protons was observed. The peak for the oxygen bonded protons also appears at a chemical shift of 1.77 ppm and thereby calculating the ratio of the area of the peaks confirms that the peaks belong to the ethylene glycol molecules in PET. Thus, the concentration of ethylene glycol can be measured by ^1H NMR spectroscopy. The reference peak used to calculate the concentration of ethylene glycol is the benzene proton peak at a chemical shift of 8.0 ppm in the NMR spectrum. The calculation for the concentration of free ethylene glycol present in the

PET sample from the ^1H NMR spectrum of PET in TCE solvent is presented below.

Benzene

Ethylene glycol

$$\text{moles of EG} = \frac{\text{Total area of carbon bonded protons of EG}}{\text{number of carbon bonded protons in one molecule of EG (4)}}$$

$$\text{moles of benzene} = \frac{\text{Total area of benzene protons}}{\text{number of protons on benzene ring in PET repeat unit (4)}}$$

number of carbon bonded protons in one molecule of EG

= number of protons on benzene ring in PET repeat unit

$$\text{Mole Ratio of EG to PET repeat unit} = \frac{\text{Total area of carbon bonded protons of EG}}{\text{Total area of benzene protons in PET}}$$

$$\text{g of EG/ g of PET} = \text{mole ratio} * 62/192$$

where the molecular weights of EG and PET repeat unit are 62 g/mol and 192 g/mol respectively.

Figure 3.30: a) NMR Spectrum for PET in TCE solvent,
 b) Expanded view of the NMR Spectrum for PET in TCE

Figure 3.31: NMR Spectrum for PET in TCE solvent on addition of pure Ethylene Glycol

3.7.1. Determination of free ethylene glycol concentration in PET resins

The ^1H NMR Spectroscopy method that had been developed was used for determination of the concentrations of EG in resin B PET pellets as functions of air stripping time at 180°C and 170°C . The concentrations obtained by the desorption technique were thought to be too high, however; the concentrations obtained by the NMR technique were also high. This confirms

that the free ethylene glycol concentrations in PET are in the orders of hundred. It has to be noted that though the thermal desorption method delivered concentrations in the same range as that obtained by NMR, the concentration values increased with increased time of desorption making the desorption technique unreliable. The ^1H NMR spectroscopy results were plotted against time as shown in Figure 3.32. The concentrations do not seem to be changing during the air stripping process at 170°C or 180°C . In Table 3.7, the initial and final concentrations of EG in resin B pellets at different temperatures are presented. The concentration of EG remained unchanged after 12 hours of air stripping at 170°C , 180°C and 190°C . This might have occurred because the boiling point of EG is 198°C and the air stripping temperatures were in the range $160^\circ\text{C} - 190^\circ\text{C}$ which are below the boiling point, making the diffusion of ethylene glycol present inside the pellets difficult. Another possible reason is that as the air stripping time increases, the density of the PET increases thereby increasing the crystallinity level. This increased crystallinity could have inhibited diffusion of the EG from the pellets and also could have an effect on the NMR results. This could be a factor, if while preparing the sample for NMR analysis by heating PET material in TCE solvent; the highly crystalline material did not dissolve even though it was heated for 2 hours at 140°C . Particularly, the pellets after 12 hrs of air stripping at 190°C are 46% crystalline and did not totally dissolve. These pellets were then flattened by heating to about 90°C , which is above

the glass transition temperature of PET, and compressing them with a laboratory press. This was done in order to break down the crystalline matrix in PET without affecting the concentration of EG. The more soluble compressed pellets were then used to prepare the sample for NMR analysis. There was; however, always some very small amount of very highly crystalline material that did not dissolve and could be seen floating in the solvent. This undissolved polymer could interfere with the calculation of EG concentration. An example of a possible deviation of the concentration is given below.

The weight of PET placed in TCE = 10mg

The weight of PET that did not dissolve in TCE < 1mg in the utmost case

The mole ratio obtained by NMR analysis for this sample = $0.5/1000 = 161$ ppm.

Where 0.5 is the area of the peak for the carbon bonded protons of EG and 1000 is the area of the benzene protons peak in the NMR spectrum.

It is considered that the PET chains arrange themselves to form crystalline material by rejecting the low molecular weight compounds, end groups and other condensates or impurities into the amorphous phase ⁽²¹⁾. Therefore, the concentration of EG within the crystalline phase can be neglected. The sample preparation dissolves the amorphous phase completely and hence all the EG molecules are assumed to be in the solution. Due to the undissolved

PET, the concentrations could be overestimated. The mole ratio obtained from ^1H NMR is for 9 mg of the PET sample in the solution and if the 1mg of undissolved PET is also taken into account, the concentration would be 145ppm. So there is a deviation by 16 ppm or 10%.

Corrected mole ratio = $0.5/1111.11 = 0.45/1000 = 145\text{ppm}$

(Area for benzene ring for 10 mg should be $1000 \times 10/9 = 1111.11$)

Considering the deviation, it can be stated that no big difference in the concentrations of EG are observed over the period of time during air stripping at these temperatures. This is a hypothetical calculation because the weight of the undissolved material floating in the solvent is so small that it cannot be filtered and weighed.

Figure 3.32: Free ethylene glycol concentrations as a function of air stripping time for PET pellets of resin B at 170°C and 180°C.

Table 3.7: Initial and final EG concentration for air stripped resin B pellets at different temperatures.

Resin B	EG Area		EG conc., ppm	
	Before	After	Before	After
170°C	0.53	0.52	171	168
180°C	0.53	0.53	171	171
190°C	0.53	0.54	171	174

Since the fact that the air stripping temperatures were below the boiling point of EG is considered to be one of the reasons for the unchanged EG concentration during air stripping, the concentrations in some commercially solid stated resins were also measured by the NMR spectroscopy method and the results are shown in Table 3.8. As commercial solid stating is generally done at temperatures of 220°C to 240°C, which are well above the boiling point of EG, it was expected that these resin samples would exhibit very low concentrations of EG. This is because the diffusivity of ethylene glycol was believed to increase with temperature. These values were higher than expected; however, we cannot determine if there was any decrease in the EG concentration of the solid stated resins compared to their precursors since the concentrations in the corresponding precursors were not known. The possible reason for high concentrations in solid stated resins considering the deviation

for the insoluble material can primarily be due to the formation of ethylene glycol during polymerization with diffusion of ethylene glycol from the pellet and moreover, during solid stating the crystallinity level increases very rapidly thereby restricting the EG molecules from easily diffusing out though the material.

Table 3.8: EG concentrations for commercially solid stated resins

PET resin	EG area	EG conc., ppm
E 0.8	0.55	178
S 0.8	0.84	271
NK	0.38	123

Therefore, in order to get an estimate of the concentration of EG in amorphous PET which can completely dissolve in TCE solvent thereby eliminating the need to correct for the insoluble highly crystalline material, three different kinds of plant resins (PR) and bench scale (BS) resins of different IV were taken for ethylene glycol analysis. As shown in Table 3.9, BS resins of 0.64 IV and 0.53 IV show a very high concentration of EG compared to the commercially solid stated resins. The lower the IV, the higher is the concentration of EG in BS resin. BS resin of 0.89 IV is crystalline PET material which was solid stated from BS resin of 0.64 IV and

shows a decrease in the concentration of EG compared to 0.64 IV resin. Thus, it is clear that solid stating helps in removal of ethylene glycol to a certain extent and that the concentration of EG in solid stated material is less than that of its precursor. Table 3.9 also shows the ethylene glycol concentration for Plant resin of different low molecular weights in the amorphous phase. But, no large difference in the concentrations is observed in this case. The Bench scale resin and Plant resin of the same IV at 0.64 show a huge difference in the ethylene glycol concentrations. Thus, the concentration of EG in the melt phase resins can depend on various factors during processing such as the effectiveness of the vacuum in removing the volatiles during the melt phase polymerization reaction.

Table 3.9: EG concentration in amorphous PET resins of different molecular weights.

Resin IV	EG Area	EG conc., ppm
BS 0.64	1.41	455
BS 0.64 to 0.89	0.98	316
BS 0.53	2.06	665
PR 0.58	0.49	158
PR 0.60	0.48	155
PR 0.64	0.51	165

3.7.2 Determination of free ethylene glycol with 30/70 (wt/wt) deuterated trifluoroacetic acid/chloroform mixture as the solvent

The free ethylene glycol concentration was determined by ^1H NMR spectroscopy using deuterated tetrachloroethane as the solvent because as already mentioned, this solvent was previously used by some researchers to determine the end group concentrations in PET. In their method the PET sample had to be rendered amorphous by heating it to 280°C in differential scanning calorimeter (DSC) so that it dissolves completely in the TCE solvent to measure the end group concentrations in PET. However, in the case of measuring ethylene glycol concentration, the PET sample was not rendered amorphous in the DSC because of the possibility of diffusion of ethylene glycol at 280°C as its boiling point is 198°C . Therefore, very tiny amounts of material were found floating in the preparation of the sample. It was suspected if this could interfere with the calculations and thus the deviation was calculated in this case.

In order to examine the accuracy of the results from the TCE solvent, the free ethylene glycol concentration has been determined by using a different solvent which could dissolve even the highly crystalline material of PET leaving no traces of undissolved material floating in the sample. A solvent consisting of 30/70 (wt/wt) deuterated trifluoroacetic acid (TFA)/chloroform has been used to dissolve some of the PET samples previously evaluated with

the TCE solvent. This was done for the purpose of comparison between the results obtained with these two different solvents. Initially, similar to the case of the TCE solvent, the peak for carbon bonded protons of ethylene glycol in TFA/chloroform was determined at 3.9 ppm chemical shift in the NMR spectrum. Once the chemical shift was determined, samples of PET were prepared by adding approximately 10mg of PET to the solvent in the NMR tube and analyzed by ^1H NMR spectroscopy, after the PET dissolves (usually in less than an hour at room temperature). The time taken for the material to dissolve depends on if the sample is a pellet or powder. Pellets take longer time to dissolve compared to the powdered PET materials. Since TFA/chloroform is an aggressive solvent, it is advised to do the NMR analysis as soon as the sample is dissolved in the solvent because the sample can degrade on waiting for longer periods of time. Table 3.10 shows the results of free ethylene glycol concentration in TFA compared to that of in TCE. It has been found that the EG concentrations obtained in both solvent systems are very close to each other. But the sample preparation is simpler with TFA/chloroform solvent compared to that with TCE solvent.

Table 3.10: Comparison of the concentrations of ethylene glycol with TCE and TFA/chloroform solvents.

PET Sample	TCE		TFA/chloroform	
	Area	Concentration, ppm	Area	Concentration, ppm
Resin B as received - 1	0.53	171	0.52	168
Resin B as received - 2			0.54	174
NK	0.38	123	0.4	129
Resin B 180°C, pellet	0.53	171	0.52	168
Resin B 190°C, pellet	0.54	174	0.52	168
Resin B 180°C, powder			0.52	168
Resin B 190°C, powder			0.53	171

3.7.3 Kinetic study of the generation and diffusion of ethylene glycol during solid state polymerization from literature

It is important to consider the reactions involved during solid state polymerization to understand the kinetics of ethylene glycol formation and therefore its concentration changes. The two main reactions that lead to significant changes in the molecular weight are polycondensation and

esterification reactions as shown in Figure 3.33. The polycondensation reaction involves the reaction between two hydroxyl ends of PET chain to form a long molecule of PET giving out an ethylene glycol molecule, while the esterification reaction involves the reaction between a hydroxyl and a carboxyl end group of PET molecules to give out a water molecule as the byproduct.

The reactions are reversible in nature with their forward and backward reaction rate constants for polycondensation and esterification reactions as k_1 & k_1' and k_2 & k_2' respectively. K_1 and K_2 are the equilibrium constants for the two reactions such that

$$K_1 = k_1/k_1'$$

$$K_2 = k_2/k_2'$$

• Polycondensation reaction

• Esterification reaction

Figure 3.33: The two main reactions during solid state polymerization of PET

Table 3.11 (a) shows the reaction rate constants for polycondensation and esterification reactions obtained by Ben Duh ⁽⁶⁷⁾ and Parashar et al. ⁽⁶⁸⁾ from experimental studies of solid stating PET at different temperatures. Ben Duh determined the rate constants for polycondensation and esterification reactions by solid state polymerization of powdered PET at 230°C with varying carboxyl end group and catalyst concentrations. In his case, the particle size is assumed to be very small, such that the resistance to the

diffusion of ethylene glycol and water is negligible. Therefore, based on these data, the average value of $k_1 > k_2$. From this it can be interpreted that, compared to the esterification reaction, the polycondensation reaction is the dominant reaction in increasing the molecular weight of the polymer, during SSP of powdered PET in the absence of diffusion resistances. On the other hand, Parashar et al. studied the solid state polymerization of pressed PET chips at 185°C and 190°C. In their case, the rate constants k_1 and k_2 were determined by neglecting the diffusion resistance of the byproducts in their calculations because of the small thickness of the chips and therefore k_1 is greater than k_2 . The present work was; however, done on PET pellets whose sizes are not small enough to neglect the diffusion resistance. As a consequence the experimental results of free ethylene glycol concentrations cannot be explained on the basis of these rate constant values.

Table 3.11(a): Rate constant values (10^6g/mol/hr) for polycondensation and esterification reaction in powdered PET and pressed PET chips at different temperatures ^(67,68)

Source	Temperature	$k_1 * 10^3$	$k_2 * 10^3$	k_2 / k_1	K_1	K_2
Ben Duh	230 C	1.40	1.19	0.85		
Parashar et al.	185 C	0.636	0.312	0.49		
Parashar et al.	190 C	0.90	0.678	0.75		

Theoretical reaction rate constant data for polycondensation and esterification reactions, during solid stating at different temperatures, from the previous work done by Kang, Mallon et al. ⁽⁶⁶⁾ and Tang et al. ⁽⁶⁷⁾ are compared in Table 3.11(b). The polymerization reactions in the melt take place in the amorphous phase and similarly the polymerization reactions during solid stating are also considered to be taking place only in the amorphous regions of the polymer, because all the chain ends are concentrated in the amorphous part of the polymer. The rate constants for the polymerization reactions at the solid stating temperatures are; therefore, obtained by extrapolating the melt polymerization data, assuming the dependence of rate constants only on the temperature.

Table 3.11(b): Rate constant values (10^6g/mol/hr) for polycondensation and esterification reaction in solid PET pellets at different temperatures ⁽⁶⁷⁾

Source	Temperature	$k_1 * 10^3$	$k_2 * 10^3$	k_2 / k_1	K_1	K_2
Kang ⁽⁵³⁾	230 C	1.326	4.134	3.12	0.5	1.25
Mallon et al. ⁽⁶⁶⁾	230 C	0.907	3.421	3.77	0.5	1.25
Tang et al.	225 C	0.201	0.783	3.86	1	1.25

The values for the equilibrium constants K_1 and K_2 are usually taken as 0.5-1 and 1.25 respectively. The K_2 value for esterification reaction indicates that

the forward reaction rate k_2 is always greater than the backward reaction rate k_2' and moreover, the water molecules that are formed as a byproduct during this reaction diffuse faster at such high temperatures aiding in the increase of molecular weight of PET. The higher rate constant value of k_2 compared to k_1 further explains that esterification reactions takes place faster than the polycondensation reaction due to the better diffusivity of small water molecules compared to the large ethylene glycol molecule at any temperature. The value of K_1 is less than 1 which signifies that the backward reaction takes place more effectively than the forward reaction in the case of polycondensation and therefore in order to increase the molecular weight of the polyester, the ethylene glycol molecules that are formed as a byproduct have to be removed to drive the polycondensation reaction forward. In the case of PET pellets, the particle size is not small as in the case of powdered PET and there is diffusion resistance within the pellets. Thus, for the ethylene glycol molecules to diffuse out from the PET pellets, temperature and crystallinity level play an important role. From the EG concentration measurements of the air stripped resin in the temperature range of 160°C – 190°C, it was mentioned that the temperature has to be above the boiling point of ethylene glycol, which is approximately 198°C, as no big change in concentration was observed. This implies that as the solid stating temperatures are well above the boiling point of EG, it was expected that the residual as well as the generated ethylene glycol would diffuse out to achieve

low levels of EG. On the contrary, the commercially solid stated resins were unable to achieve very low value of EG concentration, which could be explained by the rapid increase in crystallinity levels at such high temperatures along with the generation and diffusion of ethylene glycol by the polycondensation reaction. The crystal lattice formations inside the PET pellets obstruct the flow of ethylene glycol molecules, thus causing EG to be trapped inside the resin. Although an increase in SSP temperature could help the EG molecules to diffuse out, the crystalline structure of the PET opposes the diffusion.

From the experimental study of Ben Duh ⁽⁶⁷⁾, on the IV increase of PET pellets during SSP for samples of varying carboxyl concentrations, it was explained that the diffusion resistance of byproducts is small in the early stages of SSP where the bulk polymerization takes place at the surface. At this time, the rates of the reactions can take place in accordance with the rate constants determined by Ben Duh or Parashar et al. As the SSP proceeds, the end group concentrations at the surface decrease and the polymerization reactions take place deeper within the pellet. As a result, the diffusion resistances become larger and the results of the rate constants from Ben Duh and Parashar et al. are not valid.

It has been illustrated in section 3.2 that there is an increase in the intrinsic viscosity of PET during air stripping for 12 hours particularly at temperatures from 170°C to 190°C and that the two main reactions involved

are the polycondensation and esterification reactions. These temperatures are below the boiling point of EG and are said to inhibit the ethylene glycol removal and moreover, there is not much change in EG concentration during air stripping. This can imply that as stated by Jabarin et al. ⁽²²⁾, the polycondensation reaction is more prevalent at temperatures above EG boiling point. Below 200°C, the esterification reaction is dominant and there is not much ethylene glycol being generated during the polycondensation reaction subject to the diffusion resistance of ethylene glycol in the PET pellets. This is because unless the ethylene glycol molecules are diffused out, the polycondensation reaction cannot move forward in order to increase the molecular weight and it is possible for this to happen only above the boiling point of ethylene glycol. The IV increase at the given air stripping temperatures can; therefore, be primarily due to the esterification reaction.

The diffusion coefficients of ethylene glycol at various temperatures obtained by Kang, Mallon and Ray, Gao et al. and Ravindranath and Mashelkar ⁽⁶⁹⁾ by modeling experiments of PET are shown in Figure 3.34. The diffusivity of EG is almost negligible below 190°C from the diffusivity data of Mallon and Ray and the temperature should be at least 220°C or above, which it is typically the solid stating temperature range, in order remove ethylene glycol from PET.

Figure 3.34: Diffusion coefficients of ethylene glycol and water for solid PET at different temperatures, according to Mallon and Ray, Kang, Gao et al. and Ravindranath and Mashelkar ⁽⁶⁹⁾.

The diffusivities of ethylene glycol that have been obtained by various researchers under specific assumptions are compared to the diffusivities of acetaldehyde and water in Table 3.12. It can be noticed that the order of the

diffusivities for EG, water and acetaldehyde obtained by modeling experiments on PET are the same. The diffusivity of water is almost double the value of the diffusivity of ethylene glycol at different temperatures. Moreover, the work by Jabarin and Kim shows that the diffusivity of ethylene glycol is comparable to the diffusivity of acetaldehyde at various temperatures with different levels of crystallinity although the ethylene glycol molecule is larger in size than the acetaldehyde molecule. In reality; however, it seems that the concentrations of ethylene glycol are not comparable to that of acetaldehyde in PET at these conditions, which implies that the diffusivity of ethylene glycol is influenced by factors such as increased levels of crystallinity.

Table 3.12: Comparison of the diffusivities (cm²/sec) of ethylene glycol, water and acetaldehyde from literature

Source	T	D _{EG} *10 ⁶	D _w *10 ⁶	D _a *10 ⁶	Conditions
Mallon et al. ⁽⁶⁶⁾	220 C	1.93			Particle size = 1mm
Qiu Gao ⁽⁷⁰⁾	225 C	7.21			Pellet size 4x4x1.5 mm
Kang ⁽⁵³⁾	230 C	3.1	5.7		
Tang et al. ⁽⁶⁷⁾	230 C	2.6	5.8		
K.H. Yoon ⁽⁷¹⁾	230 C	0.056			X _c = 0.37, particle size = 0.15-0.3 mm
Jabarin & Kim ⁽²³⁾	180 C	3.00	7.91	3.77	X _c = 0.49 Effective radius = 1.25 mm
Jabarin & Kim ⁽²³⁾	190 C	3.05	8.06	3.84	X _c = 0.52 Effective radius = 1.25 mm
Jabarin & Kim ⁽²³⁾	230 C	3.14	8.57	3.99	X _c = 0.62 Effective radius = 1.25 mm
This Work	190 C			0.36	X _c = 0.46 Effective radius = 2.8mm

Many researchers ^(23,53,70) assumed that the diffusion of EG is rapid compared to the chemical reaction and therefore, the concentration of ethylene glycol is negligible or zero in their modeling experiments. Based on this work, this does not seem to be the case as shown by the significant amount of ethylene glycol measured by the ¹H NMR technique. The ethylene glycol mole ratio

value used by Qui Gao et al. ⁽⁷⁰⁾ in their modeling is approximately 1×10^{-5} compared to the value obtained from this experimental work which is approximately 50×10^{-5} and is 50 times greater than that of theoretically obtained value.

Yoon⁽⁷¹⁾ determined the diffusivity coefficient for ethylene glycol by performing a desorption experiment on the powdered PET chips and measuring the rate of mass loss of PET particles due to desorption of the volatiles at 230°C. The experimental value is much smaller than the theoretically calculated values by the rest of the authors as shown in Table 3.12 in spite of the fact that the sample was taken in the powder form. Mallon et.al carried out PET solid state experiments in a fluidized bed where the particle size was between #10 and #12 sieves (about 1mm) and determined the diffusivity of ethylene glycol as a function of temperature by modeling and data fitting as presented in Figure 3.34. On careful observation, it was found that diffusivity of ethylene glycol is almost negligible at temperatures below 200°C for their 1mm size particles and the size of pellets used in the current work is 3 times bigger than the size of particle used by Mallon and Ray for their experiments. This further supports the difficulty of ethylene glycol diffusion at 170°C, 180°C and 190°C (air stripping temperatures) and that no change in concentration of ethylene glycol was noticed during air stripping.

The main idea of measuring the free ethylene glycol in the air stripped samples was to better analyze the mechanism of the 2-methyl-1,3-dioxolane formation reaction, as ethylene glycol is one the reactants. However, it was observed that the free ethylene glycol concentration in the PET samples were many times higher than the concentrations of residual acetaldehyde and 2MD and therefore, the changes in concentrations of residual 2MD are independent of the concentrations of the free ethylene glycol because of its abundance and it would be appropriate to agree with the explanation previously given for the changes in the residual 2MD concentration with respect to the residual acetaldehyde concentration.

Chapter 4

Conclusion

The main objective of this thesis has been to study the kinetics of residual acetaldehyde removal from poly (ethylene terephthalate) by air stripping at temperatures ranging from 160°C to 190°C. The intrinsic viscosity measurements show that the molecular weight of the PET polymer increases with time and temperature of air stripping, similar to the solid stating process at these temperatures. The activation energy for polymerization during air stripping is close to that during solid stating at these temperatures. The density and crystallinity level also increases with time and temperature reaching a plateau after a few hours of air stripping.

The concentration of residual acetaldehyde could be reduced to less than 1 ppm by air stripping which needs few hours of time in the temperature range of 160°C – 190°C as indicated by the headspace analysis and gas chromatography. At these air stripping temperatures, the concentration reaches a minimum value beyond which there is no change in the residual concentration of acetaldehyde. The activation energy and diffusion coefficient or diffusivity for acetaldehyde diffusion through the cylindrical pellet at

160°C, 170°C, 180°C and 190°C temperatures has been determined by a simulation program. Higher temperatures assist in faster removal of residual acetaldehyde from the PET pellets. At higher temperatures; however, there is change in the color of the pellets because of the oxidative degradation of poly (ethylene terephthalate), if air stripping is done above 150°C for 12 hours.

The unexpected behavior of the residual 2-methyl-1,3-dioxolane concentration change with time and temperature of air stripping, which is quite different from the residual acetaldehyde concentration change, has been observed by doing headspace analysis with gas chromatography technique. In the process of removing acetaldehyde from poly (ethylene terephthalate) by air stripping, there is either addition or removal of 2-methyl-1,3-dioxolane.

According to US Patent 6864345 (Process and apparatus for producing polyethylene terephthalate), 2-methyl-1,3-dioxolane is formed by the reaction of residual acetaldehyde and free ethylene glycol present in PET giving out a water molecule. In order to validate the results of residual 2-methyl-1,3-dioxolane concentration and to give a detailed reaction mechanism for it, the concentration change with time and temperature of free ethylene glycol present in poly (ethylene terephthalate) has been determined by two different techniques. The results obtained by using the thermal desorption technique to determine the free ethylene glycol concentration in PET do not seem to be reasonable, because of the increased concentrations achieved with increased

desorption time. This is due to the generation of free ethylene glycol by solid state polymerization during the process of measurement, which has been proved by a separate experiment performed in a vacuum oven. Results indicated that the thermal desorption technique could not be used for determination of EG concentration because the boiling point of ethylene glycol is 198°C and the temperature required to evaporate it from PET had to be at least 200°C or above. This temperature is sufficient to solid state PET as a result of which additional ethylene glycol would be generated.

The concentration of free ethylene glycol in PET has been determined by ^1H NMR spectroscopy technique using two different solvents, which gave equivalent results. The concentrations of ethylene glycol in the samples air stripped at 170°C and 180°C do not show changes with time. The unchanged final concentrations of ethylene glycol after 12 hours at 170°C, 180°C and 190°C are explained by the fact that the air stripping temperatures are below the boiling point of ethylene glycol at 198°C making the diffusion of ethylene glycol through the pellets difficult. The increase in crystallinity levels during air stripping could further restrict the diffusion of ethylene glycol. The concentrations measured in the commercially solid stated resins are surprising, because although the solid stating temperatures are above the boiling point of ethylene glycol, removal of EG to low concentrations such as that of acetaldehyde was not accomplished. This can be attributed to the rapid increase in crystallinity of PET and also to the generation of ethylene

glycol by the polycondensation reaction during solid state polymerization. The concentrations of the solid stated resins; however, should to be compared to their precursors to know if there were changes in ethylene glycol concentration. The concentrations of ethylene glycol in low molecular weight amorphous resins, which are completely dissolved in the TCE solvent have been studied. The concentrations are much higher in the bench scale resin compared to the plant resin of the same IV. The bench scale PET resin of 0.89 IV solid stated from 0.64 IV show a decrease in the EG concentrations compared to the precursor. This clarifies that the solid stated resins show a lower concentrations of ethylene glycol relative to the precursor. An estimate of the concentration of ethylene glycol has thus been achieved in various kinds of PET resins. Since the concentrations of ethylene glycol are many times higher than that of acetaldehyde or 2MD, the concentration profile of 2MD with time at any temperature is more dependent on the concentration change of acetaldehyde and independent of the concentration change of ethylene glycol.

Chapter 5

Future Work Recommendations

Results obtained by desorption technique in the current work for the ethylene glycol concentrations in PET indicated that there is generation of EG during the measurement. This was clear as the concentration of EG increased with increased desorption times at 220°C on the ATD 400 during the experiment. As further confirmation of the generation of ethylene glycol during the desorption experiment at 220°C, the carboxyl and hydroxyl end group concentrations could be determined by FTIR, ¹H NMR spectroscopy or by titration method for the PET samples before and after the desorption experiment. If the end group concentration decreases at the end of the experiment, this would imply that the generation of ethylene glycol has taken place while increasing the molecular weight of PET by the consumption of the hydroxyl end groups.

The physical and chemical property analysis during air stripping could be done on the spherical underwater cut PET pellets to see if it makes any

difference compared to the cylindrical PET pellets, though it is very likely that even the spherical shaped pellets could show similar results.

Researchers, while performing modeling experiments on solid state polymerization or air stripping of PET, may consider the point that the concentration of ethylene glycol inside a PET pellet is not negligible or zero during assumptions and calculations. This could help to understand the kinetic changes during SSP or air stripping of PET.

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