Synthesis and characterization of new active barrier polymers

Kamal Mahajan

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Synthesis and Characterization of New Active Barrier Polymers

By
Kamal Mahajan

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the
Doctor of Philosophy Degree in Engineering

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The University of Toledo
May 2010
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An abstract of

Synthesis and Characterization of New Active Barrier Polymers

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For many foods and beverages, a fundamental requirement for shelf stability is the minimization of oxygen exposure and thus minimal possible reaction with the food. Common problems associated with the presence of oxygen in food products include microbial spoilage, nutrient loss, as well as flavor and odor changes. There is a need in the industry to improve the oxygen barrier properties of polyesters.

Among the approaches available to improve the barrier properties, one of the most promising approaches is the addition of an active oxygen scavenger directly into the poly(ethylene terephthalate) (PET) material. An active oxygen scavenger is a substance capable of intercepting and scavenging oxygen by undergoing a chemical reaction with it, as the oxygen permeates through the PET packaging wall. There is also a need to develop a methodology for determining the scavenging capacity of potential oxygen scavengers and to ultimately help in efficiently designing the copolymers of PET and potential scavengers with better barrier properties.
The oxygen scavengers used in this research were two simple model compounds: monoolein (MO) and 3-cyclohexene-1,1-dimethanol (CHEDM). The new active barrier copolymers were synthesized by melt polymerizing PET with the oxygen scavengers in a batch scale polymerization system. It was found using proton NMR \(^1\text{H NMR}\) and 2-D correlation spectroscopy (COSY) that PET has reacted with MO and CHEDM leading to the formation of the copolymers. The effect of oxygen scavengers on the physical properties (melting, crystallization, and rheological behavior) of PET was also studied. The effects of oxygen scavengers on the barrier properties of PET were evaluated by determining oxygen permeation rates. The oxygen barrier properties of copolymers of PET/MO and PET/CHEDM were respectively improved by about 30 and 40%. The oxidation by-products of the copolymers were determined by using gas chromatography-mass spectrometry (GC-MS).

Finally, a methodology was developed to determine the scavenging capacity of potential oxygen scavengers by studying the oxidation kinetics followed by the calculation of Thiele modulus. The oxidation kinetics of the copolymers of PET and oxygen scavengers was determined by using nuclear magnetic resonance spectroscopy (NMR) and fourier transform infrared spectroscopy (FTIR).
Dedication

This dissertation is dedicated to my family and Dr. Saleh A. Jabarin for their constant support and love.
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Table of Contents

Abstract .......................................................................................................................... iii
Dedication ..................................................................................................................... v
Acknowledgements ..................................................................................................... vi
Table of Contents ........................................................................................................ vii
List of Figures .............................................................................................................. xiii
List of Tables ............................................................................................................... xxiii

Chapter 1. Introduction ................................................................................................. 1

1.1 Active oxygen scavenger ....................................................................................... 2
1.2 Polymerization of PET/scavenger copolymers ...................................................... 4
1.3 Reaction analysis of PET/scavenger copolymers .................................................. 6
1.4 Literature review of PET copolymers ................................................................. 7
  1.4.1 PET as a passive barrier .................................................................................... 8
  1.4.1.1 Copolymerization ....................................................................................... 8
  1.4.1.2 PET nanocomposite .................................................................................. 10
1.4.2 PET modified with oxygen scavengers ......................................................... 11
  1.4.2.1 PET modified with oxidizable groups in its main chain ......................... 12
Chapter 2. Experimental

2.1 Materials.................................................................25
2.2 Melt polymerization..................................................26
2.3 Preparation of the physical blends.................................29
2.4 Extraction method......................................................29
2.5 NMR analysis..........................................................30
2.6 Melt IV/Intrinsic viscosity measurement............................33
2.7 Thermal analysis........................................................35
2.8 Solid state polymerization............................................37
2.9 FTIR analysis............................................................39
2.10 Single screw extrusion...............................................40
2.11 Barrier property measurement.....................................41
2.12 Density.................................................................42
2.13 Microscopy of PET/scavenger copolymers.........................43
2.13.1 Optical microscopy .................................................................43
2.13.2 Small angle light scattering .....................................................44
2.14 GC-MS analysis ........................................................................45
2.15 Gas chromatographic analysis .....................................................45
2.16 Oxygen scavenging capacity calculations ....................................46

Chapter 3. Results and Discussion 47

3.1 In situ polymerization of PET/scavenger copolymers .......................47
   3.1.1 Esterification reaction ...............................................................47
   3.1.2 Polycondensation reaction ........................................................47
3.2 Reaction analysis between PET and MO using NMR spectroscopy ....48
   3.2.1 $^1$H NMR spectrum of pure PET .............................................49
   3.2.2 $^1$H NMR spectrum of pure MO ..............................................51
   3.2.3 $^1$H NMR spectra of PET/MO copolymer .................................53
   3.2.4 COSY plot for PET/MO copolymer ...........................................55
   3.2.5 $^1$H NMR spectra for extracted samples of PET/MO copolymer ....59
   3.2.6 $^1$H NMR spectra for physical blend of PET/MO .......................61
   3.2.7 $^1$H NMR spectra for extracted sample of physical blend of PET/MO .61
3.3 Reaction analysis between PET and CHEDM using NMR spectroscopy 63
   3.3.1 $^1$H NMR spectrum of pure CHEDM .......................................63
   3.3.2 $^1$H NMR spectra of PET/CHEDM copolymer ..........................67
   3.3.3 $^1$H NMR spectra of physical blend of PET/CHEDM ..................69
3.4 Summary .....................................................................................71
3.5 Rheological behavior (shear viscosity versus shear rate) ........................................73
   3.5.1 For WA314 PET .................................................................73
   3.5.2 For PET/MO copolymers ...............................................74
   3.5.3 For PET/CHEDM copolymers ......................................76
3.6 Thermal properties (melting and crystallization behavior) ...............................77
   3.6.1 For WA314 PET .................................................................78
   3.6.2 For PET/MO copolymers ...............................................80
   3.6.3 For PET/CHEDM copolymers ......................................82
3.7 Melting and isothermal crystallization behavior of PET/scavenger copolymers ..........86
   3.7.1 Approach used to study isothermal crystallization behavior of PET/scavenger copolymers .................................................................88
   3.7.2 Equilibrium melting point ..............................................90
   3.7.3 Avrami kinetics ...............................................................97
   3.7.4 Half time method .............................................................111
3.8 Microscopy of PET/scavenger copolymers ..................................................115
3.9 Spherulite radii determination using SALS ..................................................118
3.10 SSP of PET/scavenger copolymers ....................................................126
3.11 Oxygen permeability .........................................................................130
   3.11.1 For PET/scavenger copolymers .......................................130
   3.11.2 Effect of catalyst on oxygen permeability .......................131
3.12 Density of PET/scavenger copolymers .................................................133
3.13 Summary .........................................................................................136
3.14 Calculation of oxygen scavenging capacity of scavengers…………………………139
  3.14.1 Theoretical calculations.................................................................139
  3.14.1.1 For Monoolein.................................................................139
  3.14.1.2 For 3-cyclohexene-1,1-dimethanol........................................141
  3.14.2 Experimental determination of oxygen scavenging capacity of
  scavengers..........................................................................................142
3.15 Effect of oxidation catalyst on rheological and thermal properties.............. 145
  3.15.1 Rheological behavior of PET/scavenger copolymers.............................146
  3.15.1.1 For PET/CHEDM copolymer..................................................146
  3.15.1.2 For PET/MO copolymer.......................................................148
  3.15.1.3 For WA314 PET....................................................................149
  3.15.2 Thermal behavior of PET/scavenger copolymers.................................151
  3.15.2.1 DSC data for PET/MO copolymer...........................................151
  3.15.2.2 DSC data for PET/CHEDM copolymer.....................................155
3.16 Summary............................................................................................160
3.17 A methodology to determine the scavenging capacity of potential O₂
  scavengers.............................................................................................161
  3.17.1 Determination of oxidation kinetics of pure MO and PET/MO copolymer.................................................................162
  3.17.2 Determination of oxidation kinetics of pure CHEDM and PET/CHEDM
  copolymer.......................................................................................199
  3.17.3 Determination of Thiele Modulus for pure scavengers and the PET/scavenger
  copolymers......................................................................................211
List of Figures

Figure 1.1: Chemical structure of PET.................................................................2

Figure 1.2: Reaction of active oxygen scavenger with oxygen .........................4

Figure 1.3: Melt polymerization steps in PET and additives...............................6

Figure 1.4: Advantage of active oxygen scavenger.........................................19

Figure 1.5: Structures of scavengers (a) Monoolein, (b) 3-cyclohexene-1,1-dimethanol.................................................................24

Figure 2.1: Schematic diagram of melt polymerization reactor.......................28

Figure 2.2: The schematic of an NMR instrument...........................................33

Figure 2.3: The calibration curve of melt intrinsic viscosity..............................35

Figure 2.4: Schematic diagram of Buhler solid state polymerization reactor........38

Figure 2.5: Diagram of small angle light scattering setup................................44

Figure 2.6: Pressure-drop (Δp) oxygen consumption test................................46

Figure 3.1: Structure of PET.........................................................................49

Figure 3.2: $^1$H NMR spectrum of pure PET...............................................50
Figure 3.3: Structure of Monoolein (MO) ............................................................51

Figure 3.4: $^1$H NMR spectrum of pure MO in a mixture of d-TFA and d-chloroform...52

Figure 3.5: $^1$H NMR spectrum of PET/MO(5wt%) copolymer ...............................54

Figure 3.6: COSY plot for PET/MO(5wt%) copolymer .........................................56

Figure 3.7: COSY plot (expanded) for PET/MO(5wt%) copolymer ......................57

Figure 3.8: $^1$H NMR spectrum of PET/MO(5wt%) copolymer ............................58

Figure 3.9: $^1$H NMR spectrum of PET/MO(5wt%) copolymer after extraction .......60

Figure 3.10: $^1$H NMR spectra for PET/MO (physical blends) .........................62

Figure 3.11: $^1$H NMR spectrum of pure CHEDM in a mixture of d-TFA and d-
chloroform (Fresh) ..................................................................................................65

Figure 3.12: $^1$H NMR spectrum of pure CHEDM in a mixture of d-TFA and d-
chloroform (After 1 day) ....................................................................................66

Figure 3.13: $^1$H NMR spectrum of PET/CHEDM(5wt%) copolymer ...............68

Figure 3.14: $^1$H NMR spectrum of physical blend of PET/CHEDM ..................70

Figure 3.15: Viscosity versus shear rate for WA314 PET ..............................74

Figure 3.16: Viscosity versus shear rate for PET/MO copolymers .......................75

Figure 3.17: Viscosity versus shear rate for PET/CHEDM copolymers ...............76

Figure 3.18: DSC plot for WA314 PET (heating after the quench) .......................79
Figure 3.19: DSC plot for WA314 PET (cooling from the melt)…………………………79

Figure 3.20: DSC plot for PET/MO copolymers (heating after the quench)………………81

Figure 3.21: DSC plot for PET/MO copolymers (cooling from the melt)………………81

Figure 3.22: DSC plot for PET/CHEDM copolymers (heating after the quench)………84

Figure 3.23: DSC plot for PET/CHEDM copolymers (cooling from the melt)…………84

Figure 3.24: DSC results from fusion of PET. The isothermal crystallization conditions were, a) 460K,b) 465K, c) 470K, d) 478K……………………………………………………………87

Figure 3.25: Multiple melting peaks of isothermally crystallized WA314 PET………91

Figure 3.26: Multiple melting peaks of isothermally crystallized PET/MO(1wt%) copolymer…………………………………………………………………………………………91

Figure 3.27: Multiple melting peaks of isothermally crystallized PET/MO(5wt%) copolymer…………………………………………………………………………………………92

Figure 3.28: Multiple melting peaks of isothermally crystallized PET/CHEDM(1wt%) copolymer………………………………………………………………………………………………………..92

Figure 3.29: Multiple melting peaks of isothermally crystallized PET/CHEDM(3wt%) copolymer………………………………………………………………………………………………………..93

Figure 3.30: Multiple melting peaks of isothermally crystallized PET/CHEDM(5wt%) copolymer………………………………………………………………………………………………………..93
Figure 3.31: Multiple melting peaks of isothermally crystallized PET/CHEDM(5wt%) copolymer………………………………………………………………………………..94

Figure 3.32: A plot used to obtain the equilibrium melting temperature ($T_{m}^{o}$) of PET/MO(1wt%) copolymer (showing melting peaks $T_{m1}$, $T_{m2}$, $T_{m3}$) versus crystallization temperature………………………………………………………………………………..95

Figure 3.33: The depression of equilibrium melting point of PET/CHEDM copolymers………………………………………………………………………………..96

Figure 3.34: The depression of equilibrium melting point of PET/MO copolymers………96

Figure 3.35: Crystallization behavior for isothermally crystallized PET/CHEDM(5wt%) copolymer………………………………………………………………………………..98

Figure 3.36: Half time plotted as a function of crystallization temperature for isothermally crystallized WA314 PET…………………………………………………………..99

Figure 3.37: Half time plotted as a function of crystallization temperature for isothermally crystallized PET/MO copolymers………………………………………………100

Figure 3.38: Half time plotted as a function of degree of undercooling for PET/MO copolymers………………………………………………………………………………..100

Figure 3.39: Half time plotted as a function of crystallization temperature for isothermally crystallized PET/CHEDM copolymers………………………………………………101

Figure 3.40: Half time plotted as a function of degree of undercooling for PET/CHEDM copolymers………………………………………………………………………………..102
Figure 3.41: $\theta_a$ versus ln(t) for isothermally crystallized WA314 PET..............106

Figure 3.42: $\theta_a$ versus ln(t) for isothermally crystallized PET/MO(5wt%) copolymer.................................................................106

Figure 3.43: $\theta_a$ versus ln(t) for isothermally crystallized PET/CHEDM(3wt%) copolymer.................................................................107

Figure 3.44: ln(-ln($\theta_a$)) versus ln(t) for isothermally crystallized WA314 PET........108

Figure 3.45: ln(-ln($\theta_a$)) versus ln(t) for isothermally crystallized PET/MO(5wt%) copolymer.................................................................108

Figure 3.46: ln(-ln($\theta_a$)) versus ln(t) for isothermally crystallized PET/CHEDM(3wt%) copolymer.................................................................109

Figure 3.47: Microphotograph of WA314 PET spherulite growth at 200°C for 120 sec.................................................................................................116

Figure 3.48: Microphotograph of PET/MO(5wt%) spherulite growth at 200°C for 120 sec.................................................................................................116

Figure 3.49: Impurities in a) WA314 PET; b) PET/MO(5wt%) copolymer sample......117

Figure 3.50: Impurities in a) PET/CHEDM(5wt%) copolymer b) Pure CHEDM compound....................................................................................118

Figure 3.51: Spherulite growth for WA314 PET during isothermal crystallization at 200°C.................................................................119
Figure 3.52: Spherulite growth for PET/MO(5wt%) copolymer during isothermal crystallization at 200°C .................................................................120

Figure 3.53: Spherulite growth for PET/CHEDM(5wt%) copolymer during isothermal crystallization at 200°C .........................................................121

Figure 3.54: WA314 PET spherulite growth from the melt at 200°C ....................124

Figure 3.55: PET/MO(5wt%) spherulite growth from the melt at 200°C ...............125

Figure 3.56: Apparent intrinsic viscosity (dL/g) versus time (min) for PET/CHEDM(3wt%) copolymer .................................................................127

Figure 3.57: Apparent intrinsic viscosity (dL/g) versus time (min) for PET/CHEDM(1wt%) copolymer .................................................................128

Figure 3.58: IV comparison of PET/CHEDM copolymers (before and after SSP reaction) .................................................................129

Figure 3.59: Oxygen permeability of PET/MO, PET/CHEDM copolymer and PET sheets .................................................................131

Figure 3.60: Average oxygen permeability for PET/MO copolymer and pure PET ......132

Figure 3.61: Average densities versus concentration of scavenger ......................134

Figure 3.62: Pressure of oxygen versus time of oxidation .....................................144

Figure 3.63: Shear viscosity versus shear rate for PET/CHEDM(1wt%) copolymer .........147

Figure 3.64: Shear viscosity versus shear rate for PET/CHEDM(5wt%) copolymer .......148
Figure 3.65: Shear viscosity versus shear rate for PET/MO(5wt%) copolymer………..149

Figure 3.66: Shear viscosity versus shear rate for WA314 PET sample………………150

Figure 3.67: Melting and crystallization behavior for PET/MO(5wt%) copolymer samples………………………………………………………………………………….152

Figure 3.68: Crystallization behavior for PET/MO(5wt%) copolymer samples………152

Figure 3.69: Melting and crystallization behavior for PET/MO(5wt%) copolymer samples………………………………………………………………………………….153

Figure 3.70: Crystallization behavior for PET/MO(5wt%) copolymer samples………153

Figure 3.71: Melting and Crystallization behavior for PET/CHEDM(5wt%) copolymer………………………………………………………………………………155

Figure 3.72: Crystallization behavior for PET/CHEDM(5wt%) copolymer sample……156

Figure 3.73: Melting and crystallization behavior for PET/CHEDM(1wt%) copolymer sample…………………………………………………………………………………..157

Figure 3.74: Crystallization behavior for PET/CHEDM(1wt%) copolymer sample……157

Figure 3.75: Crystallization behavior for PET/CHEDM copolymer (from glassy state).................................................................................................................................158

Figure 3.76: Crystallization behavior for PET/CHEDM copolymer (cooling from the melt)…………………………………………………………………………………….158

Figure 3.77: Structure of pure MO………………………………………………….….162
Figure 3.78: FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C).………………………………………………………………………………………….164

Figure 3.79: Expanded FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C).……………………………………………………………………………...….…….165

Figure 3.80: Expanded FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C).…………………………………………………………………………...….….167

Figure 3.81: Plot of ln(R/R(t0)) versus time for pure monoolein……………………………..169

Figure 3.82: Plot of normalized height of double bond peak versus time for pure monoolein………………………………………………………………………………………172

Figure 3.83: Plot of ln(-rate) versus ln(CA) for pure monoolein………………………………172

Figure 3.84: ¹H NMR spectrum of pure MO (before oxidation)……………………………….178

Figure 3.85: ¹H NMR spectrum of pure MO (after oxidation for 8 days at 50°C)………178

Figure 3.86: ¹H NMR spectrum of pure MO (after oxidation for 21 days at 50°C)……179

Figure 3.87: Plot of ln(A/A0) versus time for pure MO using NMR data…………………...181

Figure 3.88: Area under double bond peak versus time for pure MO using NMR data………………………………………………………………………………………….183

Figure 3.89: ln(-rate) versus ln(CA) for pure MO using NMR data…………………………183

Figure 3.90: ¹H NMR spectrum of PET/MO copolymer sample (before oxidation)…..189
Figure 3.91: $^1$H NMR spectrum of PET/MO copolymer (oxidized for 15 days at 50°C)......................................................................................................................................................189

Figure 3.92: $^1$H NMR spectrum of PET/MO copolymer (oxidized for 39 days at 50°C)......................................................................................................................................................190

Figure 3.93: ln($A/A_0$) versus time for PET/MO copolymer using NMR data.............192

Figure 3.94: Area under the double bond peak (A) versus time for PET/MO copolymer using NMR data.................................................................................................................................193

Figure 3.95: ln(-rate) versus ln($C_A$) for PET/MO copolymer using NMR data...........194

Figure 3.96: ln(k) versus 1/T............................................................................................198

Figure 3.97: Proposed oxidation mechanism of CHEDM compound............................200

Figure 3.98: pure CHEDM (oxidized for 4 days at 50°C).................................................201

Figure 3.99: pure CHEDM (oxidized for 7 days at 50°C)..................................................201

Figure 3.100: pure CHEDM (oxidized for 10 days at 50°C)..............................................202

Figure 3.101: pure CHEDM (oxidized for 14 days at 50°C)..............................................202

Figure 3.102: pure CHEDM (oxidized for 19 days at 50°C)..............................................203

Figure 3.103: Plot of ln($C_A/C_{A0}$) versus time for pure CHEDM using NMR..............205

Figure 3.104: ln(-rate) versus ln($C_A$) for pure CHEDM using NMR.........................207
Figure 3.105: $^1$H NMR spectrum of PET/CHEDM copolymer without catalyst (oxidized)……………………………………………………………………………………………………208

Figure 3.106: $^1$H NMR spectrum of PET/CHEDM copolymer with catalyst (oxidized for 9 days)……………………………………………………………………………………………………208

Figure 3.107: Plot of ln($C_A/C_{A0}$) versus time for PET/CHEDM copolymer using NMR……………………………………………………………………………………………………211

Figure 3.108: GC-MS of pure Air…………………………………………………………………221

Figure 3.109: GC-MS of pure Monoolein……………………………………………………222

Figure 3.110: GC-MS of PET/MO copolymer…………………………………………………222

Figure 3.111: GC-MS of pure CHEDM……………………………………………………224

Figure 3.112: GC-MS of PET/CHEDM copolymer………………………………………………224

Figure 3.113: Analysis of pure Acetaldehyde using GC………………………………………225

Figure 3.114: Analysis of pure MO (oxidized for 7 days at 50°C) using GC………………226

Figure 4.1: Potential oxygen scavengers…………………………………………………………236
List of Tables

Table 1.1: Physical properties of scavengers.................................................................23

Table 2.1: Chemical names and their usages in this research.................................26

Table 2.2: The acquisition parameters of INOVA-600 MHz NMR..........................31

Table 2.3: IR band assignments.....................................................................................40

Table 3.1: Melt IV calculation for PET/MO copolymers at shear rate = 10 sec⁻¹......75

Table 3.2: Melt IV calculation for PET/CHEDM copolymers at shear rate = 10 sec⁻¹…77

Table 3.3: Physical parameters measured for PET/MO copolymers from DSC analysis.........................................................................................................................82

Table 3.4: Physical parameters measured for PET/CHEDM copolymers from DSC analysis.........................................................................................................................85

Table 3.5: Equilibrium melting points of PET/MO, PET/CHEDM copolymers, and WA314 PET ........................................................................................................................................................................97

Table 3.6: Half time values at different crystallization temperatures for PET/scavenger copolymers, and WA314 PET......................................................................................................................103

Table 3.7: Values and mechanism of the Avrami exponents ....................................105
Table 3.8: n and k values for PET/scavenger copolymers and WA314 PET ………..110

Table 3.9: n and k values for PET/scavenger copolymers using half time method …..114

Table 3.10: Spherulite radius versus isothermal crystallization time for WA314 PET at 200°C……………………………………………………………………………………..123

Table 3.11: Spherulite radius versus isothermal crystallization time for PET/MO(5wt%) copolymer sample at 200°C…………………………………………………...………..123

Table 3.12: Spherulite radius versus isothermal crystallization time for PET/CHEDM(5wt%) copolymer sample at 200°C………………………………………………….124

Table 3.13: Calculation of specific gravity and density…………………………………135

Table 3.14: Melting and crystallization behavior for PET/MO(5wt%) copolymer samples………………………………………………………………………………….154

Table 3.15: Crystallization behavior for PET/MO(5wt%) copolymer samples………..154

Table 3.16: Melting and crystallization behavior for PET/CHEDM copolymer samples………………………………………………………………………………….159

Table 3.17: Crystallization behavior for PET/CHEDM copolymer samples………..160

Table 3.18: IR band assignments……………………………………………………163

Table 3.19: Height of double bond peak versus time of oxidation for pure MO using FTIR………………………………………………………………………………….166

Table 3.20: Order of reaction and k values for pure MO using FTIR data……………..176
Table 3.21: Area under double bond peak (A) versus time for pure MO using NMR…179

Table 3.22: Order of reaction and k values for pure MO using NMR data……………185

Table 3.23: Area under double bond peak versus time for PET/MO copolymer using
NMR………………………………………………………………………………………190

Table 3.24: Order of reaction and k values for PET/MO copolymer using NMR data…196

Table 3.25: ln(k) versus 1/T…………………………………………………………………199

Table 3.26: Area under oxidation byproduct peak versus time for pure CHEDM using
NMR………………………………………………………………………………………203

Table 3.27: Relative area under oxidation byproduct peak versus time for PET/CHEDM
copolymer using NMR…………………………………………………………………209
Chapter 1

Introduction

For many foods and beverages, a fundamental requirement for shelf stability is the minimization of oxygen exposure and thus minimal possible reaction with the food. Part of the total exposure within a plastic package is caused by desorption from and permeation through the sidewall. Common problems associated with the presence of oxygen in food products include color degradation, microbial spoilage, nutrient loss, as well as flavor and odor changes. Reduction or total removal of headspace oxygen, along with the prevention of its ingress, has been shown to minimize oxidative effects and prolong product shelf life while improving quality. A highly effective method of minimizing oxygen exposure is to provide a scavenger within the package wall, engineering its placement within a multilayer structure or incorporating it as a compatible component within a monolayer structural polymer.

Poly(ethylene terephthalate) (PET) is a commercially important aromatic polyester. It is formed by either direct esterification of ethylene glycol (EG) with terephthalic acid (TPA) or by transesterification of dimethyl terephthalate (DMT) with ethylene glycol [1,2]. The repeat unit of PET has the following molecular structure (Figure 1.1):
Figure 1.1 Chemical structure of PET

PET is a widely used packaging polymer because of its balance of features, including excellent transparency, good gas and flavor component barrier, ease of melt processing, high strength, thermal resistance, environmental safety, and recyclability [2,3]. Its oxygen barrier properties; however, are not adequate for highly oxygen sensitive food and beverage products that include components that can be readily oxidized at ambient shelf-storage conditions. Adding an active oxygen scavenger directly into PET material can significantly improve the oxygen barrier properties of PET.

1.1 Active oxygen scavenger

An active oxygen scavenger is a substance capable of intercepting and scavenging oxygen by undergoing a chemical reaction with the oxygen, as the oxygen permeates through the polyester packaging wall (as shown in Figure 1.2). An important feature of active oxygen scavengers is their ability not only to intercept oxygen permeating through the polyester packaging wall, but also to eliminate unwanted oxygen from within the container’s headspace. Active oxygen scavenging implies transformation of a material incorporated in the package as it reacts with and depletes oxygen. The material is gradually consumed so that the active oxygen scavenging ability is ultimately depleted.
This eventual depletion of the active oxygen scavenging moiety can be adjusted so that the depletion occurs only well after the required oxygen free shelf life of the copolyester container.

There are at least two separate considerations involved in development of materials and methods that could be used to improve the oxygen scavenging properties of PET. First, it is necessary to identify a list of materials which may possess high oxygen scavenging capacity so that only small amounts of such materials would be required for use in fabricated form. Second, it is necessary to devise means for incorporating the more promising scavenging substances into the polyesters bottles to form desirable oxygen scavengers.

Preferred materials

- Branched diols with mono-unsaturation in short side chain
- Branched diols with cycloalkene unsaturation in side chain
- Branched diols with mono- or di-unsaturation in fatty acid (C$_{18}$) side chain; possibility of thermal cyclization to cyclopentenyl or cyclohexenyl ring
- Branched (disubstituted) diols with no tertiary H and mono-unsaturation on each branch
- Co(II) salts of selected fatty acids, with chain structure selected for potential co-crystallization
- Co(II) complexes, with complexation (ligands) chosen for miscibility in modified polymer and demonstrated catalytic activity for oxidation and polymerization in unsaturated systems
1.2 Polymerization of PET/scavenger copolymers

PET/scavenger copolymers can be prepared by two major approaches differing in the starting raw materials used: the terephthalic acid (TPA) and ethylene glycol (EG) approach, and the dimethyl terephthalate (DMT) and EG approach. In both methods, the diester bishydroxyethyl terephthalate (BHET) is formed either by the direct esterification of TPA and EG or by the transesterification of DMT and EG, with water or EG as the byproduct. The melt phase polycondensation of BHET and scavenger produces PET/scavenger copolymer and EG at a higher temperature than the melting point of the copolymer and well above the boiling point of EG. Diethylene glycol (DEG) can be formed as a byproduct in the last stage of esterification or the early stage of polycondensation of BHET. DEG contents can be varied according to temperature,
residence time, type of catalyst, and TPA/EG ratio [4,5,6,7]. The catalysts used in melt phase polycondensation of PET include acetates of antimony (Sb), zinc (Zn) or lead (Pb), oxides of Sb, Pb, or germanium (Ge) and organotin compounds [2]. The conditions and steps for melt phase polymerization are shown in Figure 1.3.

Although melt phase polymerization can increase molecular weight higher than a molecular weight value corresponding to an intrinsic viscosity value of 0.80 dL/g, that process can lead to resin quality problems due to the degradation caused by high temperatures and long residence times. Solid state polymerization (SSP) is done under relatively moderate thermal conditions. The important roles of solid state polymerization are to increase molecular weight with less thermal degradation than melt phase polymerization and to reduce the levels of byproducts such as acetaldehyde, and oligomers to acceptable levels. The normal SSP temperature range is from 200-220°C and this temperature can be changed according to melting point of PET [4]. Many variables can be involved in the SSP process. Precursor molecular weight, pellet size, and SSP temperature are the most important factors, because these factors influence SSP kinetics [8].

The basis for the concept that active oxygen scavenger will be added in melt phase polymerization (in situ polymerization) is that the end-groups of active oxygen scavenger can react with the end-groups of PET. This allows the random distribution of scavenger in the copolymer, because of the random distribution of end groups of PET. Active
oxygen scavenger can be added during the early stage of esterification or the early stage of polycondensation of BHET.

\[
\begin{align*}
[1^{\text{st}} \text{step in melt polymerization}] & \\
\text{DMT} + 2 \text{EG} & \xrightarrow{\text{catalyst}} \text{BHET} + 2 \text{CH}_3\text{OH} \\
& \text{190~230°C} \\
\text{TPA} + 2 \text{EG} & \xrightarrow{\text{pressure}} \text{BHET} + 2 \text{H}_2\text{O} \\
& \text{210~240°C} \\
[2^{\text{nd}} \text{step in melt polymerization}] & \\
\text{BHET} & \xrightarrow{270~290°C} \text{PET} + \text{EG} \\
& \text{catalyst, colorant, stabilizer, vacuum}
\end{align*}
\]

Where,

\[
\begin{align*}
\text{DMT}; & \\
\text{TPA}; & \\
\text{EG}; & \\
\text{BHET};
\end{align*}
\]

Figure 1.3 Melt polymerization steps in PET and additives

### 1.3 Reaction analysis of PET/scavenger copolymers

The most common techniques used to elucidate copolymer structures are nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The reaction-monitoring techniques that can be used for in-situ observation of chemical changes in reactive scavengers are the following:
In nearly all forms of packaging, oxygen is introduced to the food products from three major sources. The most obvious source of oxygen is the headspace gas [9], which surrounds the product in all non-vacuum packages. A modified atmosphere package (MAP) environment is commonly used with oxygen sensitive products. In a MAP situation, the initial air is removed from the package and replaced with a single gas or mixture of gasses, usually with reduced oxygen. With even the best MAP flushing systems, it is difficult to remove all of the oxygen from the package headspace. The result is free oxygen in the package, which is available to interact with the product.

The second source of oxygen is ingress oxygen through the package itself. Although barrier technology has advance greatly over time, the perfect oxygen barrier for flexible polymeric films remains elusive. Glass and metal are considered to be total oxygen barriers but their incorporation into flexible packaging has consistently posed problems. Over the shelf life of a product, oxygen is constantly permeating into the package. The
reduced oxygen environment in vacuum and MAP packages creates a partial pressure
difference and a driving force, which can in effect increase the rate of oxygen permeation
into the package. Even with the use of high barrier packaging materials, extended shelf
lives can result in detrimental amounts of oxygen reaching the product.

Air, which is entrapped in the product itself, is the final source of oxygen available
for oxidative reactions. Entrapped or dissolved oxygen is commonly overlooked or
ignored during the packaging process. Over time, this trapped oxygen can migrate out of
the product and into the headspace resulting in elevated oxygen levels. Increased
microbial activity or color change reactions are a common result. Oxygen that remains
trapped in the food product can accommodate accelerated oxidation reactions due to the
autocatalytic nature of these reactions.

Some attempts have been made to modify PET in order to reduce its inherent
oxygen permeability as a passive (non reactive) polymer as discussed in the following
section.

1.4.1 PET as a passive barrier

1.4.1.1 Copolymerization

These attempts generally involve either copolymerization or reactive processing
(such as reactive extrusion) in order to introduce main-chain segments with increased
polarity (amide groups) [10], increased polarizablity (naphthalene groups) [11] or a kink
in the main chain (isophthalate groups) [12] to achieve better packing. The resultant
copolymers (at roughly 1-12 % comonomer substitution for the terephthaloyl unit) have
varied degrees of randomness along the linear chain and may be classified as either polyesteramides or copolyesters.

Copolymerization has been widely used in commercial bottle-grade PET to maintain clarity during processing, by retarding crystallization. Here, the resin manufacturer [13] often utilizes a cycloaliphatic diol (cyclohexanediol), which disrupts long-range order somewhat and provides an increased manifold of conformational states (i.e. degrees of freedom) that can be adopted along the main chain. At 1-5 mole% comonomer substitution, these copolymers achieve high transparency, slightly less density (packing is poorer) and slightly more flexibility (the cyclohexane ring is much less rigid than benzene ring) than homopolymer PET. This flexibility in the chains leads to slightly higher permeability to small molecules.

The underlying assumption in the approaches just mentioned is that the primary structure of the linear polymer – the components of the repeat unit, its spatial regularity and connectivity – determines both the interchain attraction and the effectiveness of packing in phases that may develop during processing. Interchain attraction is measured by an indicator such as cohesive energy density (CED) and the effectiveness of packing is measured by an indicator such as free volume f(V). Maximal CED and minimal f(V) lead to very low permeabilities for small molecules such as oxygen.
1.4.1.2 PET nanocomposite

There are many companies developing PET nanocomposites having enhanced gas barrier properties, but commercialization is still to come. The Poly(ethylene terephthalate) (PET)/clay nanocomposites have been studied since 1990. The primary objective of the development of PET/clay nanocomposites is to improve the oxygen barrier property that is required for beverage and food packaging. These nanocomposites are commonly based on polymer matrices reinforced by nanofillers such as layered polysilicates and silica-titania oxides, silica beads, cellulose whiskers, zeolites as well as colloidal dispersion of rigid polymers and many others [14,15,16,17]. The major drawbacks in PET/clay nanocomposites are discoloration, haze, and agglomerated clay particles in the PET matrix [18,19,20,21,22,23,24]. The improvement in barrier properties has generally not been up to the expected level, because of agglomeration of the clay particles [18]. Another disadvantage of PET/clay nanocomposites is that with this system the headspace oxygen cannot be removed. The oxygen will be available to interact with the food products inside the container and ultimately will reduce product shelf life.

Another approach can be taken with PET as the starting point. Instead of trying to modify the chain to reduce (passive) permeability, one can conceive of chain modifications designed to improve the oxygen barrier properties by the use of oxygen scavengers.
1.4.2 PET modified with oxygen scavengers

The most conventional approach has been the use of a metal-based scavenger such as iron. In these systems, the finely powdered activated metal enters the oxide state when exposed to the appropriate humidity condition, effectively binding oxygen in the process. Metal-based scavengers can exist in several forms. The most common form is the sachet, where the ground metal is packaged in a highly permeable pouch. Other metal-based scavengers include labels, coatings and extrusion additives, which incorporate the metal compound. A disadvantage of the iron-based oxygen scavenger is that it is dependent on moisture to initiate and maintain the scavenging reaction.

The second approach uses low molecular weight organic reducing agents, such as ascorbic acid and sodium ascorbate, and enzymic oxygen scavenger systems, glucose oxidase or ethanol oxidase, which would be incorporated into sachets, adhesive labels, or immobilized onto packaging film surfaces.

The third approach uses polymer modifications designed to enhance reactivity with oxygen, in other words to utilize the modified PET itself as an oxygen scavenger. The two main avenues to this approach include:

(i) Introducing more-readily oxidizable groups into the main chain, or

(ii) Introducing oxidizable pendant groups (side chains) which are not present in unmodified PET
1.4.2.1 PET modified with oxidizable groups in its main chain

The aforementioned polyesteramide [10] is actually an unintentional example of approach avenue (i), because the amide linkage –C(O)–N(H)– is considerably more susceptible to oxidation than the ester linkages –C(O)–O–.

Another example of approach avenue (i) is the classic Oxbar® system [25]. It consists of an extruded blend of the aromatic polyamide MXD6 and PET, along with a metal (oxidation) catalyst. It is likely that significant amide-ester interchange occurs during the extrusion process at 280 - 300°C forming a polyesteramide component within the resultant multiphase polymer dispersion. The Oxbar® system has been demonstrated to react with oxygen at room temperature for long periods of time, thus reducing transmission rates to near zero in monolayer or multilayer structures. This material is a highly effective scavenger system, when incorporated into packaging. The reaction with oxygen, however, results in chain scission, which ultimately results in low MW products as amide sites are attacked along the chain. The blends of MXD6 and PET do not generally show good clarity, since they are incompatible and hence produce a multiphase blend.

A copolyester has been prepared with PET, using a long-chain fatty diol (the C36 dimer of two unspecified C18 chains with unspecified degree or location of unsaturation, having terminal α,ω hydroxyl groups) [10]. This copolyester is technically a ‘linear’ polymer with no pendant chain, but the C18 segments are geometrically in a pendant disposition relative to the main chain axis and may be readily oxidizable at the double bonds. Such an oxidation will result in chain scission although the MW of most scission
products will be fairly large (chain length of 12 – 30 carbons plus one or two terephthaloyl units). Some of the oxidative cleavage products will be low MW if the C₃₆ dimer is highly unsaturated. However, as with most oxidations of unsaturated compounds [26], oxidative cleavage (chain scission) will compete with other oxidative reactions at the double bonds that do not result in chain cleavage, for example, epoxidation followed by ring opening by active hydrogens to form ether linkages, hydroxyl functionalities or adjacent hydroxyls (α-diols). These are propagation-like reactions leading to cross-linking and network formation.

A patent, which is the basis for at least some of the Amosorb® technology developed by BP Amoco, discloses the preparation of copolyesters incorporating polybutadiene segments (blocks) into the main chain of PET or the trimethylene (PTMT) or butylenes (PBT) analogs [27]. The copolyesters are formed (presumably by transesterification) during reactive extrusion in which the starting materials are PET and α, ω – hydroxy polybutylene oligomers of approximately MW 1000-3000, along with a metal (Co) catalyst. These are believed to be linear copolymers, and when incorporated at loadings of 4 – 12 wt% in the copolymer, the polybutadiene segments confer significant oxygen-absorbing capacity. Interestingly, the polybutadiene segments are long enough and mobile enough to be able to aggregate into more or less organized olefin-rich domains of diameters of approximately 0.5 to 1 μm, thus substantially affecting the optical properties of the solid copolyester.
1.4.2.2 Advantages of PET modified with oxidizable groups versus sachet and iron based films

The benefits of using an oxygen scavenging film versus a sachet are numerous: Oxygen scavenging films are designed to overcome the harmful effects of oxygen with food. The films absorb residual headspace oxygen that even the best gas flushing and vacuum systems cannot remove. Entrapped or dissolved oxygen is pulled away from the food product resulting in improved flavor and color profiles in highly oxygen sensitive products. Finally, oxygen scavenging films act as a total active barrier layer, stopping oxygen ingress before it reaches the food product.

Iron based oxygen scavengers (films or sachets) generally are dependent on moisture to initiate and maintain the scavenging reaction. Oxygen scavenging films are completely independent of moisture.

Oxygen scavenging films address both consumer and producer needs. The scavenger is invisible and does not change the package appearance. Product quality is enhanced through reduced oxidative reactions, providing fresher, more natural food products, without the use of chemical antioxidants.

Finally, the system is capable of reducing headspace O₂ levels from 1% to ppm levels in 4 - 10 days - comparable with oxygen scavenging sachets. The system works in a wide range of environments from ambient storage to refrigeration. No moisture or external stimulus is needed to sustain the reaction and the reaction is not affected by the presence of other headspace gasses such as nitrogen or carbon dioxide.
1.4.2.3 Disadvantages of PET modified with oxidizable groups

The reaction with oxygen of PET modified with oxygen scavengers in its main chain (for example, blends of MXD6 and PET) results in chain scission, which ultimately results in low MW products as amide sites are attacked along the chain. This problem can be overcome if PET is modified with oxidizable pendant side groups. The idea is that when oxygen will react with the oxidizable pendant groups, then it will not lead to chain scission of the main PET chain and also, it will not impart oxidation byproducts to the packaged material.

Another disadvantage of the blends of MXD6 and PET is that they do not generally show good clarity, since they are incompatible and hence produce a multiphase blend.

1.4.3 PET with non-oxidizable pendant groups

It has been found that there are no intentional examples of approach avenue (ii) in the literature of polyesters, for example, deliberate introduction of oxidizable pendant groups for the purpose of promoting reaction with oxygen. Branched diols have been used to prepare mono- or disubstituted polyesters [28] with –O–CH(CH₃)–C–O– or –O–C(CH₃)₂–C–O– aliphatic linkages, where the pendant group is the unreactive methyl. Longer branched diols such as 2,5-hexanediol, 2-methyl-2,4-pentanediol and 3-methyl-2,4-pentanediol have been used in forming copolyesters with PET [29]; here too the pendant group is methyl. It has been noted that these substitutions affect thermal properties (T_g, T_m) and inhibit crystallization, but that the methyl-substituted polymer or copolymer is compatible with PET and does not phase separate.
Other copolymers of PET have been prepared [30] with longer branched diols including ethyl, n-butyl and longer alkyl chains up to C\textsubscript{19}. All of these were saturated alkyl chains and thus not reactive. Major effects were found for melt viscosity, crystallization and melting behavior and thermal shrinkage as side chains became longer than C\textsubscript{12}. Increase in dye uptake and moisture regain were also found, since these characteristics are enhanced by larger free volume. Increased resistance to alkali hydrolysis at the ester linkage and presumably also at the ether linkage was found for gem-disubstituted copolymer (i.e., containing repeat units from a 2,2-dialkyl-1,3-propanediol comonomer). This lower reactivity was attributed to steric hindrance from the bulky alkyl groups. A separate melting peak was observed for copolymers with C\textsubscript{16} or C\textsubscript{19} side chains. This implies an organized side-chain phase in the solid.

Substitution on the aryl ring of phthalate polyesters can be considered a modification that introduces pendant groups. Examples exist of methyl, halogen or sulfonate substitution on the ring of PET or of polyethylene isophthalate or of the similar poly(p-oxybenzoyl) [31,32]; these polymers are not particularly oxidatively unstable. I do not find published examples of PET with longer chain ring substituents.

A branched modification of PET has been achieved [33] by co-reacting a trifunctional or tetrafunctional polyol (glycerol or pentaerythritol, respectively) with the normal PET monomers; the polymer structure may be considered to be a linear PET copolymer with random side chains (at 2 to 7 mole\% of the linear repeat units) of PET. Depending on the functionality (3 or 4), the substitution is either mono- (using glycerol) or gem-disubstitution (using pentaerythritol) on the linear chain. These polymers are not
expected to have especially oxidizable side chains, although it was noted that the hydrolytic stability was decreased relative to that of normal PET.

1.4.4 PET with oxidizable pendant groups

It has been found that there are no published attempts to prepare side-chain modified PET in which pendant groups can be readily (or controllably) oxidized. The current research will therefore focus on the use of pendant C=C double bonds that will be designed to minimize rupture of the polymer backbone during oxidation. Substituted aliphatic unsaturated compounds and substituted cyclic olefinic compounds can be potential scavengers which can be incorporated into PET to improve its active barrier properties.

In this research, the approach of using autoxidation of unsaturated groups on a polymer as a basis for oxygen scavenging has been used. The oxidizable moieties are cyclohexene side group, and unsaturated side group bound to the backbone. The novelty in the process of using cyclohexene side group lies in its apparent “tasteless” achievement of oxygen removal [34]. The earlier approaches involving autoxidation of non-cyclic side groups are claimed to have imparted some taste to the food.

1.4.5 Projected advantages of PET modified with oxidizable pendant groups

The following advantages can be achieved by modifying PET with oxidizable pendant groups:

- Transparency – probably will not crystallize
- Compatibility with PET – should be fully miscible
• Oxidative cleavage of reactive groups should not result in linear (PET) chain scission
• Oxidation of selected side chains (cycloalkenes) should result in no low-MW products [35]

1.5 Oxygen transmission rate / Permeability

There are four different types of technologies which are used for improvement in barrier technology [36]:

1. Coatings (vacuum deposited and organic barrier)
2. Blends of barrier polymers and existing polymers
3. Nanocomposite materials
4. New active barrier polymers

One common objective of these four technologies is to develop plastic containers capable of protecting the contents from oxidation for longer period of time. Some of these technologies have been commercially available, but others are still under development.

Barrier property improvements with new active barrier polymers are still a developing area so that only very few patents and articles have been reported. The Oxbar® system is reported to provide virtually total barrier to oxygen ingress for as long as the reactants are present. For example, in 1-liter PET only versus PET/MXD6 (4%)/Cobalt blend bottles, the reference PET bottle shows an oxygen transmission value of 3.5 cc/m²/day at room temperature, whereas the equivalent Oxbar® variable has a transmission value of less than 0.04 cc/m²/day [25]. According to the Amosorb®
technology, polybutadiene segments, when copolymerized at loadings of 4 – 12 wt% with PET, provide significant improvement in the oxygen barrier properties of PET [27].

The idea of adding active oxygen scavenger into the PET matrix is that the scavenger could delay the induction time period of oxygen transmitted into the PET container and then after some time, achieve a steady state similar to that of pure PET as shown in Figure 1.4.

![Figure 1.4 Advantage of active oxygen scavenger](image)

1.6 **Rationale and objectives**

In order to improve the gas barrier properties of a PET material, it can be modified with oxygen scavengers. In the packaging industry, the clarity of the container is also important. The most important factor required to achieve a low haze value is that the
scavenger should be compatible with PET or in other words, it should be fully miscible with PET. When the scavenger is compatible with PET or the scavenger is reactive with PET and the PET/scavenger copolymer is stretched and oriented, then there will not be any phase separation which will prevent haze and also, the copolymer will have better barrier properties because of the absence of microvoids in the copolymer after stretching. It has been seen that the generation of microvoids after stretching can lead to an increase in the oxygen permeability through PET/clay nanocomposite [18].

Another important aspect of this research is the selection of active oxygen scavengers. The type of scavenger selected will play an important role in PET/scavenger copolymer formation, because the nature of the scavenger will influence the rheological properties, the release of oxidation by-products, and the improvement of properties.

The overall objective of this project is to synthesize and characterize new active barrier polymers. When the active oxygen scavengers are incorporated into a PET matrix, significant improvement in its oxygen barrier property is expected. There are very few patents/articles available on PET modified with oxidizable pendant groups in the literature. In this research, an in situ polymerization method is selected to develop PET/scavenger copolymer and two different scavengers have been used. The current research investigates in detail the effectiveness of the active oxygen scavengers in reducing the oxygen concentration, which is desorbed from and permeated through the polymer and this research also involves the development of a methodology to determine the scavenging capacity of potential oxygen scavengers. The two scavengers, used in this
research, will be analyzed in terms of their: reaction with PET, overall reduction of oxygen, and effects upon the properties of PET. According to these considerations, the detailed objectives are categorized into three parts.

The first step of this study will be to focus on the in situ polymerization method for synthesis of PET/scavenger copolymer and evaluation of the reaction between PET and the scavengers. Several studies [12,13,18,24,37-43] have been reported concerning synthesis of PET copolymer and PET nanocomposite by an in situ polymerization method; however, I have been unable to find a synthesis process and detailed studies such as the effect of polymerization variables on properties obtained for a PET/scavenger copolymer. The best conditions for melt polymerization were set up with the melting point of PET/scavenger copolymers. Nuclear magnetic resonance (NMR) spectroscopy was performed to evaluate the reaction between PET and the active oxygen scavengers by studying the reactions between end-groups of PET and the hydroxyl end-groups of scavengers.

The addition of oxygen scavenger may affect the physical properties (e.g., melt viscosity, thermal and crystallization behavior) of PET. Improving the barrier properties of PET is a concern, however, not at the cost of sacrificing the overall physical appearance and properties of PET. The second objective in this research is to investigate the effect of scavenger on properties such as thermal, rheological, and barrier properties of PET/scavenger copolymer.

The third step of this study will be to focus on determining oxidation kinetics of PET/scavenger copolymers. This will be performed by studying the unsaturated peak
(i.e., double bond peak, where oxygen reacts with scavenger) present in scavenger using IR and NMR spectroscopy. Finally, a methodology will be developed to determine the scavenging capacity of potential oxygen scavengers. This will enable prediction of the applicability of the potential oxygen scavengers to scavenge oxygen efficiently, even before synthesizing the copolymer of PET/scavenger.

An additional objective in this research is to investigate the effects of catalyst (added to enhance the rate of oxidation) on thermal and rheological properties of PET/scavenger copolymers. The cobalt octoate catalyst is added just before extruding sheets of the copolymers using single screw extruder. This investigation will give an understanding about the degradation resulting from the addition of a catalyst after extruding sheets of PET/scavenger copolymers.

1.7 Selection of active oxygen scavengers for this research

The oxygen scavengers which have been used in this research are monoolein (MO), which is a branched diol with mono-unsaturation in its side chain and 3-cyclohexene-1,1-dimethanol (CHEDM), which is a branched diol with cycloalkene unsaturation in its side chain. Advantages of these scavengers are described below: Both scavengers have hydroxyl end-group which can react with end-groups of PET forming copolymers. There will not be a multiphase structure and therefore there will not be a phase separation which can, otherwise, cause the haze problem. MO as well as CHEDM scavengers are both auto-oxidizable compounds.
Another important advantage of selecting CHEDM compound is that it does not fragment as it oxidizes, thus avoiding the problem of imparting oxidation byproducts to the packaged material. In addition to these advantages, both of these scavengers will be present as side chains to the main long PET chains, therefore, if the oxidative cleavage occurs it will occur at the double bond which is not a part of main PET chain and ultimately, there will not be any significant molecular weight loss. The physical properties of these scavengers are tabulated in Table 1.1. Structures of both of these scavengers are given in Figure 1.5.

Table 1.1 Physical properties of the scavengers

<table>
<thead>
<tr>
<th>Factors</th>
<th>Monoolein</th>
<th>3-Cyclohexene-1,1-dimethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Pale Yellow Semi-Solid/Oily Liquid</td>
<td>White – Beige Crystalline Powder</td>
</tr>
<tr>
<td>Melting Point</td>
<td>35 – 36 °C</td>
<td>88 – 90 °C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>238 – 239 °C</td>
<td>-</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C_{21}H_{40}O_{4}</td>
<td>C_{8}H_{14}O_{2}</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>356.55 g/mol</td>
<td>142.2 g/mol</td>
</tr>
</tbody>
</table>
Figure 1.5 Structures of scavengers (a) Monoolein, (b) 3-Cyclohexene-1,1-dimethanol
Chapter 2

Experimental

2.1 Materials

Terephthalic acid (TPA) was kindly donated by Amoco Chemical Company, USA. Ethylene glycol (EG) (polyester grade) was purchased from Superior Solvents and Chemicals, USA. Monoolein (MO) was obtained from City Chemical, USA. 3-cyclohexene-1, 1-dimethanol (CHEDM), cobalt acetate, tetramethylammonium hydroxide, phosphoric acid, and antimony trioxide were obtained from Acros Organics, USA. Chloroform and trifluoroacetic acid (d-TFA) were purchased from Fisher Chemicals, USA. Chloroform (deuterated) was purchased from Cambridge Isotope Laboratories Inc., USA and cobalt octoate was provided by Shepherd Chemicals, USA. All the monomers supplied were polymerization grades, so that they could be used without any further purification. Table 2.1 shows all the chemical names and their usages in this research.
Table 2.1 Chemical names and their usages in this research

<table>
<thead>
<tr>
<th>Name</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalic acid (TPA)</td>
<td>Monomer</td>
</tr>
<tr>
<td>Ethylene glycol (EG)</td>
<td>Monomer</td>
</tr>
<tr>
<td>Monoolein (MO)</td>
<td>Active oxygen scavenger</td>
</tr>
<tr>
<td>3-cyclohexene-1,1-dimethanol (CHEDM)</td>
<td>Active oxygen scavenger</td>
</tr>
<tr>
<td>Cobalt acetate</td>
<td>Colorant</td>
</tr>
<tr>
<td>Antimony trioxide</td>
<td>Catalyst</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>Metal stabilizer</td>
</tr>
<tr>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>Diethylene glycol (DEG) suppressor</td>
</tr>
<tr>
<td>Cobalt octoate</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>

2.2 Melt polymerization

The copolymer of PET and active oxygen scavenger (AOS) was melt polymerized in a batch scale polymerization system (RTI Engineering Co. Ltd., South Korea) equipped with 2 reactors (esterification reactor and polycondensation reactor). Each reactor has a 3 liter capacity so that 1–2 kg PET resin per batch can be produced. An anchor type stirrer was used in the esterification reactor, whereas the polycondensation reactor was equipped with a helical type stirrer to increase stirring efficiency as shown in Figure 2.1. The copolymer melt polymerization process consisted of 2 steps (esterification and polycondensation).
In the first step, TPA and EG were mixed and reacted at 220~245°C under 1 kgf/cm² of N₂ in the esterification reactor in order to prepare BHET. Tetramethyl ammonium hydroxide (100 ppm) was also added as diethylene glycol (DEG) suppressor. 1 Kg TPA was used to react with 560 g of EG, so the mole ratio of ethylene glycol/terephthalic acid was 1.5:1. During the reaction, the byproduct, which is water, was removed from the reaction mixture. At the end of the esterification reaction, BHET was removed from the reactor and collected in a container. It took about 355 minutes to complete the esterification reaction. The mole ratio of ethylene glycol/terephthalic acid was calculated as follows:

\[
\begin{align*}
\text{EG} & \quad - \quad 560 \text{ grams} \\
\text{TPA} & \quad - \quad 1000 \text{ grams} \\
\text{Molecular weight of one molecule of EG} & \quad = \quad 62 \text{ g/mol} \\
\text{Molecular weight of one molecule of TPA} & \quad = \quad 166 \text{ g/mol} \\
\text{Therefore,} \\
\text{Moles of EG} & \quad = \quad 9.03 \text{ moles} \\
\text{Moles of TPA} & \quad = \quad 6.02 \text{ moles} \\
\text{Mole ratio of EG/TPA} & \quad = \quad 1.5:1
\end{align*}
\]

In the second step, crushed BHET of 1250 g was dried at 130°C overnight, and then melted in the polycondensation reactor at 250°C for 2 hours under nitrogen (0.2 kgf/cm² pressure). After BHET was melted, active oxygen scavenger, catalyst (antimony trioxide), colorant (cobalt acetate), and a thermal stabilizer (phosphoric acid) were added.
and then pressurized with N₂. The amounts of additives used for the polycondensation reaction were 250 ppm Sb, 30 ppm Co, 20 ppm P, and 12.5-62.5 g of scavenger. These were added in the early stage of the polycondensation reaction. These additives were put into the reactor at the same time with stirring and nitrogen flowing to prevent thermo-oxidation while the additives were added. Before adding the additives, antimony trioxide was mixed with ethylene glycol and heated up to 150°C for 2 hrs to form antimony glycolate. Cobalt acetate was mixed with hot ethylene glycol to prepare an additive solution. The polycondensation reaction was performed at 270~280°C under high vacuum (1~2 torr) for about 285-345 minutes.

Figure 2.1 Schematic diagram of melt polymerization reactor

* Each reactor size: 3 liter capacity
* Additives
- Monoolein (1wt% and 5wt%)
- 3-cyclohexene-1,1-dimethanol (1wt%, 3wt% and 5wt%)
- 250 ppm Sb, 30 ppm Co, 20 ppm P (these all are elements amounts and ppm in terms of total reaction mixture)
- Antimony trioxide was mixed with ethylene glycol and heated up to 150°C and held at this temperature for 2 hours
- Cobalt acetate was mixed with hot ethylene glycol and heated up to 150°C and held at this temperature for 30 minutes

2.3 Preparation of the physical blends

To confirm the reaction between PET and the scavengers, the samples of the PET/scavenger copolymers (synthesized through the in situ polymerization process) were compared with the physical blends of the PET/scavenger using NMR spectroscopy. For this analysis, physical blends of the PET/scavenger were prepared by grinding WA314 PET (i.e. pure PET) to powder form and then physically dry mixing it with the scavengers using a magnetic stirrer.

2.4 Extraction method

To evaluate evidence in order to prove the occurrence of an interchange reaction between PET and the scavengers, the samples of PET/scavenger copolymers (synthesized through the in situ polymerization process) and the physical blends of PET/scavenger were extracted using chloroform as a solvent. In separate procedures, about 1.5 g of each
ground sample was placed in a Kontes separatory funnel with a stopper. Then 20 ml of chloroform was put into the glass separatory funnel and the contents were shaken 2-3 times and allowed to wait until the PET settled to the top. Since the scavengers (Monoolein and 3-cyclohexene-1,1-dimethanol) are soluble in chloroform, they were extracted from the PET/scavenger copolymer samples (if the scavenger is not bonded to PET chains) and the physical blends of PET/scavenger. The solvent containing scavenger was drained through the stopcock valve leaving behind sample enriched in PET. In order to completely remove or minimize the scavenger content from the copolymers and the physical blends, the above process was repeated 3 times for each sample and the remaining polymer sample was collected in an aluminum pan. After extraction, the remaining polymer sample was vacuum dried at about 65⁰C for 5-6 hours to make sure that chloroform was completely removed.

2.5 NMR analysis

Solution proton NMR (¹H NMR) was used to study the copolymer synthesis or in other words to evaluate the occurrence of an interchange reaction between the PET chains and scavenger and it was also used to study the oxidation kinetics of the scavenger and PET/scavenger copolymers. A 70/30 (wt/wt) deuterated chloroform/trifluoroacetic acid mixture was used as a solvent to dissolve the ground samples for NMR measurements. Some of the samples exhibited overlapping peaks, thus a high resolution INOVA–600 MHz spectrometer manufactured by Varian Association Inc was used to
broaden the peaks. The following data acquisition parameters were used, in order to obtain the data and perform the required spectral analyses, as shown in Table 2.2:

Table 2.2 The acquisition parameters of INOVA-600 MHz NMR

<table>
<thead>
<tr>
<th>Spectrometer receiver frequency or field strength</th>
<th>599.876648 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectra width or spectral frequency window</td>
<td>16000 Hz</td>
</tr>
<tr>
<td>Nucleus</td>
<td>$^1$H</td>
</tr>
<tr>
<td>Original points count</td>
<td>48000</td>
</tr>
<tr>
<td>Points count</td>
<td>48000</td>
</tr>
<tr>
<td>Acquisition time</td>
<td>3 sec</td>
</tr>
<tr>
<td>Relaxation delay</td>
<td>1 sec</td>
</tr>
<tr>
<td>Numbers of transients</td>
<td>16 - 64</td>
</tr>
<tr>
<td>Line broadening</td>
<td>0.3 Hz</td>
</tr>
<tr>
<td>Spinning rate</td>
<td>20 Hz</td>
</tr>
<tr>
<td>Temperature</td>
<td>29°C</td>
</tr>
</tbody>
</table>

NMR (nuclear magnetic resonance) is a physical phenomenon based upon the quantum mechanical magnetic properties of an atom’s nucleus. All nuclei that contain odd numbers of protons or neutrons have an intrinsic magnetic moment and angular momentum. The most commonly measured nuclei are hydrogen-1 (the most receptive isotope at natural abundance) and carbon-13, although nuclei from isotopes of many other elements can also be observed. Figure 2.2 displays the instrumentation schematic of
an NMR machine. NMR studies magnetic nuclei by aligning them with a very powerful external magnetic field and perturbing this alignment using an electromagnetic field. The resulting response to the external perturbing electromagnetic field is the phenomenon that is exploited in nuclear magnetic resonance spectroscopy.

When an atom is placed in a magnetic field, its electrons circulate in the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction $\sigma$.

$$B = B_0(1-\sigma)$$

Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. Since this frequency is dependent on the strength of the magnetic field, it is converted into a field-independent value known as the chemical shift. The chemical shift is reported as a relative measure from a specific reference resonance frequency. For the nuclei $^1$H and $^{13}$C, TMS (tetramethylsilane) is commonly used as a reference. This difference between the frequency of the signal and the frequency of the reference is divided by frequency of the reference signal to give the chemical shift. The units of chemical shift are parts per million (ppm) because the difference in frequencies is usually in hertz while the frequency of the reference signal is in megahertz. By understanding different chemical environments, the chemical shift can be used to obtain some structural information about the molecule in question and to assign signals to a specific atom or a group of atoms.

$$\text{Chemical Shift (}\delta\text{)} = \frac{\text{shift observed/reference frequency}}{} \times 10^6 \equiv \text{ppm}$$
2.6 Melt IV/Intrinsic viscosity measurement

Melt IV has been reported as the equivalent intrinsic viscosity (IV) of PET. Traditionally, the intrinsic viscosity of PET is determined by a solution method. In order to simplify the measurement procedure, a standard rheometer based melting method was used to determine the intrinsic viscosity of PET. The IV of PET, obtained by this melting process, is called melt IV of PET. The procedure involves testing two sets of samples; the unknown samples, and standard PET samples. The intrinsic viscosity of standard PET samples had previously been obtained by a solution method. The zero-shear viscosities of different samples are also measured from the flow curves of the materials, where in the range the zero-shear viscosity is the viscosity which is independent of shear rate. The viscosity of materials at a shear rate of 10 sec$^{-1}$ was used to represent the zero-shear viscosity. The following relationship between melt IV and the viscosity can be obtained:

$$\text{IV (melt IV)} = m \ln(\eta^*) + b$$
Here $\eta^*$ is the complex viscosity at a shear rate of 10 sec$^{-1}$, m and b are constants, calculated by calibrating the instrument with pure PET samples of known IV’s and in this study, $m = 0.136$, $b = -0.115$. Figure 2.3 displays the relationship between complex viscosity and intrinsic viscosity of PET resin. The melt IV was measured using a Rheometric Scientific RDA III instrument. A double parallel plate geometry was used to perform the dynamic test on the polymer melt sample. The visco-elastic properties of the copolymer melt were studied as a function of frequency at a temperature of 280°C in the presence of nitrogen gas (to avoid oxidation).

Test conditions:

Diameter of die = 25 mm

Frequency sweep = 10 rad/sec

Strain = 20%

Gap between parallel plates = 1 mm

Initial frequency = 1 rad/sec

Final frequency = 100 rad/sec
2.7 Thermal analysis

Differential scanning calorimetry (DSC) was carried out on the PET/scavenger copolymer samples under a dry nitrogen atmosphere in order to study their glass transition, melting, and crystallization behaviors while heating from the glassy state and while cooling from the melt. The isothermal and non-isothermal crystallization behaviors of the PET/scavenger copolymers were also investigated. A Perkin-Elmer DSC-7 model calorimeter equipped with Pyris software for data acquisition and analysis was used for this purpose. In the thermal analysis experiment, the pellet samples were first ground into powder form and then dried in vacuum oven for about 12 hours at 120°C. The weights of the samples used for thermal experiments were between 5 mg to 10 mg. The experiment procedure was as follows:
Non-isothermal crystallization steps were:

1. Heat from 40°C to (260°C - 280°C) at 10°C/min
2. Hold for 5 min at (260°C - 280°C)
3. Cool from (260°C - 280°C) to 40°C at 300°C/min
4. Hold for 5 min at 40°C
5. Heat from 40°C to (260°C - 280°C) at 10°C/min
6. Hold for 5 min at (260°C - 280°C)
7. Cool from (260°C - 280°C) to 40°C at 10°C/min

Isothermal crystallization and remelting steps were:

1. Heat from 40°C to 260°C at 300°C/min
2. Hold for 5 min at 260°C
3. Cool from 260°C to (185°C - 220°C) at 300°C/min
4. Hold for 60 min at (185°C - 220°C)
5. Cool from (185°C - 220°C) to 40°C at 300°C/min
6. Hold for 5 min at 40°C
7. Heat from 40°C to 270°C at 10°C/min

The melting temperature \( T_m \) was determined as the temperature at which the peak maximum of the melting transition appeared in the heating run, and the heat of fusion \( \Delta H_f \) was additionally measured. From the measured thermal analysis curves, the glass transition temperature \( T_g \) was taken as the midpoint of the step change in baseline as shown in the heating run. The crystallization peak temperature \( T_c \) was determined from the peak minimum of the DSC thermogram. In addition, the heat of crystallization \( \Delta H_c \)
was measured. During isothermal crystallization of the PET/AOS copolymers and WA314 PET, all the samples were kept at a particular crystallization temperature for 60 minutes. The reason for crystallizing all the samples for 60 minutes was that the typical half time for PET/scavenger copolymers and WA314 PET is about 5 to 8 minutes at low crystallization temperatures and typically, the PET samples are crystallized for about 10 times their crystallization half times.

2.8 Solid state polymerization

From the literature [44], the application of post polymerization techniques, such as drying, further polymerization (especially solid state polymerization), to PET/scavenger copolymers in a manner similar to the techniques used on unmodified polymers has proven unsatisfactory because of problems encountered such as loss of oxygen scavenging capacity and discoloration or loss of clarity of the oxygen scavenging copolymers.

The post treatments were performed in a manner which does not significantly reduce the oxygen scavenging performance nor the clarity of the oxygen scavenging copolymer. The post treatment was done through careful vacuum drying and heating.

Solid state polymerization was utilized in order to further increase the molecular weight of the PET/CHEDM copolymer samples. In order to prepare the thermoplastic pelletized oxygen scavenging copolymer samples for the solid state polymerization operation, each material was placed in a vacuum oven capable of obtaining a vacuum of 30 inch Hg. After 15 minutes under vacuum at room temperature, the oven was slowly heated over a 1 to 2 hour period under vacuum to 140°C and was maintained at that
temperature under vacuum overnight to crystallize the product. The increased crystallinity was beneficial to prevent the pellets from sticking at the solid state polymerization temperature. After pre-crystallization, the heat was turned off and the oven was allowed to cool to reach 60°C. When the temperature reached 60°C, the vacuum was broken by introduction of nitrogen gas. The product was quickly removed and placed in the solid state polymerization reactor.

A reactor from Buhler Company, with a 1000 gm sample capacity, was used to conduct the solid state polymerization of PET/CHEDM copolymer samples at a temperature of 210°C. A schematic diagram of the SSP reactor is shown in Figure 2.4.

![Figure 2.4 Schematic diagram of Buhler Solid State Polymerization Reactor](image)
The cylindrical, stainless steel reactor with an inner diameter of 90 mm and a height of 250 mm is equipped with a gas inlet situated below the sample chamber, to permit preheated purge gas to pass through the pellet bed during solid stating. The purge nitrogen gas passes through the sample chamber in order to heat the pellets, as well as to remove volatile reaction products from the pellet atmosphere. Thermocouples at three individual locations within the reaction chamber are used to monitor pellet bed temperatures during polymerization.

The reactions times are counted only after the temperature in the middle of the reactor had reached 5°C lower than the desired reaction temperature. During the SSP process, samples were removed from the reactor at specified time intervals for further analysis.

In these experiments, the SSP temperature was 210°C. The total SSP time for each run was 8 hours and the nitrogen flow rate was 1500 L/hr. The first sample was taken from the reactor for analysis after 4 hours and subsequent samples were removed every 2 hours.

2.9 FTIR analysis

In this research, a Perkin Elmer 1600 Series fourier transform infrared spectroscopy (FTIR) instrument was used to study the oxidation kinetics of pure scavengers. A very thin layer of pure MO on a potassium bromide disc was prepared and oxidized at 50°C for different time periods. Sixty-four scans were performed for each determination. Instrument resolution was 4 cm⁻¹.
Three spectral ranges (highlighted in red in Table 2.3) have been carefully examined in relation to the interest of study; although a full range of 400 – 4000 cm\(^{-1}\) was scanned for every run. Transmission FTIR technique was applied in all the experiments. Table 2.3 represents the few important IR band assignments for IR spectrum of pure monoolein. Measurements of the heights of the peaks were performed in the absorbance mode.

Table 2.3 IR band assignments\(^{45}\)

<table>
<thead>
<tr>
<th>Wave number (cm(^{-1}))</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>723 m</td>
<td>Cis C=CH planar bend</td>
</tr>
<tr>
<td>1170 s</td>
<td>C(O)-C ester vibration</td>
</tr>
<tr>
<td>2855-2893 vs-sh</td>
<td>CH stretch (–CH(_2)- asymmetric and –CH(_3) asymmetric)</td>
</tr>
<tr>
<td>2926-2955 vs-sh</td>
<td>CH stretch (–CH(_2)- symmetric and –CH(_3) symmetric)</td>
</tr>
<tr>
<td>3010 w</td>
<td>Cis C=CH symmetric stretch</td>
</tr>
<tr>
<td>3451-3600 m (broad)</td>
<td>O-H stretch</td>
</tr>
</tbody>
</table>

* m = medium, s = strong, vs-sh = very strong-shoulder, w = weak

### 2.10 Single screw extrusion

A laboratory scale Brabender single screw extrusion was performed on PET/scavenger copolymers in order to obtain the sheet samples to be used for determination of oxygen permeability. Due to the hygroscopic nature of the PET/scavenger copolymer samples, the pelletized samples were dried overnight at a temperature of 130°C in a vacuum oven before extrusion. Extrusion temperature was 270°C in all zones and the screw speed was 80 rpm. Resin was melted by the externally
supplied heat and some shear heating between screw and barrel wall clearance. Melted resin was homogenized by screw design and passed through a sheet die. Emerging extrudate ran through a set of chilled squeeze rolls prior to collection.

Cobalt in the form of cobalt octoate (0.2wt%) was also added to a portion of the PET/scavenger(5wt%) copolymer. This cobalt octoate is a transition metal catalyst that was added before the pellets were processed through single screw extruder in order to enhance the uptake of oxygen [46]. The catalyst was essential to be added to reduce the activation energy of the oxidation reaction of the scavenger and oxygen or in other words, the catalyst is causing the oxidation reaction to occur at room temperature.

The pellets of the samples listed below were made into sheets about 0.01-0.02 cm thick by using a sheet die. All the sheet samples were stored in metal containers in the presence of nitrogen. The following sheet samples were prepared:

- PET/MO(5wt%)
- PET/MO(5wt%)/cobalt octoate
- PET/CHEDM(5wt%)
- PET/CHEDM(5wt%)/cobalt octoate
- Pure WA314 PET

2.11 Barrier property measurement

Oxygen permeability was determined by measuring the oxygen transmission rate at steady state using a whole package MoCon tester. The oxygen transmission rate is the
rate of oxygen gas passing through a film or sheet per unit of time. This test method is a
coulometric method, which follows ASTM D3985 with a test temperature of 23°C and
100% internal relative humidity. The test gas was oxygen at 50% external relative
humidity. Samples were brought to steady state, equilibrium conditions in order to obtain
reported oxygen transmission rates.

The oxygen transmission rate (GTR) was measured by the difference in the partial
pressure of oxygen between the two surfaces of the sample. The GTR was measured with
a coulometric sensor. The following equation was used to measure the GTR:

\[ GTR = (AV - BV) \times IF = \text{cc(STP)/day} \]

Where,  
- **AV** is the voltage for oxygen permeation in mV
- **BV** is the baseline voltage in mV
- **IF** is an instrument factor which accounts for the cell area and the
  conversion factor for the detector. For this experiment, IF = 1/6 cc(STP)/mV*day

Oxygen permeation is the stable value of GTR per unit of oxygen partial pressure
difference between the two surfaces. Oxygen permeability coefficient is the oxygen
permeation of unit thickness. The unit of oxygen permeability is:
\[ \text{cc(STP)*mil/100in}^2\text{*day*atm}. \]

### 2.12 Density

The density of the PET/scavenger copolymers was calculated by first determining
specific gravity of the samples and then by using appropriate correlation between specific
gravity and density. This method follows ASTM D792-98.
The specific gravity of the copolymers can then be calculated as

\[
\text{Sp gr.} = \frac{a}{a + w - b}
\]

Where,

\[a = \text{apparent weight of specimen without wire in air}\]
\[b = \text{apparent weight of specimen completely immersed and of the wire partially immersed in liquid}\]
\[w = \text{weight of wire submerged as when the sample is measured in water}\]

The density can be calculated as:

\[D_{23^\circ C} = \text{sp gr.}^{23^\circ C} \times \text{density of water at test temperature}\]

**2.13 Microscopy of PET/scavenger copolymers**

In order to elucidate the differences in growth mechanisms or differences between nucleation courses, optical microscopy and light scattering techniques were utilized.

**2.13.1 Optical microscopy**

Optical polarized light microscopy (OM) was used to observe the spherulite formation during crystallization from the molten state. OM involves looking at a sample through a high-powered Carl Zeiss Standard Universal Microscope equipped with Sony CCD-IRIS/RGB color video camera. Due to the polarization effects of spherulites, they can be seen under crossed polarized films. A detailed discussion of the theory can be found in articles written by Keith and Padden [47-48].
To crystallize the samples, a Metler FP-82 hot stage with a Metler FP90 digital controller was used. The temperature accuracy of the unit was +/- 1°C. The ground copolymer samples and WA314 PET were dried in a vacuum oven at 120°C overnight before analysis in order to minimize the hydrolytic degradation during crystallization. Following the drying period, each sample was melted at 260°C to 280°C between a glass slide and a cover slip in the hot-stage. While in the molten state, the samples were thinned by applying pressure to the top of the cover slide. The hot stage was set at the desired crystallization temperature, and the samples were crystallized isothermally. Spherulite growth was halted at a given time of crystallization by removing the slide from the hot stage at that time and then quenching it between metal plates.

2.13.2 Small angle light scattering (SALS)

The average spherulitic radius of the spherulites of each PET/scavenger copolymer samples was calculated by using small angle light scattering. The samples were prepared by using a Metler FP-82 hot stage. Figure 2.5 shows a diagram of the small angle light scattering apparatus used. The laser was a Uniphase model number 155SL-1. It emits red light at a wavelength of 0.6358 microns.

![Diagram of small angle light scattering setup](image)

Figure 2.5 Diagram of small angle light scattering setup
2.14 GC-MS analysis

During the oxidation of PET/scavenger copolymers and pure scavengers, small molecules of oxidation product can be released into the atmosphere. In this research, GC-MS (Gas chromatography-Mass spectrometry) was used to identify the oxidation products. GC-MS was performed with a Hewlett-Packard HP-G1800B GCD coupled to a mass detector operated in the electron ionization (EI) mode. The injection rate was 3 ml/hr. EI mass spectra were obtained over the range m/z = 10-200 using a column (Agilent Technologies Column HP-1) temperature of 83°C.

The five different GC sample bottles (pure air, pure MO, pure CHEDM, PET/MO copolymer, and PET/CHEDM copolymer) were put inside an oven to oxidize at 50°C for 12 days. After 12 days of oxidation, a GC syringe was used to take out 5 µl of gas from each GC sample and injected it into a GC-MS machine in order to obtain each individual GC-MS spectrum. The spectrum of pure air was used as a reference.

2.15 Gas chromatographic analysis

To further analyze the oxidation product that is released into the atmosphere after oxidizing the samples of pure scavengers, headspace analysis of the glass viles containing pure scavengers was done. The headspace measurement was performed with the use of a Perkin-Elmer TurboMatrix 40 Headspace Sampler and a Perkin-Elmer AutoSystem XL Gas Chromatograph. The gas chromatograph contains a Stabilwax®-DA column; with 30 meters by 0.32 mm ID as its dimensions. The detector is a flame ionization detector (FID). The column temperature was 60°C and included a helium gas purge.
2.16  Oxygen scavenging capacity calculations

The apparatus shown in Figure 2.6 was used to determine the oxygen scavenging capacity of the scavengers experimentally. In this apparatus, there is a pressure gauge connected with the metal tube containing scavenger and oxygen. This apparatus was designed based on the idea that a known number of moles of oxygen and scavenger are placed inside this metal tube. Initially a greater number of moles of oxygen were placed in the chamber as compared to the number of moles of scavenger in order that an equilibrium stage with respect to moles of oxygen could be achieved when the entire scavenger was consumed over the experimental time.

Figure 2.6 Pressure-drop (Δp) oxygen consumption test
Chapter 3

Results and Discussion

3.1 In situ polymerization of PET/scavenger copolymers

The process of in situ polymerization was used to prepare two different active barrier PET copolymers. In each case, active barrier oxygen scavenger was added at the early stage of the polycondensation reaction. The preparation of the copolymers allowed me to determine the properties of the PET/scavenger copolymers prepared by an in situ polymerization method and also, to study the effects of the scavengers on the oxygen barrier properties of PET.

3.1.1 Esterification reaction

In the first stage of copolymer preparation, esterification time was measured from the time when heating started to the time when esterification was completed. The factors responsible for the termination of the esterification reaction were the temperature of the top part of the distillatory, the transparency of the BHET, and the amount of water accumulated as a byproduct. It took about six hours for each additive to finish the esterification reaction for BHET preparation.

3.1.2 Polycondensation reaction

Active oxygen scavenger (AOS) was added in the PC reactor because the total residence time for AOS decreases in comparison to a case in which it would have been
added to the ES reactor. This shorter residence time ultimately reduces the loss in oxygen scavenging capacity of the scavengers. It generally takes about 360 minutes for pure PET to finish the polycondensation reaction. Polycondensation time was respectively reduced to 320 and 285 minutes with 1 and 5wt% of monoolein. It was similarly reduced to 345, 320, and 300 minutes with the addition of 1, 3, and 5wt% of 3-cyclohexene-1,1-dimethanol. This accelerated polycondensation reaction could be related to the reaction at relatively high temperature, compared with the PET polymerization conditions. If the PET/scavenger copolymer has a lower melting temperature, the reaction at PET polycondensation conditions becomes relatively faster for PET/scavenger copolymers. The polycondensation reaction was stopped at the same torque value of about 0.80 kW in each case.

The polycondensation temperature for pure PET is generally 280°C. This temperature was reduced to 270°C for the preparation of 95wt% PET/5wt% MO and to 275°C for the 95wt% PET/5wt% CHEDM copolymers.

3.2 Reaction analysis between PET and MO using NMR spectroscopy

After synthesizing the copolymers of PET/scavenger, we needed to evaluate experimental evidence in order to prove that a reaction had occurred between PET and the scavenger. To confirm an interchange reaction between the PET and monoolein units, NMR spectroscopy measurements were performed in six stages:

1. $^1$H NMR spectrum of pure PET;

2. $^1$H NMR spectrum of pure monoolein;
3. $^1$H NMR spectrum of PET/MO copolymer;

4. $^1$H NMR spectrum of a physical blend of PET/MO;

5. $^1$H NMR spectrum of extracted sample of PET/MO copolymer;

6. $^1$H NMR spectrum of extracted sample of a physical blend of PET/MO

3.2.1 $^1$H NMR spectrum of pure PET

Figure 3.1 shows the structure of pure PET and Figure 3.2 represents the $^1$H NMR spectrum of pure PET. The peak at $\delta = 8.13$ ppm is attributed to the protons of the terephthalic acid ring of the PET. The peak at $\delta = 4.79$ ppm belongs to protons of the ethylene glycol segment of the PET.

![Figure 3.1 Structure of PET](image)

The other resonances in the range from $\delta = 4.00$ to 4.75 ppm in $^1$H NMR spectrum of pure PET are attributed to the methylene protons of diethylene glycol (DEG) in the PET. DEG is formed when two molecules of EG react with each other. During the polymerization process, this DEG can then become part of the PET chain or PET/scavenger copolymer chain.
Figure 3.2 $^1$H NMR spectrum of pure PET
3.2.2 $^1$H NMR spectra of pure monoolein (MO)

Figure 3.3 gives the structure of pure monoolein. Figure 3.4 depicts the $^1$H NMR spectrum of pure monoolein when this material was dissolved in a 70/30 (wt/wt) deuterated chloroform/trifluoroacetic acid mixture. There are four main peaks appearing in the spectrum. The peak at $\delta = 5.40$ ppm belongs to the signal of protons of the double bond (CH=CH) of the monoolein structure. The peak at $\delta = 3.95$ ppm belongs to the resonance of protons at position 2 of monoolein structure. The peak at $\delta = 4.2$ ppm is associated with proton at position 7 of monoolein structure. The peak at $\delta = 4.36$ ppm is the signal of protons at position 3 of monoolein structure.

![Figure 3.3 Structure of Monoolein](image-url)
Figure 3.4 1H NMR spectrum of pure Monoolein in a mixture of d-TFA and d-chloroform
3.2.3  \(^{1}\text{H NMR spectra of PET/MO copolymer}

Figure 3.5 represents the \(^{1}\text{H NMR spectrum of PET/MO}\) (95/5 by weight) copolymer synthesized through the in situ polymerization process. Comparing Figure 3.5 with Figures 3.2 and 3.4, it is evident that the peak appearing at \(\delta = 4.78\) ppm is the signal of protons of EG unit of PET in the copolymer as in the case of \(^{1}\text{H NMR spectrum of pure PET}\). Peaks appearing between \(\delta = 0.85 - 2.44\) ppm are the resonances of the protons of MO in the copolymer as in the case of \(^{1}\text{H NMR spectrum of pure MO}\). When the PET and MO react together, the molecular interaction influences the chemical environment of each component. The chemical shifts of the components in the copolymer should be different from those of their pure state. The interchange reaction leads to the formation of new copolymer. The protons of the new copolymer should display their own chemical shifts in the NMR spectra.

For a PET/MO copolymer (shown in Figure 3.5), we found two new signals at \(\delta = 5.94\) ppm and \(\delta = 4.87\) ppm attributed to the protons of a new copolymer resulting from the interchange reaction between PET and monoolein. However, we were expecting three new signals corresponding to the protons at positions 9, 10, and 20; because PET will react with MO at positions 9 and 20 by replacing \(-\text{H}\) atom of \(-\text{OH}\) end groups of MO. Therefore, there will be a change in chemical environment around protons at positions 9, 10, and 20 (as shown in Figure 3.5) and the chemical shift of the protons corresponding to these three positions should be different from that of their pure state. This leads us to perform 2-D correlation spectroscopy (COSY) experiment for further analysis.
Figure 3.5 $^1$H NMR spectrum of PET/MO(5wt%) copolymer
3.2.4 COSY plots for PET/MO copolymer

In order to further substantiate the existence and assignment of the new copolymer peaks, a two-dimensional COSY experiment was performed as shown in Figure 3.6 to determine the connectivity of a molecule by determining which protons are spin-spin coupled. In Figures 3.6 and 3.7, the proton spectrum for PET/MO (95/5 by weight) copolymer (synthesized by in situ polymerization process) is plotted on each of the two axes. Note that the diagonal within the box is also the spectrum for copolymer as seen from "above". Off-diagonal peaks are denoted through bond coupling between protons on adjacent carbons. Note the coupling of the proton at \( \delta = 5.94 \) ppm to the methylene protons (adjacent to position 9 after reaction) at \( \delta = 4.80 \) ppm and methylene protons at \( \delta = 4.87 \) ppm. The \( \text{CH}=\text{CH} \) peak at \( \delta = 5.34 \) ppm is coupled with methylene protons of position 30 and 33 at \( \delta = 1.99 \) ppm.

The COSY experiment proves that the peak at \( \delta = 5.94 \) ppm has four cross-peaks between \( \delta = 4.80 \) ppm and \( \delta = 4.9 \) ppm and among these four peaks, the two important cross-peaks appear at \( \delta = 4.80 \) ppm and \( \delta = 4.87 \) ppm (shown in Figure 3.7). It means the peak corresponding to \( \delta = 5.94 \) ppm is directly connected to these two cross-peaks. This leads us to draw the conclusion that these two cross-peaks are corresponding to protons of positions 10 and 20.
Figure 3.6 COSY plot for PET/MO(5wt%) copolymer
Figure 3.7 COSY plot (expanded) for PET/MO(5wt%) copolymer
From the conclusions which are made from the COSY plot, the spectrum in Figure 3.5 is expanded, the two new peaks at $\delta = 4.80$ ppm and 4.87 ppm can be seen as shown in Figure 3.8.
3.2.5  $^1$H NMR spectra for extracted samples of PET/MO copolymer

To further support our previous results of sections 3.2.3 and 3.2.4, $^1$H NMR spectroscopy was performed on the extracted sample of PET/MO copolymer. The extraction was performed to remove any unbounded MO by using chloroform as a solvent. The idea behind doing extraction of the PET/MO copolymer sample is that if MO is not bounded to the PET chain, then MO should come out of the copolymer sample because MO is completely soluble in the chloroform.

Figure 3.9 represents the $^1$H NMR spectrum of an extracted sample of PET/MO (95/5 by weight) copolymer synthesized through the in situ polymerization process. From Figure 3.9, it is evident that the peak appearing at $\delta=4.79$ ppm is the signal of protons of EG unit of PET in the copolymer as in the case of $^1$H NMR spectrum of pure PET. Peaks appearing between $\delta=0.85$ - 2.44 ppm are the resonances of the protons of MO in the copolymer as in the case of $^1$H NMR spectrum of pure MO. As shown in Figure 3.9, the new peak at $\delta=5.95$ ppm is attributed to the new chemical shift for proton at position 9 which was at $\delta=4.2$ ppm in pure MO. The CH=CH peak has a similar chemical shift of $\delta=5.34$ ppm as seen in pure MO, because this group is quite far from the position where the reaction has occurred. Since there is a change in the environment around the proton at position 9, there would be a change in the chemical shift of protons at positions 10 and 20. The new peak at $\delta=4.80$ ppm is attributed to the protons at position 10, which was at $\delta=4.36$ ppm in pure MO and the other new peak at $\delta=4.87$ ppm is assigned to the protons at position 20, which was at $\delta=3.95$ ppm in pure MO. From the analysis of the above spectrum, we can say that, MO units are still bonded to the PET chain resulting in
the presence of copolymer even after extraction. This confirms the reaction between the PET and MO units.

Figure 3.9 $^1$H NMR spectrum of PET/MO (5 wt%) copolymer after extraction.
3.2.6 $^1$H NMR spectra for physical blend of PET/MO

For a comparison, NMR analysis was performed on samples of physical blends of PET/MO (95/5 by weight) before and after extraction. In Figure 3.10 (upper spectrum for the physical blend of PET/MO (95/5 by weight) before extraction), the peak at $\delta = 5.39$ ppm is attributed to the CH=CH group of monoolein and the various peaks at the lower chemical shift region are also attributed to the monoolein unit. But it is clear from the spectrum that the three important peaks at $\delta = 5.95$ ppm, $\delta = 4.80$ ppm, $\delta = 4.88$ ppm are not present in the physical blend. The reason for the absence of these three peaks is that it is just a physical blend, so there is no interchange reaction between the PET and monoolein.

3.2.7 $^1$H NMR spectra for extracted sample of physical blend of PET/MO

In Figure 3.10 (lower spectrum for the physical blend of PET/MO (95/5 by weight) after extraction), it is evident that now even the peak at $\delta = 5.39$ ppm belonging to CH=CH group is not present. The reason for the disappearance of this peak is that chloroform has extracted monoolein from the physical blend during the extraction process. The above mentioned peak and the peaks where the change in chemical shift has occurred due to the reaction between PET and MO, are all present in the spectrum of copolymer of PET/MO copolymer synthesized through the in situ polymerization process even after extraction.
Figure 3.10 $^1$H NMR spectra for PET/MO (physical blends)
3.3 Reaction analysis between PET and CHEDM using NMR spectroscopy

To verify that an interchange reaction has occurred between the PET and CHEDM units, NMR spectroscopy measurements were performed in four stages as follows:

1. $^1$H NMR spectrum of pure PET;
2. $^1$H NMR spectrum of pure CHEDM compound;
3. $^1$H NMR spectrum of PET/CHEDM copolymer;
4. $^1$H NMR spectrum of a physical blend of PET/CHEDM

3.3.1 $^1$H NMR spectra of pure CHEDM

Figure 3.11 depicts the $^1$H NMR spectrum of pure CHEDM in a 70/30 (w/w) deuterated chloroform/trifluoroacetic acid mixture. There are three main peaks appearing in the spectrum. The first main peak appearing at $\delta = 3.78$ ppm and $\delta = 4.35$ ppm belongs to the signal of protons at positions 7 and 9 of the CHEDM structure. The chemical environment of protons at positions 7 and 9 is very similar; therefore they should have one peak instead of two peaks. Figure 3.12 illustrates the $^1$H NMR spectrum of pure CHEDM dissolved in a solvent for one day. It is evident from Figure 3.12 that the peaks corresponding to protons at positions 7 and 9, which were at $\delta = 3.78$ ppm and $\delta = 4.35$ ppm in Figure 3.11, have emerged as one peak now and appeared at $\delta = 4.34$ ppm. This may be due to the reason that NMR was run on a freshly prepared sample and the $-\text{CH}_2$ groups of pure CHEDM were still moving when dissolved in a solvent. After the sample was kept dissolved in a solvent for one day, then the $-\text{CH}_2$ groups had sufficient time to relax and therefore they appear as one peak. The second main peak at $\delta = 5.75$ ppm
belongs to the resonance of the proton at position 5 of the CHEDM structure. The third main peak at $\delta = 5.62$ ppm is associated with the proton at position 4 of the CHEDM structure. The peaks between $\delta = 1.88 - 2.07$ ppm are the signals of protons of positions 2, 3, and 6 of the CHEDM structure. It can also be seen from Figures 3.11 and 3.12 that the peaks between $\delta = 1.88 - 2.07$ ppm are changing their chemical shifts with time. This may be due to hydrogen bonding between the d-TFA and CHEDM molecules.
Figure 3.11 $^1$H NMR spectrum of pure CHEDM in a mixture of d-TFA and d-chloroform (Fresh)
Figure 3.12 $^1$H NMR spectrum of pure CHEDM in a mixture of d-TFA and d-chloroform (After 1 day)
3.3.2 $^1$H NMR spectra of PET/CHEDM copolymer

Figure 3.13 represents the $^1$H NMR spectrum of PET/CHEDM (95/5 by weight) copolymer synthesized through the in situ polymerization process. Now, comparing Figure 3.13 with Figures 3.2 and 3.12, it is evident that the peak appearing at $\delta = 4.81$ ppm is the signal of protons of EG unit of PET in the copolymer as in the case of $^1$H NMR spectrum of pure PET. Peaks appearing at $\delta = 1.85$ ppm, and $\delta = 2.19$ are the resonances of the protons of CHEDM in the copolymer as in the case of $^1$H NMR spectrum of pure CHEDM. When PET and CHEDM react together, the molecular interaction influences the chemical environment of each component. The interchange reaction leads to the formation of a new copolymer. The protons of the new copolymer should display their own chemical shifts in the NMR spectra.

For a PET/CHEDM copolymer, we find new signals attributed to the protons of a new copolymer, which are the product of the interchange reaction between the PET and CHEDM units (shown in Figure 3.13). The peak at $\delta = 4.46$ ppm (shown in Figure 3.13) is attributed to the new chemical shift for protons of positions 7 and 11, which was at $\delta = 4.34$ ppm in the $^1$H NMR spectrum of pure CHEDM molecule. The protons at positions 4 and 5 have the similar chemical shift of $\delta = 5.69$ and $\delta = 5.80$ ppm, respectively, as in $^1$H NMR spectrum of pure CHEDM, because this group is quite far from the position where the reaction will occur.

From Figure 3.13, the area under the peaks at $\delta = 5.69$ and $\delta = 5.80$ ppm is ‘1’ each and the area under the peak at $\delta = 4.46$ ppm is ~ 4. This ratio should be 1:1:4, respectively, because the positions 4 and 5 have ‘1’ proton each and the positions 7 and 11 have ‘4’ protons in total. The area under the peaks satisfies this ratio.
Figure 3.13 $^1$H NMR spectrum of PET/CHEDM(5wt%) copolymer
3.3.3  $^1$H NMR spectra of physical blend of PET/CHEDM

To further substantiate the result that the reaction between PET and CHEDM unit has occurred (shown in section 3.3.2), the copolymer sample of PET/CHEDM was compared with the physical blend of PET/CHEDM. The idea behind preparing a physical blend is that there should not be a change in chemical shift for protons of positions 7 and 11 in case of a physical blend, whereas there was a change in chemical shift for protons of positions 7 and 11 in the case of a copolymer synthesized through the in situ polymerization process.

For a comparison, in the $^1$H NMR spectrum of a physical blend of PET/CHEDM(5wt%) (shown in Figure 3.14), the peaks at $\delta = 5.63$ ppm and $\delta = 5.75$ ppm are attributed to the protons of positions 4 and 5 of CHEDM units, respectively, and the three peaks at the lower chemical shift region are also attributed to the CHEDM unit. It is clear from the spectrum that the important peak at $\delta = 4.46$ ppm, which corresponds to the protons of positions 7 and 11 after PET reacts with the CHEDM units, is not present in the physical blend. The reason for the absence of this peak is that it is just a physical blend, therefore there in no interchange reaction between PET and the CHEDM molecule.
Figure 3.14 $^1$H NMR spectrum of physical blend of PET/CHEDM
3.4 Summary

Two PET/scavenger copolymers were synthesized with two different scavengers (monoolein and 3-cyclohexene-1,1-dimethanol) each with different concentrations, at temperatures between 270-280°C using a batch scale melt polymerization system. Proton NMR spectroscopy and 2-D correlation spectroscopy (COSY) were performed to confirm that interchange reactions between PET and the scavenger units had occurred. The summary of this section has been discussed as follows:

- Scavengers were added in the early stage of the polycondensation reaction, the residence time of ~5 hours, at PET melt polymerization conditions. This shorter residence time reduced the loss in oxygen scavenging capacity of the scavengers in comparison to a case in which it would have been added during the esterification reaction.
- Polycondensation reaction was accelerated by ~20% due to the addition of 5wt% monoolein and it was accelerated by ~15% due to the addition of 5wt% 3-cyclohexene-1,1-dimethanol.
- \(^1\)H NMR spectroscopy and 2-D COSY proved that there is an interchange reaction between PET and the MO and CHEDM scavenger units during melt phase polymerization leading to the formation of PET/scavenger copolymers.
- \(^1\)H NMR spectroscopy also proved that in the case of physical blends of PET/scavenger, there is no interchange reaction between PET and the MO and CHEDM scavenger units.
- \(^1\)H NMR spectroscopy proved that the reaction peaks were still present in the spectra of PET/scavenger copolymers extracted with chloroform. This indicated that the MO
and CHEDM units were still bonded to the PET chains even after extraction with chloroform and ultimately proved that the reaction between PET and the MO and CHEDM scavenger units had occurred
3.5  **Rheological behavior (shear viscosity versus shear rate)**

Improving the oxygen barrier properties of PET is a concern, however, not at the cost of sacrificing the overall physical appearance and properties of PET. It is very important, therefore, to study the overall benefits of the addition of scavenger in terms of the physical properties of PET. Rheological and thermal properties of the prepared copolymers were evaluated and compared to those of unmodified commercially prepared high IV WA314 PET.

The study of rheological behavior helps to determine the visco-elastic properties of the PET/scavenger copolymers. This analysis is done on the PET/scavenger copolymer pellets. The study of rheological behavior also helps to determine the degradation caused as a result not only of processing but also by the addition of cobalt octoate catalyst. This analysis is done on the PET/scavenger copolymer sheet samples and will indicate any degradation that has occurred through the addition of the cobalt octoate catalyst.

Sample evaluations included in the following discussions have utilized commercial WA314 PET resin as well as the copolymer resins of PET/MO and PET/CHEDM prepared through in situ polymerization. Additional evaluations require the preparation of extruded sheets of each material.

### 3.5.1 For WA314 PET

Figure 3.15 illustrates change in melt viscosity as a function of shear rate measured for WA314 PET sample. From Figure 3.15, it is evident that the commercially prepared WA314 pure PET resin sample shows Newtonian behavior up to the measured shear rate (\(\dot{\gamma}\)) values, which is a typical rheological behavior for pure PET.
In this research, the viscosity of WA314 PET at a shear rate of 10 sec\(^{-1}\) was used to represent the zero-shear viscosity and the results are tabulated in Table 3.1.

![Figure 3.15 Viscosity versus shear rate for WA314 PET](image)

Figure 3.15 Viscosity versus shear rate for WA314 PET

### 3.5.2 For PET/MO copolymers

Figure 3.16 illustrates changes in melt viscosity as functions of shear rates measured for copolymer samples with 1wt\% and 5wt\% MO and WA314 PET. The copolymer sample of PET/MO(1wt\%) synthesized by in situ polymerization process shows Newtonian behavior up to low values of shear rate (\(\gamma\)) similar to that of pure WA314 PET. The copolymer sample of PET/MO(5wt\%) synthesized by in situ polymerization process, however, shows non-Newtonian behavior even at low shear rates. The reason for this behavior may be that “branching” occurs among the PET and monoolein chains.
With the increase of the minor component, the melt viscosity increased. This increase may be attributed to the chain rigidity imparted by PET/MO copolymer synthesis.

In this research, the viscosity of materials (PET equivalent) at a shear rate of 10 sec\(^{-1}\) was used to represent the zero-shear viscosity to obtain the results tabulated in Table 3.1.

![Figure 3.16 Viscosity versus shear rate for WA314 PET and PET/MO copolymers](image)

Table 3.1 Melt IV calculation for PET/MO copolymers at shear rate = 10 sec\(^{-1}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Melt IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA314 PET</td>
<td>0.73</td>
</tr>
<tr>
<td>Copolymer of PET/MO(1wt%)</td>
<td>0.72</td>
</tr>
<tr>
<td>Copolymer of PET/MO(5wt%)</td>
<td>non-Newtonian</td>
</tr>
</tbody>
</table>
3.5.3 For PET/CHEDM copolymers

The dynamic viscosity, obtained for the copolymer samples of PET/CHEDM and WA314 PET at a temperature of 280°C, is presented as a function of shear rate as shown in Figure 3.17. It was noted that the copolymer samples of PET/CHEDM with three different compositions of CHEDM (1, 3, and 5wt%) synthesized through the in situ polymerization process show Newtonian behavior up to the measured shear rate (\(\gamma\)) values similar to that of pure WA314 PET.

The calculation of melt IV (PET equivalent) for the copolymers was done as described earlier in section 3.4.2. The results are given in Table 3.2.

![Figure 3.17 Viscosity versus shear rate for PET/CHEDM copolymers](image)
Table 3.2 Melt IV calculation for PET/CHEDM copolymers at shear rate = 10 sec\(^{-1}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>Melt IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer of PET/CHEDM(1wt%)</td>
<td>0.63</td>
</tr>
<tr>
<td>Copolymer of PET/CHEDM(3wt%)</td>
<td>0.63</td>
</tr>
<tr>
<td>Copolymer of PET/CHEDM(5wt%)</td>
<td>0.58</td>
</tr>
</tbody>
</table>

3.6 Thermal properties (melting and crystallization behavior)

As discussed in section 3.2, NMR results have shown that the PET reacts with the oxygen scavengers to form copolymers. The influences of the interchange reactions on the melting behaviors and the morphologies of the PET/scavenger copolymers have also been investigated. The investigation of thermal properties is important because these properties dictate the processing conditions, for injection molding and stretch blow molding, needed for a particular resin. Changes in the glass transition temperature (T\(_g\)), crystallization behavior and melting behavior were evaluated for both MO and CHEDM copolymer samples.

In order to study the melting and crystallization behaviors, differential scanning calorimetry (DSC) was used. The isothermal and non-isothermal crystallization behaviors of the copolymers were studied as functions of the type of the scavenger and the content of the scavenger.

Thermal analysis was carried out on the PET/scavenger copolymer samples under a dry nitrogen atmosphere in order to study their glass transition, melting, and
crystallization behaviors while heating samples that had previously been quenched from the melt to the glassy state. While cooling samples from the melt at 10°C per minute, crystallization behavior was also monitored. In the thermal analysis experiment, the pellet samples were first ground into powder form and then dried under vacuum for about 12 hours at 120°C. The weight of the samples used for thermal experiment was between 5 - 10 mg.

In order to remove the previous thermal history of the copolymer samples, all the samples were quenched very quickly at 300°C/min (step 3, details are included in section 2.7) after their first heating. The quenched samples were heated again (step 5) at 10°C/min to evaluate their glass transition temperature, crystallization, and melting behaviors. To determine the crystallization behavior while cooling from the melt, all the samples were cooled at 10°C/min (step 7) after their second heating.

3.6.1 For WA314 PET

Reheat after quench (step 5)

The DSC thermogram of WA314 PET (shown in Fig 3.18) indicates that the glass transition temperature is 78°C, the crystallization peak temperature is 165°C, and the melting point of the polymer is 242°C. These data are summarized in Table 3.3.

Cooling from the melt (step 7)

Figure 3.19 shows the crystallization behavior of the WA314 PET as it is cooled from the melt at 10°C per minute. The crystallization peak temperature of 177°C is also included in Table 3.3.
Figure 3.18 DSC plot for WA314 PET (heating after the quench)

Figure 3.19 DSC plot for WA314 PET (cooling from the melt)
3.6.2 For PET/MO copolymers

Reheat after quench (step 5)

The DSC thermogram of PET/MO copolymers given in Figure 3.20 indicates that the glass transition temperature of the copolymer with 1wt% MO is 75°C and with 5wt% MO is 71°C. The data for 1wt% and 5wt% MO content are indicative of the increase in crystallization temperature with increasing MO content in the copolymer. It means that the higher the MO content, the slower is the crystallization. In addition to the increase in crystallization temperature, the melting point of the copolymer decreases with increasing MO content in the range of 1wt% to 5wt%, enabling us to process the PET/MO copolymers at lower temperatures than PET homopolymer. PET/MO copolymers have lower melting points ($T_m = 242°C$ for 1wt% MO and $T_m = 234°C$ for 5wt% MO) and have lower crystallization rates compared to the pure PET. These data are summarized in Table 3.3. The results of melting and crystallization behaviors of PET/MO copolymer samples cannot be compared with the results of melting and crystallization behavior of WA314 PET. This is due to the fact that WA314 PET is commercially prepared SSP resin and therefore, it has different synthesis process in comparison to the synthesis process for the PET/MO copolymer samples.

Cooling from the melt (step 7)

Figure 3.21 shows the crystallization behavior of the PET/MO copolymer as it is cooled from the melt at 10°C per minute. It is evident that the crystallization peak temperature ($T_{cc}$) decreases as MO content increases in the copolymer. This is consistent
with the crystallization behavior while reheating after quench. These data are included in Table 3.3.

Figure 3.20 DSC plot for PET/MO copolymers (heating after the quench)

Figure 3.21 DSC plot for PET/MO copolymers (cooling from the melt)
Table 3.3 Physical parameters measured from DSC analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Heating from the quench</th>
<th>Cooling from the melt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melting</td>
<td>Crystallization</td>
</tr>
<tr>
<td></td>
<td>$T_g$ (°C)</td>
<td>$T_m$ (°C)</td>
</tr>
<tr>
<td>Copolymer with 1wt% MO</td>
<td>75.0</td>
<td>242.0</td>
</tr>
<tr>
<td>Copolymer with 5wt% MO</td>
<td>71.0</td>
<td>234.0</td>
</tr>
</tbody>
</table>

3.6.3 For PET/CHEDM copolymers

Reheat after quench (step 5)

The DSC thermogram of PET/CHEDM copolymer synthesized through the in situ polymerization process (shown in Figure 3.22) indicates that the glass transition temperature of the copolymer of PET with 1wt% CHEDM is 79.0°C, with 3wt% CHEDM is 78.0°C and with 5wt% CHEDM is 78.0°C. The crystallization data for 1, 3, and 5wt% CHEDM content are indicative of the increase in crystallization temperature with increasing comonomer (CHEDM) content in the copolymer. It means that the higher the CHEDM content in the copolymer, the slower is the crystallization. In addition to the
increase in crystallization temperature, the melting point of the copolymers decreases with increasing CHEDM content in the range of 1wt% to 5 wt%, enabling us to process the PET/CHEDM copolymers at lower temperatures than PET homopolymer. PET copolymers have lower melting points (T_m = 245.0°C for 1wt% CHEDM, T_m = 240.0°C for 3wt% CHEDM, and T_m = 232.0°C for 5wt% CHEDM) (shown in Figure 3.22). The depression of melting temperature could be attributed to the transesterified CHEDM units which restrict PET crystallization, and reduce PET crystallite size. It may also be caused by the broadening of the interfacial region from the introduction of the CHEDM block. These data are summarized in Table 3.4. The results of melting and crystallization behaviors of PET/CHEDM copolymer samples cannot be compared with the results of melting and crystallization behavior of WA314 PET. This is due to the fact that WA314 PET is commercially prepared SSP resin and therefore, it has different synthesis process in comparison to the synthesis process for the PET/CHEDM copolymer samples.

**Cooling from the melt**

Figure 3.23 shows the crystallization behavior of the PET/CHEDM copolymer sample as it is cooled from the melt at 10°C per minute. It is evident that the crystallization temperature (T_{cc}) decreases as CHEDM content increases in the copolymer. This is consistent with the crystallization behavior while reheating after quench. These data are included in Table 3.4.
Figure 3.22 DSC plot for PET/CHEDM copolymers (heating after the quench)

Figure 3.23 DSC plot for PET/CHEDM copolymers (cooling from the melt)
### Table 3.4 Physical parameters measured from DSC analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Heating from the quench</th>
<th>Crystallization from the melt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Melting</td>
<td>Crystallization</td>
</tr>
<tr>
<td></td>
<td>$T_g$ ($^\circ$C)</td>
<td>$T_m$ ($^\circ$C)</td>
</tr>
<tr>
<td>Copolymer with 1wt% CHEDM</td>
<td>79.0</td>
<td>245.0</td>
</tr>
<tr>
<td>Copolymer with 3wt% CHEDM</td>
<td>78.0</td>
<td>240.0</td>
</tr>
<tr>
<td>Copolymer with 5wt% CHEDM</td>
<td>78.0</td>
<td>232.0</td>
</tr>
</tbody>
</table>
3.7 Melting and crystallization behavior of PET/scavenger copolymers: Theory of polymer melting and crystallization

Poly(ethylene terephthalate) (PET) is a semi-crystalline polymer, some of whose properties are dependent upon its melting and crystallization behavior. The relative level of crystallinity is a main factor determining the melting behavior of PET resin. PET resins, when crystallized under various conditions; exhibit the multiple melting endotherms during differential scanning calorimetric heating measurements. The phenomenon of multiple melting endotherms, observed by many researchers [49-57], is not limited to PET resin. This phenomena has also been found for the case of other polymers and copolymers, such as Nylon66 [58], PEN [59], PET/MXD6 blends [60]. There are many interpretations concerning the origins of these melting peaks.

S.B. Clough et al [54] investigated the melting behavior of PET. Figure 3.24 displays three melting endotherms in the melting curve of isothermally crystallized PET. The peaks are labeled I, II, III starting with the lowest temperature endotherm. Peak I, which is approximately 10°C above the $T_c$ (crystallization temperature), was attributed to the melting of the crystals formed during secondary crystallization. Peak II was attributed to the melting of the crystals formed during the primary crystallization stage. Peak III, which does not change appreciable with the increasing $T_c$, was attributed to the crystals formed as a results of recrystallization on heating.

F.J. Medellin-Rodriguez et al [61] mentioned that PET spherulites included two structural elements. One was the dominant branches, which were composed of lamellae; the other was the subsidiary branches, which had amorphous component molecules in the vicinity of the dominant lamellae. They indicated that the melting process of PET was
just the reverse of the isothermal crystallization process. In the melting process both dominant and subsidiary branches, which consisted of the PET spherulites, melt. The three melting endotherms, appearing in the melting curve of PET, were related to the melting of these two branched structures. Endotherm I was due to the melting of small metastable branches, endotherm II was due to the melting of main metastable branches, and endotherm III was related with dominant branches, which underwent some recrystallization on heating.

Figure 3.24 DSC results from fusion of PET. The isothermal crystallization conditions were, a) 460K, b) 465K, c) 470K, d) 478K [61]
3.7.1 Approach used to study the isothermal crystallization behavior of PET/scavenger copolymers

To study the isothermal crystallization kinetics of the copolymers, crystal growth analysis is generally done. There have been many attempts to develop theories to explain the important aspects of crystallization [62,63]. The most widely accepted approach to the analysis of the crystal growth rates is the kinetic description due to Lauritzen and Hoffmann [62]. The general expression of crystal growth as described by Lauritzen and Hoffman is:

\[ G = G_0 \exp\left(-\frac{U^*}{R(T_c - T_\infty)}\right) \exp\left(-\frac{K_g}{T_c \Delta Tf}\right) \quad (1) \quad [62] \]

Where

- \( G \) = growth rate
- \( G_0 \) = growth rate constant
- \( U^* \) = activation energy for polymer diffusion
- \( R \) = gas constant
- \( T_c \) = crystallization temperature (°K)
- \( T_\infty \) = \( T_g - 30 \) (°K)
- \( \Delta T \) = degree of undercooling = \( T_m^0 - T_c \)
- \( f \) = correction factor
- \( K_g \) = nucleation rate constant = \( j b_0 \sigma c T_m^0 / k \Delta h_f \) \quad (2)

Where

- \( b_0 \) = width of the chain
\[ \sigma = \text{lateral surface free energy} \]
\[ \sigma_e = \text{fold surface free energy} \]
\[ T_{m}^0 = \text{equilibrium melting temperature (°K)} \]
\[ k = \text{Boltzmann constant} \]
\[ \Delta h_f = \text{heat of fusion} \]
\[ j \text{ is determined by the operating regime (regime I, II, III)} \]

From equations 1, it is clear that the crystal growth rate is dependent on the degree of undercooling and nucleation rate constant. From equation 2, it can also be seen that the nucleation rate constant is further dependent on the equilibrium melting temperature \( T_{m}^0 \). Therefore, the determination of \( T_{m}^0 \) and degree of undercooling \( (\Delta T) \) is essential to study the isothermal crystallization kinetics of the PET/scavenger copolymers.

The equilibrium melting point, \( T_{m}^0 \), of a polymer is defined as the melting temperature of a stack of several fully extended polymer chains, which constitute the perfect polymer crystalline structure. The equilibrium melting point is obtained through extrapolative procedures. Two general methods have been devised for the evaluation of equilibrium melting points of semicrystalline polymers: the Hoffmann-Weeks [64] and the Gibbs-Thomson procedures [65].

In order to determine their equilibrium melting points \( T_{m}^0 \), samples were crystallized at various temperatures for one hour.
3.7.2 Equilibrium melting point

Figures 3.25 to 3.31 show the multiple melting peaks of WA314 PET (pure), PET/MO copolymer, and PET/CHEDM copolymer samples. Isothermal crystallization temperatures are noted on the respective melting curves of each figure. Isothermally crystallized WA314 PET has three melting peaks, namely, $T_{m1}$, $T_{m2}$ and $T_{m3}$ (as shown in Figure 3.25). Isothermal crystallization temperatures were from 195°C to 210°C. Isothermally crystallized PET/MO and PET/CHEDM copolymer samples have three melting peaks. Isothermal crystallization temperatures were from 180°C to 220°C. In section 1.6, we discussed the reasons for the occurrence of multiple melting peaks in the crystallized polycondensates (polymers or copolymers). There are many different interpretations about the phenomena of multiple melting peaks. I prefer the interpretation indicating that the melting peak $T_{m1}$ is associated with the melting of crystals formed in secondary crystallization, the melting peak $T_{m2}$ is due to the melting of crystals formed in primary crystallization, and the melting peak $T_{m3}$ is related with the melting of crystals formed from reorganization during heating.
Figure 3.25 Multiple melting peaks of isothermally crystallized WA314 PET

Figure 3.26 Multiple melting peaks of isothermally crystallized PET/MO(1wt%) copolymer
Figure 3.27 Multiple melting peaks of isothermally crystallized PET/MO(5wt%) copolymer

Figure 3.28 Multiple melting peaks of isothermally crystallized PET/CHEDM(1wt%) copolymer
Figure 3.29 Multiple melting peaks of isothermally crystallized PET/CHEDM(3wt%) copolymer

Figure 3.30 Multiple melting peaks of isothermally crystallized PET/CHEDM(5wt%) copolymer
In Figures 3.26 to 3.31, there are also three melting peaks in the melting curves of isothermally crystallized copolymer samples of PET/MO and PET/CHEDM. The occurrence of these three melting peaks, appearing in Figures 3.26 to 3.31, are related to the melting of crystalline components in the PET/MO and PET/CHEDM copolymers. As shown in Figures 3.26 to 3.31, with increasing isothermal crystallization temperatures, the positions of $T_m1$ and $T_m2$ shift to higher temperatures. The position of $T_m3$ does not change.

From Figure 3.32, if we extrapolate the $T_m2$ line to higher temperatures, it will intercept with the $T_m = T_c$ line. On the basis of the calculation method of Hoffman-Weeks equation [66], the interception point is the equilibrium melting point ($T_m^o$) of the copolymer sample of PET/MO(1wt%).
Figure 3.32 A plot used to obtain the equilibrium melting temperature ($T_m^o$) of PET/MO (1wt%) copolymer (showing melting peaks $T_{m1}$, $T_{m2}$, $T_{m3}$) versus crystallization temperature

Similar plots were constructed for other copolymer samples and WA314 PET. Figures 3.33 and 3.34, respectively, indicate the melting behaviors of copolymer samples of PET/CHEDM and PET/MO. It is evident that the equilibrium melting point ($T_m^o$) is depressed with increasing CHEDM and MO content. A summary of the equilibrium melting point ($T_m^o$) values for all the samples is given in Table 3.5.
Figure 3.33 The depression of equilibrium melting point of PET/CHEDM copolymers

Figure 3.34 The depression of equilibrium melting point of PET/MO copolymers
Table 3.5 Equilibrium melting points of PET/MO, PET/CHEDM copolymers, and WA314 PET

<table>
<thead>
<tr>
<th>Material</th>
<th>Scavenger (wt%)</th>
<th>$T_m^o$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA314 PET</td>
<td>0</td>
<td>257</td>
</tr>
<tr>
<td>PET/MO</td>
<td>1</td>
<td>263</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>257</td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>1</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>264</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>255</td>
</tr>
</tbody>
</table>

3.7.3 Avrami kinetics

After studying the melting behavior, we studied the crystallization behavior observed while the samples were isothermally crystallized at various temperatures. Figure 3.35 shows the crystallization behavior recorded for the PET/CHEDM(5wt%) copolymer after cooling the sample to a particular crystallization temperature from the melt and holding the sample at that crystallization temperature for an hour. It can be seen from Figure 3.35 that as the crystallization temperature increases, the crystallization peak time increases. Isothermal crystallization temperatures are indicated with appropriate cooling curves in this figure. The other prepared samples were found to exhibit similar behavior under equivalent isothermal crystallization conditions. Data recorded for these samples have been evaluated in terms of crystallization half time.
Figure 3.35 Crystallization behavior for isothermally crystallized PET/CHEDM(5wt%) copolymer

Crystallization half time is the time at which the relative crystallinity of the polymers achieves the value of 50% of the total crystallinity achieved at that temperature. The crystallization half time can reflect the overall crystallization rate of the polymers. In Figures 3.36 to 3.40, the crystallization behavior of the pure PET and the PET/scavenger copolymers is displayed in terms of crystallization half time.

From Figure 3.36, it is evident that as the crystallization temperature increases for WA314 PET, the half time also increases. From Figure 3.37, as the crystallization temperature increases for PET/MO copolymers, the half time also increases. It can also be observed that as the concentration of MO increases, the half time increases. This result is consistent with the non-isothermal crystallization behavior for PET/MO copolymers, which shows that the higher the MO content in the copolymer the slower is the crystallization.
The true driving force of crystallization of polymers is the degree of undercooling. This is the difference between the equilibrium melting point ($T_m^0$) of the polymers and the crystallization temperature ($T_c$). The degree of undercooling is important because the equilibrium melting points of the PET/scavenger copolymers are different as a result of the copolymer. The crystallization data will be more meaningful if the results of the crystallization half time for different copolymer samples are compared at the same degree of undercooling.

Figure 3.38 illustrates the plot of half time as a function of degree of undercooling for PET/MO copolymer samples. As the MO content increases in the copolymer, the crystallization half time also increases at the same degree of undercooling, therefore the crystallization rate of PET/MO copolymer decreases.

Figure 3.36 Half time plotted as a function of crystallization temperature for isothermally crystallized WA314 PET
Figure 3.37 Half time plotted as a function of crystallization temperature for isothermally crystallized PET/MO copolymers

Figure 3.38 Half time plotted as a function of degree of undercooling for PET/MO copolymers
The PET/CHEDM copolymer samples were treated in a manner similar to that described for the PET/MO copolymer samples. From Figure 3.39, it can be seen that as the CHEDM content increases, the half time also increases when the samples are crystallized at the same crystallization temperature (especially at higher crystallization temperatures). It means that the higher the CHEDM content, the slower is the crystallization. Figure 3.40 illustrates the plot of half time as a function of degree of undercooling for PET/CHEDM copolymer samples. It shows that there is no significant difference in the crystallization behavior for PET/CHEDM copolymer samples with different concentrations of CHEDM at the same degree of undercooling; however, the non-isothermal crystallization data shows that the higher the CHEDM content, the slower is the crystallization because of changes in $T_m$. 

![Figure 3.39 Half time plotted as a function of crystallization temperature for isothermally crystallized PET/CHEDM copolymers](image)
Figure 3.40 Half time plotted a function of degree of undercooling for PET/CHEDM copolymers

Table 3.6 summarizes the results for isothermal crystallization half times for WA314 PET, PET/MO copolymers, and PET/CHEDM copolymers at different isothermal crystallization temperatures.
Table 3.6 Half time values at different crystallization temperatures for PET/scavenger copolymers, and WA314 PET

<table>
<thead>
<tr>
<th>Isothermal crystallization temperature (T_c), (ºC)</th>
<th>Crystallization half time (t_{1/2}), (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WA314 PET</td>
</tr>
<tr>
<td>180</td>
<td>-</td>
</tr>
<tr>
<td>185</td>
<td>-</td>
</tr>
<tr>
<td>190</td>
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<tr>
<td>195</td>
<td>658</td>
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<tr>
<td>200</td>
<td>925</td>
</tr>
<tr>
<td>205</td>
<td>1031</td>
</tr>
<tr>
<td>210</td>
<td>1379</td>
</tr>
<tr>
<td>215</td>
<td>-</td>
</tr>
<tr>
<td>220</td>
<td>-</td>
</tr>
</tbody>
</table>
In addition to the half time analyses, the previously discussed data were also used to determine the crystallization kinetics parameters using Avrami expressions. The recorded crystallization data for WA314 PET, PET/MO copolymers, and PET/CHEDM copolymers from section 3.7.2 was used to plot $\theta_a$ (fraction of uncrystallized material) as a function of ln(crystallization time). The crystallization kinetics of the polymers is analyzed in terms of the Avrami expression given by:

$$\theta_a = e^{-kt^n} \quad (3)$$

Where $\theta_a$ is the fraction of uncrystallized material, $k$ is the kinetic rate constant, $t$ is the time, and $n$ is the Avrami exponent, describing the mechanism of crystallization.

The mathematical formulation of the kinetic phase change and the derivation of the Avrami equation can be found in many sources [67,68]. In the Avrami expression, the kinetic rate constant, $k$, is a function of the nucleation and the growth rates. The Avrami exponent provides qualitative information on the nature of nucleation and the growth processes.

From the literature [69], the values of the Avrami exponent, for various types of nucleation and growth are given in Table 3.7:
Table 3.7 Values and mechanism of the Avrami exponents

<table>
<thead>
<tr>
<th>n</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Spherulitic growth from sporadic nuclei</td>
</tr>
<tr>
<td>3</td>
<td>Spherulitic growth from instantaneous nuclei</td>
</tr>
<tr>
<td>3</td>
<td>Disc-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>2</td>
<td>Disk-like growth from instantaneous nuclei</td>
</tr>
<tr>
<td>2</td>
<td>Rod-like growth from sporadic nuclei</td>
</tr>
<tr>
<td>1</td>
<td>Rod-like growth from instantaneous nuclei</td>
</tr>
</tbody>
</table>

Figures 3.41 to 3.43 give the variation of $\theta_a$ with crystallization time at various crystallization temperatures for WA314 PET and the copolymer samples. All the isotherms have a sigmoidal shape typical of polymer crystallization behavior. From Figures 3.41, it can be seen that as the crystallization temperature increases for WA314 PET, the value of the fraction of uncrystallized material increases when the WA314 PET was crystallized for the same crystallization time period. Similar behaviors were observed for PET/MO(5wt%) copolymer sample (shown in Figure 3.42) and PET/CHEDM(3wt%) copolymer sample (shown in Figure 3.43).
Figure 3.41 $\theta_a$ versus ln(t) for isothermally crystallized WA314 PET

Figure 3.42 $\theta_a$ versus ln(t) for isothermally crystallized PET/MO(5wt%) copolymer
The kinetic parameters are obtained from Eq.(3) by plotting the data according to Eq. (4).

\[
\ln(-\ln \theta_a) = \ln k + n (\ln t) \quad (4)
\]

Therefore, a plot of \(\ln(-\ln \theta_a)\) vs. \(\ln t\) yields a straight line; the slope is equal to \(n\) and the intercept is equal to \(\ln k\).

Typical Avrami plots for the crystallization behavior of WA314 PET and copolymer samples of PET/MO and PET/CHEDM are given in Figures 3.44 to 3.46. Similar plots were constructed for other copolymer samples.
Figure 3.44 $\ln(-\ln(\theta_a))$ versus $\ln(t)$ for isothermally crystallized WA314 PET

Figure 3.45 $\ln(-\ln(\theta_a))$ versus $\ln(t)$ for isothermally crystallized PET/MO(5wt%) copolymer
A summary of the n and k values obtained for the crystallization behavior of pure PET and the copolymer samples of PET/MO and PET/CHEDM is given in Table 3.8. The rate constant, k, in Eq. (3) determines the rates of the nucleation and the growth processes which control the crystallization. As seen in Table 3.8, a change of $10^6$ is obtained for a change of crystallization temperature of $35^\circ C$ in the case of copolymer samples of PET/CHEDM(5wt%), a change of $10^1$ is obtained for a change of crystallization temperature of $15^\circ C$ in the case of copolymer samples of PET/MO(1wt%) and PET/CHEDM(3wt%) and WA314 PET, a change of $10^1$ is obtained for a change of crystallization temperature of $20^\circ C$ in the case of copolymer sample of PET/CHEDM(1wt%).
Table 3.8 n and k values for PET/scavenger copolymers and WA314 PET

<table>
<thead>
<tr>
<th>Isothermal crystallization temperature (°C)</th>
<th>WA314 PET</th>
<th>PET/MO (1wt%)</th>
<th>PET/MO (5wt%)</th>
<th>PET/CHEDM (1wt%)</th>
<th>PET/CHEDM (3wt%)</th>
<th>PET/CHEDM (5wt%)</th>
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<tr>
<td>180</td>
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</tr>
<tr>
<td></td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>1.2*10⁻¹¹</td>
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<tr>
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<td>-</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
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<td>8.7*10⁻⁷</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>190</td>
<td>n</td>
<td>-</td>
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<td>5.1</td>
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<tr>
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<td>k, sec⁻¹</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>7.6*10⁻¹²</td>
</tr>
<tr>
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<td>n</td>
<td>2.0</td>
<td>2.2</td>
<td>-</td>
<td>4.7</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
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<td>7.2*10⁻⁷</td>
<td>-</td>
<td>8.4*10⁻¹¹</td>
<td>2.9*10⁻¹²</td>
</tr>
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<td>n</td>
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<td>2.1</td>
<td>2.3</td>
<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>3.2*10⁻⁶</td>
<td>6.2*10⁻⁷</td>
<td>6*10⁻⁶</td>
<td>2.5*10⁻¹¹</td>
<td>1.0*10⁻¹²</td>
</tr>
<tr>
<td>205</td>
<td>n</td>
<td>2.0</td>
<td>2.5</td>
<td>2.1</td>
<td>-</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>1.6*10⁻⁶</td>
<td>3.2*10⁻⁷</td>
<td>4.8*10⁻⁷</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<td>4.9</td>
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<td>k, sec⁻¹</td>
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<td>2.2*10⁻⁷</td>
<td>-</td>
<td>2.6*10⁻⁶</td>
<td>1.9*10⁻¹²</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1*10⁻¹⁵</td>
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<td>215</td>
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<td>-</td>
<td>2.2</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>-</td>
<td>1.8*10⁻⁷</td>
<td>-</td>
<td>1.8*10⁻⁶</td>
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<td>220</td>
<td>n</td>
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<td>2.4</td>
<td>-</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>-</td>
<td>3.1*10⁻⁸</td>
<td>-</td>
<td>1.0*10⁻⁷</td>
<td>-</td>
</tr>
</tbody>
</table>
The values of n and k are different for different copolymer samples of PET/MO and PET/CHEDM. This indicates that the crystallization mechanism (shown in Table 3.8) is different for different copolymer samples. Although the copolymers of PET/CHEDM(1, 3, and 5wt%) exhibit similar IV, the rate of crystallization of copolymer sample of PET/CHEDM(5wt%) is significantly lower.

The results given in Table 3.8 show that the n values for WA314 PET, PET/MO copolymer samples, and PET/CHEDM(1wt%) copolymer sample varies between 2 and 3, which indicate that these copolymer samples and WA314 PET have spherulitic growth from instantaneous nuclei. However, the n value varies from 4.8 to 5.5 for the copolymer sample of PET/CHEDM(5wt%) and it varies from 4.4 to 4.7 for the copolymer sample of PET/CHEDM(3wt%).

It is clear that the values of Avrami exponent (n) for the copolymer samples of PET/CHEDM(3 and 5wt%) are varying from 4 to 6 and these values are too high to conclude anything about the geometry of the crystallization. Therefore, it leads us to use another method called “Half time method” to determine the values of n and k.

3.6.4 Half time method

In order to further investigate the crystallization characteristics of the PET/CHEDM copolymers, the half time of crystallization as a measure of the rate and n values was used.

According to the half time method [2],

Plot \( \theta_a \) vs. \( \ln t \) (shown in Figures 3.41 to 3.43) and
\[ S = -0.35 \times n \]

Where, \( S \) is the slope at half time.

\[ k = 0.69 / t_{1/2}^n \]

Here, \( k \) is a combined function of \( t_{1/2} \) and \( n \).

A summary of the \( n \) and \( k \) values for the crystallization behavior of the PET/MO and PET/CHEDM copolymer samples determined by the half time method is given in Table 3.9. As seen in Table 3.9, a change of \( 10^5 \) is obtained for a change of crystallization temperature of \( 35^\circ C \) in the case of copolymer samples of PET/CHEDM(5wt\%), a change of \( 10^2 \) is obtained for a change of crystallization temperature of \( 15^\circ C \) in the case of copolymer sample of PET/CHEDM(3wt\%), a change of \( 10^1 \) is obtained for a change of crystallization temperature of \( 15^\circ C \) in the case of copolymer sample of PET/CHEDM(1wt\%), a change of \( 10^1 \) is obtained for a change of crystallization temperature of \( 20^\circ C \) in the case of copolymer sample of PET/MO(1wt\%), and a change of \( 10^1 \) is obtained for a change of crystallization temperature of \( 25^\circ C \) in the case of copolymer sample of PET/MO(5wt\%).

From Table 3.9, the \( n \) value varies from 2.6 to 3.5 for the copolymer sample of PET/CHEDM(5wt\%) and it varies from 2.6 to 3.0 for the copolymer sample of PET/CHEDM(3wt\%). On comparing the values of \( n \) and \( k \) for the copolymer samples of PET/CHEDM(3 and 5wt\%) determined by Avrami expression (Table 3.8) and half time method (Table 3.9), it can be seen that the half time method gives lower values of \( n \) and higher values of \( k \) as compared to Avrami expression. However, both methods give comparable values of \( n \) and \( k \) for the copolymer samples of PET/MO(1 and 5wt\%) and PET/CHEDM(1wt\%).
The results given in Tables 3.8 and 3.9 show that the n value varies between 2 and 3 at different crystallization temperatures for PET/scavenger copolymer and WA314 PET samples. This kind of behavior has been observed by other workers [70,71] and it indicates that the mechanism of crystallization is different for different copolymer samples.
Table 3.9 n and k values for PET/scavenger copolymers using half time method

<table>
<thead>
<tr>
<th>Isothermal crystallization temperature (°C)</th>
<th>PET/MO (1 wt%)</th>
<th>PET/MO (5 wt%)</th>
<th>PET/CHEDM (1 wt%)</th>
<th>PET/CHEDM (3 wt%)</th>
<th>PET/CHEDM (5 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>n</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8.4*10⁻⁷</td>
</tr>
<tr>
<td>185</td>
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<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>-</td>
<td>4.2*10⁻⁶</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>190</td>
<td>n</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>k, sec⁻¹</td>
<td>-</td>
<td>-</td>
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<td>2.3*10⁻⁷</td>
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<td>n</td>
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<td>3.0</td>
</tr>
<tr>
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<td>k, sec⁻¹</td>
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<td>2.1*10⁻⁶</td>
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<td>3.3*10⁻⁷</td>
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<td>1.5*10⁻⁶</td>
<td>2.3*10⁻³</td>
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<td>9.8*10⁻⁸</td>
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<td>k, sec⁻¹</td>
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<td>3.3*10⁻⁷</td>
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<tr>
<td></td>
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<td>-</td>
<td>1.9*10⁻⁶</td>
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<td></td>
<td></td>
<td>5*10⁻¹²</td>
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<td>2.2</td>
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</tr>
<tr>
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<td>k, sec⁻¹</td>
<td>4.4*10⁻⁷</td>
<td>-</td>
<td>1.1*10⁻⁶</td>
<td>-</td>
</tr>
</tbody>
</table>
3.8 Microscopy of PET/scavenger copolymers

In order to further elucidate the differences in growth mechanisms or differences between nucleation courses, we used optical microscopy and small angle light scattering techniques.

**Optical Microscopy and Small Angle Light Scattering**

Optical microscopy (OM) and small angle light scattering (SALS) were used to determine the crystallization kinetics of WA314 PET and the copolymer samples. In particular, the linear growth rates of the spherulites were determined. The study of the effect of the crystallization time on the morphology of the spherulites was performed using SALS and OM.

**Optical Microscopy**

Figures 3.47 and 3.48 show sample photo microphotographs of spherulites obtained for WA314 PET and PET/MO copolymer samples crystallized at 200°C for 120 sec from the molten state. It can be seen that the spherulites formed are approximately 5µ in diameter for WA314 PET as well as for PET/MO copolymer.
Figure 3.47 Microphotograph of WA314 PET spherulite growth at 200°C for 120 sec

Figure 3.48 Microphotograph of PET/MO(5wt%) spherulite growth at 200°C for 120 sec
Impurities in the copolymers

In addition to observation of spherulite formation, it was also noted that in some cases significant levels of impurities were present. Virgin WA314 PET contained no visible impurities, while a PET/MO copolymer sample had some impurities and a PET/CHEDM copolymer sample contained many impurities as shown in Figures 3.49 and 3.50. In Figure 3.50 (b) (for pure CHEDM compound), we melted pure CHEDM compound and even then we could see impurities through cross polarizers. These impurities may have contributed to increase the rate of crystallization for PET/CHEDM copolymers.

a) WA314 PET (50*1.25) b) PET/MO(5wt %) copolymer

Figure 3.49 Impurities in a) WA314 PET; b) PET/MO(5wt%) copolymer sample
3.9 Spherulite radii determination using SALS

After confirming spherulite formation using optical microscopy, we used small angle light scattering to calculate the average spherulitic radii of the crystallized samples of the PET/scavenger copolymers and WA314 PET.

At 200°C, a series of samples crystallized for various times were created using WA314 PET and the PET/scavenger copolymer samples. Spherulite growth was halted at a given time of crystallization by removing the slide from the hot stage at that time and then quenching it between cold metal plates.

Cloverleaf patterns such as those shown in Figure 3.51 indicate that spherulitic superstructure is present. Avrami’s exponent is related to the form of nucleation (heterogeneous or homogeneous) and crystal growth (spheres, plates, rods) of the WA314 PET and the copolymers. Figures 3.51 to 3.53 respectively represent the spherulite
growth for WA314 PET, and the copolymer samples of PET/MO(5wt%) and PET/CHEDM(5wt%) during isothermal crystallization at 200°C.

Figure 3.51 Spherulite growth for WA314 PET during isothermal crystallization at 200°C
Figure 3.52 Spherulite growth for PET/MO(5wt%) copolymer during isothermal crystallization at 200°C
Figure 3.53 Spherulite growth for PET/CHEDM(5wt%) copolymer during isothermal crystallization at 200°C
**Determination of the spherulites radii**

Rhodes and Stein [72] found that equation 5 could be used to calculate the bulk average spherulitic radius at a given time.

\[
4.1 = \frac{4\pi R \sin(\theta_{\text{max}}^*/2)}{\lambda} \tag{5}
\]

Where

- \( R \) = Average spherulite radius (microns)
- \( \lambda \) = Wavelength of light in the scattering medium = \( \lambda_0/\eta \)
- \( \lambda_0 \) = Wavelength of light in air
- \( \eta \) = Refractive index of sample
- \( \theta_{\text{max}}^* \) = Scattering angle where intensity is maximum

It can be seen from equation 5 that the spherulite radius is inversely proportional to the scattering vector. The scattering vector is the distance from the primary beam to that of the brightest point in the lobe. As a result, the scattering pattern decreases as the spherulites increase in size. Figure 3.51 shows the light scattering patterns for WA314 PET as a function of crystallization time. As is shown, the scattering pattern shrinks with increased crystallization time. In addition, the overall intensity of the scattering pattern increases with increasing crystallization time. This indicates that the level of crystallinity in the sample is increasing. Using a scale, the scattering vector to one of the four lobes
was measured, in which the brightest point in the lobe was taken as the center point. This value was used in the calculation of the spherulite radius according to equation 5. Similar treatments were applied to the other samples.

Tables 3.10 to 3.12 respectively summarize the results of spherulites radii vs. crystallization time at 200°C for WA314 PET, PET/MO copolymer and PET/CHEDM copolymer.

Table 3.10 Spherulite radius versus isothermal crystallization time for WA314 PET at 200°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (sec)</th>
<th>R (μ)</th>
<th>t_{1/2}(sec) (using DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WA314 PET</td>
<td>200</td>
<td>150</td>
<td>3.02</td>
<td></td>
</tr>
<tr>
<td>WA314 PET</td>
<td>200</td>
<td>210</td>
<td>3.94</td>
<td></td>
</tr>
<tr>
<td>WA314 PET</td>
<td>200</td>
<td>260</td>
<td>4.46</td>
<td></td>
</tr>
<tr>
<td>WA314 PET</td>
<td>200</td>
<td>340</td>
<td>5.74</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.11 Spherulite radius versus isothermal crystallization time for PET/MO(5wt%) copolymer sample at 200°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (sec)</th>
<th>R (μ)</th>
<th>t_{1/2} (sec) (using DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/MO</td>
<td>200</td>
<td>150</td>
<td>3.79</td>
<td></td>
</tr>
<tr>
<td>PET/MO</td>
<td>200</td>
<td>210</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>PET/MO</td>
<td>200</td>
<td>260</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>PET/MO</td>
<td>200</td>
<td>300</td>
<td>5.51</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.12 Spherulite radius versus isothermal crystallization time for PET/CHEDM(5wt%) copolymer sample at 200°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (sec)</th>
<th>R (μ)</th>
<th>t₁/₂ (sec) (using DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/CHEDM</td>
<td>200</td>
<td>460</td>
<td>2.11</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>200</td>
<td>600</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>200</td>
<td>750</td>
<td>2.26</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>200</td>
<td>900</td>
<td>2.38</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.54 shows the change in spherulite size resulting from the crystallization of WA314 PET from the molten state at a crystallization temperature of 200°C.

Figure 3.54 WA314 PET spherulite growth from the melt at 200°C

![Crystallization Growth Rate](image)

Figure 3.54 WA314 PET spherulite growth from the melt at 200°C

\[
y = 0.014x + 0.910
\]

\[
R^2 = 0.995
\]
The crystal growth rate with units of microns per second (µ/sec) is the slope of the plot of spherulite radii vs. crystallization time.

From Figure 3.54,

\[
\text{crystal growth rate} = 0.014 \, \mu/\text{sec}
\]

Figure 3.55 shows the change in spherulite size resulting from the crystallization of PET/MO(5wt%) copolymer sample from the molten state at a crystallization temperature of 200°C.

![Crystallization Growth Rate](image)

Figure 3.55 PET/MO(5wt%) spherulite growth from the melt at 200°C

From Figure 3.55,

\[
\text{crystal growth rate} = 0.011 \, \mu/\text{sec}
\]

It can be seen that the crystal growth rate for the PET/MO(5wt%) copolymer sample is approximately the same as for the WA314 PET.
From Table 3.12, it is clear that to determine the average spherulitic radius of the PET/CHEDM(5wt%) copolymer sample crystallized from the molten state, the sample was crystallized for longer times as compared to PET/MO copolymer and WA314 PET samples. The reason for crystallizing the sample for longer periods of time is that it was difficult to obtain data points in the linear growth region for PET/CHEDM copolymer. Therefore, we were not able to calculate the crystal growth rate. This could be due to the large nucleation densities of the PET/CHEDM(5wt%) copolymer sample.

### 3.10 SSP of PET/scavenger copolymers

The melt IV of the PET/CHEDM copolymer samples (PET equivalent) obtained from the reactor is not sufficiently high to extrude sheets. In order to further increase the molecular weight of the PET/CHEDM copolymer samples, solid state polymerization of the samples has been done. The copolymer samples of PET/MO have sufficient IV for sheet preparation; therefore, SSP was not carried out on these copolymer samples.

During melt extrusion, the higher processing temperature and longer processing times, however, can lead to degradation of the copolymers. Degradation of the copolymers can then result in discoloration of the final products and decrease of the melt IV. In order to avoid the degradation problems, solid state polymerization has been carried out on the copolymer at a temperature of 210°C.
Figure 3.56 Apparent intrinsic viscosity (dL/g) versus time (min) for PET/CHEDM(3wt%) copolymer

Figure 3.56 shows that in the process of solid state polymerization of PET/CHEDM(3wt%) copolymer sample, the change of apparent intrinsic viscosity is very fast initially. This result implies that the SSP reaction kinetics of the PET/CHEDM(3wt%) copolymer sample is different from that of pure PET, because the apparent intrinsic viscosity of pure PET has a linear relationship with time in the solid state polymerization process [73]. The reason for this kind of SSP behavior of PET/CHEDM(3wt%) copolymer sample may be the existence of the CHEDM component (to a significant amount) which could influence the solid state polymerization kinetics of PET in the copolymers.
Figure 3.57 Apparent intrinsic viscosity (dL/g) versus time (min) for PET/CHEDM(1wt%) copolymer

Figure 3.57 shows that in the process of solid state polymerization of PET/CHEDM(1wt%) copolymer sample, the changes of apparent intrinsic viscosity are uniform with the SSP time. This result implies that the SSP reaction kinetics of the PET/CHEDM(1wt%) copolymer sample is similar to that of pure PET.

After solid state polymerization, the apparent intrinsic viscosity of the PET/CHEDM(3wt%) copolymer sample is higher than that of PET/CHEDM(1wt%) copolymer sample (as shown in Figure 3.58) when both copolymers were solid state polymerized for the same time period at 210°C.
For the copolymer sample of PET/CHEDM(3wt%), the increase in IV is greater than that for the copolymer sample of PET/CHEDM(1wt%); when the samples are solid state polymerized for the same amount of time at a temperature of 210ºC (as shown in Figure 3.58). This could have occurred because the level of crystallinity is less for the 3wt% copolymer than for the 1wt% copolymer and therefore, the diffusion rate of the byproducts for the 3wt% copolymer would be higher as compared to the 1wt% copolymer.
3.11 Oxygen permeability

One of the most important objectives of this research is to achieve improvements in the oxygen barrier properties of PET. In order to determine if this objective had been met, WA314 PET and each of the copolymer samples were extruded into sheets suitable for oxygen permeability property measurements. After extruding the sheets of PET/scavenger copolymers and WA314 PET using a single screw extruder, oxygen barrier property measurements were done by measuring the oxygen transmission rate at steady state using a whole package MoCon tester. All the sheet samples were supported on standard impermeable fixtures and Epoxy 53 adherent prevented leaks between the sample sheet and the fixture. The areas of samples were about 7.8 - 8.0 cm².

3.11.1 For PET/scavenger copolymers

Figure 3.59 shows plots of permeability versus number of days of exposure for PET/MO(5wt%), PET/CHEDM(5wt%) copolymer sheets with cobalt octoate catalyst and WA314 PET sheet. From Figure 3.59, it can be seen that the average permeability values for PET/MO, PET/CHEDM copolymers, and WA314 PET are 6.6, 5.4, and 9.2 cc*mil/100in²*day*atm, respectively. It can be seen that there is an improvement of about 30 and 40% in permeability value for PET/MO and PET/CHEDM copolymers in comparison to that of WA314 PET.

For the initial period of time, it was expected that we would observe very low values of permeability (or flux) for the PET/scavenger copolymer. That value was then expected to increase to reach a steady state value (as shown in Figure 1.4). In contrast; however, we found that the permeability values for the PET/scavenger copolymer samples were
almost constant during the entire time period of measurement as shown in Figure 3.59. This could be due to the slow rate of reaction of the scavenger and oxygen as compared to the rate of diffusion of oxygen. For cases when the rate of reaction is slow as compared to the rate of diffusion, the time lag approaches that of diffusion alone and the slope of the plot of flux or permeability versus time remains almost constant [74]. This is similar to the behavior that was observed for the PET/scavenger copolymers.

![Figure 3.59 Oxygen permeability of PET/MO, PET/CHEDM copolymer and PET sheets](image)

3.11.2 Effect of catalyst on oxygen permeability

In order to enhance oxygen uptake or improve the rate of reaction between the oxygen scavenger and permeating oxygen, cobalt octoate catalyst was added to each of the dried copolymer pellets in the glass beaker just before extruding sheets. Figure 3.60 shows a plot comparing average oxygen permeability of pure PET and PET/MO copolymer with catalyst and without catalyst. This figure shows that the oxidation catalyst (cobalt octoate) does not have significant effect on oxygen barrier properties of PET/MO copolymer samples. In this figure, the oxygen permeability of Mylar film has
also been plotted and the idea of plotting permeability value of Mylar film was to achieve the same level of permeability by modifying PET with the oxygen scavengers.

![Comparison of Permeability Values]

Figure 3.60 Average oxygen permeability for PET/MO copolymer and pure PET

In the case of PET/CHEDM copolymer sample, the effect of cobalt octoate catalyst was also not found to be significant similar to the case of PET/MO copolymer sample with catalyst. The possible reason, that we could not see the effect of catalyst on the oxygen permeability value, may be that we started actual measurements for the amount of oxygen transmitted through the PET/scavenger sheets after 3 days of the installation of the samples to allow the system to purge residual oxygen as well as to achieve a steady state value. Therefore, it is possible that we might have lost the effect of catalyst during that time period.
3.12 Density of PET/scavenger copolymers

From section 3.11, it can be seen that the improvement in oxygen barrier properties was greater for the PET/CHEDM copolymer than for the PET/MO copolymer. Since the density of a polymeric material can have an influence on its oxygen barrier properties, densities of the copolymers were measured. The density of the PET/scavenger copolymers was calculated by first determining specific gravity and then by using a correlation between specific gravity and density (as explained in section 2.12).

The specific gravity of pure PET and the copolymers was calculated as

\[
\text{sp gr.} = a/(a+w-b)
\]

\[
\therefore \text{specific gravity} = 0.3440/(0.3440+0.1473-0.2339) = 1.3364
\]

The density was calculated as:

\[
D^{22.5^\circ C} = \text{sp gr.}^{22.5^\circ C} \times \text{density of water at test temperature}
\]

Now, density of water at 22.5\(^\circ\)C = 0.99768 g/cc

\[
\therefore \text{Density of pure PET} = 1.3364 \times 0.99768 = 1.333 \text{ g/cc}
\]

Similarly the specific gravity and density of the copolymers were also calculated and reported as shown in Table 3.13. Density results given in Table 3.13 have been plotted as functions of scavenger concentrations in Figure 3.61. From Figure 3.61, it can be observed that the average density of PET/MO(1wt%) and PET/CHEDM(1wt%) copolymer samples is similar to that of pure PET and the average density decreases as the scavenger concentration increases from 1wt% to 5wt%. It can also be observed that the average density of PET/MO(5wt%) copolymer is lower than that of the
PET/CHEDM(5wt%) copolymer sample. This occurs because PET/CHEDM copolymer packs well as compared to PET/MO copolymer because of the long side chain of MO unit. This outcome supports the previous result that the oxygen permeability of PET/CHEDM copolymer is lower in comparison to that of the PET/MO copolymer.

Figure 3.61 Average densities versus concentration of scavenger
Table 3.13 Calculation of specific gravity and density

<table>
<thead>
<tr>
<th>Sample</th>
<th>a</th>
<th>b</th>
<th>w</th>
<th>Specific gravity (22.5/22.5°C)</th>
<th>Density (gm/cm³)</th>
<th>Average density (gm/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>0.3440</td>
<td>0.2339</td>
<td>0.1473</td>
<td>1.3364</td>
<td>1.333</td>
<td>1.334</td>
</tr>
<tr>
<td></td>
<td>0.3420</td>
<td>0.2331</td>
<td>0.1473</td>
<td>1.3349</td>
<td>1.332</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5430</td>
<td>0.2879</td>
<td>0.1500</td>
<td>1.3404</td>
<td>1.337</td>
<td></td>
</tr>
<tr>
<td>PET/MO 1wt%</td>
<td>0.1244</td>
<td>0.1808</td>
<td>0.1494</td>
<td>1.3375</td>
<td>1.334</td>
<td>1.334</td>
</tr>
<tr>
<td></td>
<td>0.1325</td>
<td>0.1829</td>
<td>0.1494</td>
<td>1.3384</td>
<td>1.335</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1714</td>
<td>0.1919</td>
<td>0.1494</td>
<td>1.3378</td>
<td>1.334</td>
<td></td>
</tr>
<tr>
<td>PET/MO 5wt%</td>
<td>0.0990</td>
<td>0.1730</td>
<td>0.1494</td>
<td>1.3130</td>
<td>1.310</td>
<td>1.313</td>
</tr>
<tr>
<td></td>
<td>0.0983</td>
<td>0.1733</td>
<td>0.1494</td>
<td>1.3212</td>
<td>1.319</td>
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<tr>
<td></td>
<td>0.0565</td>
<td>0.1632</td>
<td>0.1497</td>
<td>1.3140</td>
<td>1.311</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM 1wt%</td>
<td>0.6664</td>
<td>0.3170</td>
<td>0.1496</td>
<td>1.3355</td>
<td>1.333</td>
<td>1.333</td>
</tr>
<tr>
<td></td>
<td>0.6780</td>
<td>0.3202</td>
<td>0.1496</td>
<td>1.3362</td>
<td>1.333</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM 3wt%</td>
<td>0.5723</td>
<td>0.2922</td>
<td>0.1496</td>
<td>1.3319</td>
<td>1.328</td>
<td>1.329</td>
</tr>
<tr>
<td></td>
<td>0.5534</td>
<td>0.2884</td>
<td>0.1496</td>
<td>1.3348</td>
<td>1.331</td>
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</tr>
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<td></td>
<td>0.3299</td>
<td>0.2323</td>
<td>0.1501</td>
<td>1.3319</td>
<td>1.328</td>
<td></td>
</tr>
<tr>
<td>PET/CHEDM 5wt%</td>
<td>0.7430</td>
<td>0.3332</td>
<td>0.1509</td>
<td>1.3251</td>
<td>1.322</td>
<td>1.322</td>
</tr>
<tr>
<td></td>
<td>0.6843</td>
<td>0.3189</td>
<td>0.1509</td>
<td>1.3254</td>
<td>1.322</td>
<td></td>
</tr>
</tbody>
</table>
3.13 Summary

In the previous section, the synthesis of the PET/scavenger copolymers was done followed by the evaluation of experimental evidence to prove that the reaction between PET and scavengers had occurred. In this section, the effects of the scavengers on thermal, rheological, and barrier properties of the PET copolymers were monitored in order to characterize the synthesized PET/scavenger copolymers. The equilibrium melting points (T_m^o) of the PET/scavenger copolymer samples were determined by crystallizing the samples at various temperatures for one hour. The crystallization kinetic parameters were determined by using Avrami expressions and half time method. The summary of this section has been discussed as follows:

- T_g and T_m of the PET/MO copolymers were decreased as the MO content was increased from 1wt% to 5wt%. This decrease was due to the higher contents of flexible parts provided by long side chain of MO in the copolymer. The T_g values of the PET/CHEDM copolymers did not change as the CHEDM content was increased from 1wt% to 5wt%; however, the melting peak temperatures (T_m) were found to decrease. The depression of melting temperature could be attributed to the transesterified CHEDM units which restrict PET crystallization, and reduce PET crystallite size. It may also be caused by the broadening of the interfacial region from the introduction of the CHEDM block.

- Crystallization rates of the PET/MO copolymers were affected by the MO content. As the MO content in the copolymer was increased from 1wt% to 5wt%, it delayed the crystallization. Similar crystallization behavior was observed for the PET/CHEDM
copolymers, as the CHEDM contents in the copolymer were increased from 1wt% to 5wt%, it delayed the crystallization

- Pure WA314 PET showed Newtonian behavior up to the measured values of shear rate, whereas, the copolymer sample of PET/MO(1wt%) showed Newtonian behavior up to the low values of shear rate; however, the copolymer sample of PET/MO(5wt%) showed non-Newtonian behavior even at low shear rates. The reason for this behavior was that the branching occurs among the PET and MO chains

- The copolymer samples of PET/CHEDM with three different compositions of CHEDM (1, 3, and 5wt%) showed Newtonian behavior up to the measured shear rate values in a manner similar to that of pure PET

- Three melting peaks were observed in the melting curves of isothermally crystallized samples. With increasing isothermal crystallization ($T_c$), the positions of $T_{m1}$ and $T_{m2}$ shifted to higher temperatures and the position of $T_{m3}$ did not change

- The equilibrium melting point ($T_m^o$) of the copolymers was found to be depressed with increasing MO and CHEDM contents in the copolymers

- With the increase of the MO content in the PET/MO copolymers, the crystallization half time was increased at the same degree of undercooling and therefore, the crystallization rate of the PET/MO copolymer was decreased. This isothermal crystallization behavior of the PET/MO copolymer was consistent with the non-isothermal crystallization behavior of the PET/MO copolymer

- With the increase of the CHEDM content in the PET/CHEDM copolymers, the crystallization half time was increased and therefore, the crystallization rate of the PET/CHEDM copolymer was decreased. This isothermal crystallization behavior of
the PET/CHEDM copolymer was consistent with the non-isothermal crystallization behavior of the PET/CHEDM copolymer

- The crystallization kinetic parameters (n and k) determined by Avrami expression and half time method indicated that the crystallization mechanism was different for different copolymer samples with n values varying between 2 and 3
- Spherulite radii increase as the crystallization time increases for WA314 PET, and the copolymer samples of PET/MO using small angle light scattering. However, we were not able to determine the average spherulite radius of the PET/CHEDM copolymer samples crystallized from the molten state, because it was difficult to obtain data points in the linear growth region. This could be due to their large nucleation densities
- There was an improvement of about 30 and 40% in oxygen permeability for the PET/MO and PET/CHEDM copolymer sample in comparison to that of WA314 PET
- The average density values of the PET/MO(1wt%) and PET/CHEDM(1wt%) copolymer samples were similar to that of pure PET and the average specimen density was found to decrease as the scavenger concentration was increased from 1wt% to 5wt%
- It was also observed that the average density of the PET/MO(5wt%) copolymer was lower than that of the PET/CHEDM(5wt%) copolymer sample. This occurred because PET/CHEDM copolymer packs well as compared to PET/MO copolymer because of the long side chain of MO unit. This outcome supported the previous result that the oxygen permeability of the PET/CHEDM copolymer was lower in comparison to that of the PET/MO copolymer
3.14 Calculation of oxygen scavenging capacity of scavengers

After determining the effect of scavenger on thermal, rheological, and oxygen barrier properties of PET, it is also important to calculate the theoretical oxygen scavenging capacity of the scavengers in order to determine their efficiency. We have successfully developed a technique to determine the oxygen scavenging capacity of these materials experimentally. The experimental values have then been compared with the theoretical values to verify the results.

3.14.1 Theoretical calculations

3.14.1.1 For Monoolein

In order to perform the theoretical calculations, we know that one molecule of monoolein has one double bond with which oxygen molecules can react.

Let us assume that one double bond of a molecule of monoolein can react with only one oxygen molecule.

Let us take 1 mole of terephthalic acid (TPA), 1.462 moles of ethylene glycol (EG) and 0.038 moles of monoolein.

1 mole of TPA   =   166.14 g
1.462 moles of EG   =   90.75 g
0.038 mole of monoolein   =   13.55 g
Total weight   =   270.44 g

TPA   =   61.4 wt%
EG   =   33.6 wt%
Monoolein = 5 wt%

1 mole of monoolein = 6.02\times10^{23} molecules of monoolein

0.038 mole of monoolein = 2.29\times10^{22} molecules of monoolein

This copolymer can absorb 2.29\times10^{22} molecules of oxygen because each monoolein molecule has one double bond.

From the ideal gas law,

\[ PV = nRT \]

Where,

\[ P = \text{pressure of oxygen at STP conditions} = 100 \text{ kpa} \]

\[ V = \text{volume of oxygen, which can be absorbed} \]

\[ n = \text{number of moles of oxygen} \]

\[ R = \text{gas constant} = 8.314 \text{ m}^3\text{pa/mol.}^\circ\text{K} \]

\[ T = \text{temperature at STP conditions} = 273^\circ\text{K} \]

Therefore,

\[ V = 0.038\times8.314\times273\times10^6/100\times10^3 \]

\[ = 862.5 \text{ cm}^3 \]

\[ V' = 862.5/270.44 = 3.2 \text{ cm}^3 \text{ oxygen/g copolymer} = 63.6 \text{ cm}^3 \text{oxygen/g scavenger} \]
3.14.1.2 **For 3-cyclohexene-1,1-dimethanol (C$_8$H$_{14}$O$_2$)**

One molecule of 3-cyclohexene-1,1-dimethanol (CHEDM) has one double bond with which oxygen molecules can react.

Let us assume that one double bond of a molecule of CHEDM can react with only one oxygen molecule.

Let us take 1 mole of TPA, 1.405 moles of EG and 0.095 moles of CHEDM.

\[
\begin{align*}
1 \text{ mole of TPA} & = 166.14 \text{ g} \\
1.405 \text{ moles of EG} & = 87.21 \text{ g} \\
0.095 \text{ mole of CHEDM} & = 13.55 \text{ g} \\
\text{Total weight} & = 266.9 \text{ g}
\end{align*}
\]

TPA = 62.2 wt%
EG = 32.8 wt%
CHEDM = 5 wt%

\[
\begin{align*}
1 \text{ mole of CHEDM} & = 6.02 \times 10^{23} \text{ molecules of CHEDM} \\
0.095 \text{ mole of CHEDM} & = 5.72 \times 10^{22} \text{ molecules of CHEDM}
\end{align*}
\]

This copolymer can absorb $5.72 \times 10^{22}$ molecules of oxygen because each CHEDM molecule has one double bond.
From the ideal gas law,

\[ PV = nRT \]

Where,
\[ P = \text{pressure of oxygen at STP conditions} = 100 \text{ kpa} \]
\[ V = \text{volume of oxygen, which can be absorbed} \]
\[ n = \text{number of moles of oxygen} \]
\[ R = \text{gas constant} = 8.314 \text{ m}^3\text{pa/mol.}^\circ\text{K} \]
\[ T = \text{temperature at STP conditions} = 273^\circ\text{K} \]

Therefore,
\[ V = 0.084 \times 8.314 \times 273 \times 10^6 / 100 \times 10^3 \]
\[ = 2156.2 \text{ cm}^3 \]
\[ V' = 2156.2 / 266.9 = 8.1 \text{ cm}^3 \text{ oxygen/g copolymer} = 159.1 \text{ cm}^3 \text{ oxygen/g scavenger} \]

### 3.14.2 Experimental determination of oxygen scavenging capacity of scavengers

To experimentally determine the oxygen scavenging capacity of the scavengers, we have developed a technique utilizing the apparatus shown in section 2.16. The calculation for the determination of O\(_2\) scavenging capacity of the scavengers is as follows:

- Total volume of metal tube = 50 cm\(^3\)
- Volume of monoolein taken = 0.5 cm\(^3\)
- Density of monoolein = 0.942 g/cm\(^3\)
- Weight of monoolein taken = 0.471 g
- Moles of monoolein taken = 0.0013 moles
Gauge pressure of oxygen \(= 19.7 \text{ psi} = 1.34 \text{ atm}\)

For our lab,

Absolute pressure \(= 1.34 + 1 = 2.34 \text{ atm} = 34.4 \text{ psi}\)

Modified absolute pressure \(= 35.0 \text{ psi}\) (by taking into account the effect of change in room conditions)

Headspace volume \(= 49.5 \text{ cm}^3 + \pi r^2 l \text{ cm}^3 = 49.5 \text{ cm}^3 + 4.25 \text{ cm}^3 = 53.75 \text{ cm}^3\)

At \(P_1 = 35.0 \text{ psi}\) (pressure of oxygen at the beginning of the scavenging reaction)

\[
P_1 V_1/T_1 = P_2 V_2/T_2
\]

\[
35.0 \times 53.75/296 = 14.7 \times V_2/273
\]

\(\Rightarrow\) Volume of oxygen at STP conditions \(= V_2 = 118.03 \text{ cm}^3\)

We know, \(V_2/n_2 = 22.414 \text{ m}^3/\text{kmol at } 0^\circ \text{C and } 101.325 \text{ kpa}\)

\(n_2 = \# \text{ of moles of oxygen at the beginning of scavenging reaction} = 5.27 \times 10^{-3} \text{ mol}\)

Figure 3.62 shows the plot of variation of pressure of oxygen inside the metal tube with time. It is clear from the plot that as the time of oxidation increases, the amount of oxygen inside the metal tube decreases because it is consumed by the scavenger and eventually attains an equilibrium value.
At $P_3 = 27.7$ psi (pressure of oxygen at the end of 76 days of scavenging reaction)

$$P_3V_3/T_3 = P_4V_4/T_4$$

$$27.7 \times 53.75/296 = 14.7 \times V_4/273$$

$\Rightarrow$ Volume of oxygen remaining at STP conditions $= V_4 = 93.4 \text{ cm}^3$

Also, $V_4/n_4 = 22.414 \text{ m}^3/\text{kmol}$ at $0°C$ and 101.325 kpa

$n_4 = \# \text{ of moles of oxygen remaining} = 4.17 \times 10^{-3} \text{ mol}$

$\# \text{ of moles of oxygen consumed} = n_2 - n_4 = (5.27 - 4.17) \times 10^{-3}$

$\Rightarrow n_2 - n_4/\text{gm scavenger} = 1.1 \times 10^{-3}/0.471$

$= 2.3 \times 10^{-3} \text{ moles of oxygen consumed/g scavenger}$

$\Rightarrow$ Volume of oxygen consumed (cm$^3$)/g of scavenger $= 52.3$
\[ \text{Scavenger Capacity (SC)} \] = \# of moles of oxygen consumed/g scavenger
\[ = 2.3 \times 10^{-3} \text{ moles of oxygen consumed/g scavenger} \]
\[ = \frac{2.3 \times 10^{-3} \times 6.02 \times 10^{23}}{0.017 \times 10^{23}} \text{ molecules of oxygen consumed} \]
\[ \text{SC} = 0.81 \text{ molecules of oxygen consumed/molecule of monoolein} \]

The experimental results are consistent with the theoretical calculations used to determine the oxygen scavenging capacity of the scavengers. The above results also validate our assumption made during our theoretical calculations that one double bond of a molecule of scavenger can react with only one oxygen molecule.

3.15 Effect of oxidation catalyst on rheological and thermal properties

As previously discussed, the cobalt octoate catalyst was added to PET/scavenger copolymer pellets just before extruding the sheets in order to enhance oxygen uptake. In this section, we have evaluated the effects of the catalyst on rheological and thermal properties of the extruded copolymers.

To study the effect of oxidation catalyst on rheological and thermal properties, the following samples were used:

- Solid state polymerized PET/CHEDM(1wt%) copolymer sample (pellets from two different batches)
- Solid state polymerized and extruded sheet sample of PET/CHEDM(1wt%) copolymer with two different concentrations of catalyst
Solid state polymerized PET/CHEDM(5wt%) copolymer sample (pellets from two different batches)

Solid state polymerized and extruded sheet sample of PET/CHEDM(5wt%) copolymer with two different concentrations of catalyst

PET/MO(5wt%) copolymer sample (pellets from two different batches)

Extruded sheet samples of PET/MO(5wt%) copolymer with two different concentrations of catalyst

Extruded sheet sample of PET/MO(5wt%) copolymer without catalyst

WA314 PET (unprocessed)

WA314 PET (processed with the addition of 400 ppm catalyst)

WA314 PET (processed without catalyst)

3.15.1 Rheological behavior of PET/scavenger copolymers

3.15.1.1 For PET/CHEDM copolymer

Figures 3.63 and 3.64 illustrate the effect of catalyst on the shear viscosity (or melt IV) of PET/CHEDM copolymer samples. From Figure 3.63, it is clear that the shear viscosity of two different batches of PET/CHEDM(1wt%) copolymer samples decreases significantly after adding two different concentrations of catalyst. The melt IV (PET equivalent) was calculated from shear viscosity data at a shear rate of 10 sec\(^{-1}\) for all the copolymer samples. The melt IV of the first batch of PET/CHEDM(1wt%) copolymer sample decreases from 0.77 to 0.67 after adding 200 ppm catalyst to it and the melt IV of
second batch of PET/CHEDM(1wt%) copolymer sample decreases from 0.76 to 0.56 after adding 400 ppm catalyst to it.

![Shear Viscosity vs Shear Rate](image.png)

**Figure 3.63** Shear viscosity versus shear rate for PET/CHEDM(1wt%) copolymer

From Figure 3.64, it is clear that the shear viscosity of two different batches of PET/CHEDM(5wt%) copolymer samples decreases significantly after adding two different concentrations of catalyst. The melt IV (PET equivalent) was calculated from shear viscosity data at a shear rate of 10 sec\(^{-1}\) for all the copolymer samples. The melt IV of first batch of PET/CHEDM(5wt%) copolymer sample decreases from 0.79 to 0.73 after adding 200 ppm catalyst to it and the melt IV of second batch of PET/CHEDM(5wt%) copolymer sample decreases from 0.81 to 0.57 after adding 400 ppm catalyst to it.
Figure 3.64 Shear viscosity versus shear rate for PET/CHEDM(5wt%) copolymer

3.15.1.2 For PET/MO copolymer

Figure 3.65 illustrates the effect of catalyst on the shear viscosity of PET/MO copolymer samples. From Figure 3.65, it is clear that the shear viscosities of two different batches of PET/MO(5wt%) copolymer samples decrease after adding 400 ppm and 250 ppm catalyst to the copolymer samples.

To see the effect of processing on the shear viscosity without adding catalyst, we extruded PET/MO(5wt%) copolymer sample through an Instron capillary rheometer. From Figure 3.65, it can be seen that the shear viscosity of PET/MO(5wt%) copolymer sample decreases to a small extent after processing without catalyst. However, the decrease in shear viscosity for PET/MO(5wt%) copolymer sample after processing without catalyst is not significant as compared to the decrease in shear viscosity for PET/MO(5wt%) copolymer sample after processing with catalyst in it.
3.15.1.3 For WA314 PET

Figure 3.66 illustrates the effect of catalyst on the shear viscosity or melt IV (calculated at a shear rate of 10 sec\(^{-1}\)) of WA314 PET sample. From Figure 3.66, it is clear that the shear viscosity of WA314 PET sample decreases significantly after processed it with the addition of a catalyst. The melt IV was calculated from shear viscosity data at a shear rate of 10 sec\(^{-1}\) for WA314 PET sample. The melt IV of WA314 PET sample decreases from 0.73 to 0.62 after adding 400 ppm catalyst in it.

To see the effect of processing on the shear viscosity without the addition of a catalyst, we extruded WA314 PET sample through single screw extruder. From Figure 3.66, it can be seen that the shear viscosity of WA314 PET sample decreases to a small
extent from 0.73 to 0.70 after processing without catalyst, however, the decrease in melt IV is not significant as compared to the decrease in the melt IV after adding catalyst.

Figure 3.66 Shear viscosity versus shear rate for WA314 PET sample

Therefore, we can say that the oxidation catalyst is causing the degradation of the PET/scavenger copolymers and WA314 PET.
3.15.2 Thermal behavior of PET/scavenger copolymers

In this section, we have evaluated the effect of the oxidation catalyst on the thermal properties of the PET/scavenger copolymers and WA314 PET. The same samples were used for the thermal analysis as were used for the rheological study in section 3.13.1.

3.15.2.1 DSC data for PET/MO copolymer

It is clear from Table 3.14 and Figures 3.67 and 3.69 that the crystallization temperature ($T_c$) decreases after processing PET/MO(5wt%) copolymer sample through an Instron capillary rheometer at 265°C without the addition of the catalyst, while heating from the quench. The $T_c$ decreases more significantly when both the batches of PET/MO(5wt%) copolymer samples were processed with the addition of the catalyst in single screw extruder at 265°C. The reason for this behavior is that the catalyst is causing the oxidative degradation (or lowering the IV) of the PET/MO copolymer samples and this decrease in molecular weight leads to faster crystallization. There is no effect of catalyst on $T_g$ and $T_m$ of the PET/MO(5wt%) copolymer samples.

From Table 3.15 and Figures 3.68 and 3.70, it can be clearly seen that the crystallization behavior ($T_{cc}$) for PET/MO(5wt%) copolymer samples follows the same trend as above, while cooling from the melt.
Figure 3.67 Melting and crystallization behavior for PET/MO(5wt%) copolymer samples

Figure 3.68 Crystallization behavior for PET/MO(5wt%) copolymer samples
Figure 3.69 Melting and crystallization behavior for PET/MO(5wt%) copolymer samples

Figure 3.70 Crystallization behavior for PET/MO(5wt%) copolymer samples
Table 3.14 Melting and crystallization behavior for PET/MO(5wt%) copolymer samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Status</th>
<th>Shear Viscosity</th>
<th>Heating from quench</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Melting</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$T_g$ (°C)</td>
</tr>
<tr>
<td>PETMO5_061808</td>
<td>From Reactor</td>
<td>non-Newtonian</td>
<td>68</td>
</tr>
<tr>
<td>PETMO5_061808</td>
<td>Processed with 400ppm catalyst</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>From Reactor</td>
<td></td>
<td>67</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>Processed</td>
<td></td>
<td>66</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>Processed with 250ppm catalyst</td>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>

Table 3.15 Crystallization behavior for PET/MO(5wt%) copolymer samples

<table>
<thead>
<tr>
<th>Material</th>
<th>Status</th>
<th>Shear Viscosity</th>
<th>Cooling from the melt, $T_{cc}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PETMO5_061808</td>
<td>From Reactor</td>
<td>non-Newtonian</td>
<td>150</td>
</tr>
<tr>
<td>PETMO5_061808</td>
<td>Processed with 400ppm catalyst</td>
<td></td>
<td>166</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>From Reactor</td>
<td></td>
<td>153</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>Processed</td>
<td></td>
<td>166</td>
</tr>
<tr>
<td>PETMO5_062408</td>
<td>Processed with 250ppm catalyst</td>
<td></td>
<td>173</td>
</tr>
</tbody>
</table>
3.15.2.2 DSC data for PET/CHEDM copolymer

It is clear from Figures 3.71 that the crystallization temperature \( (T_c) \) of the PET/CHEDM(5wt\%) copolymer sample decreases when it is processed with the catalyst in single screw extruder at 265°C. It is also noted that the higher the catalyst content, the faster is the crystallization. There is no effect of catalyst on \( T_g \) and \( T_m \) of the copolymer samples.

From Figure 3.72, it is observed that the crystallization behavior \( (T_{cc}) \) for PET/CHEDM(5wt\%) copolymer sample follows the same trend as above, while cooling from the melt. Therefore, we can say that the catalyst is reducing the molecular weight of the copolymer due to oxidative degradation and making the crystallization faster for PET/CHEDM(5wt\%) copolymer samples.

Figure 3.71 Melting and crystallization behavior for PET/CHEDM(5wt\%) copolymer
From Figures 3.73 and 3.75, it is noted that the crystallization temperature ($T_c$) of PET/CHEDM(1wt%) copolymer sample decreases when it is processed with catalyst in single screw extruder at 275°C. It is also clear that the higher the catalyst content, the faster is the crystallization. However, there is no effect of catalyst on $T_g$ and $T_m$ of the copolymer samples.

From Figures 3.74 and 3.76, it can be seen that the crystallization behavior ($T_{cc}$) for PET/CHEDM(1wt%) copolymer sample follows the same trend as above, while cooling from the melt. Therefore, the catalyst is reducing the molecular weight of the copolymer due to oxidative degradation and making the crystallization faster for PET/CHEDM(1wt%) copolymer samples.
Figure 3.73 Melting and crystallization behavior for PET/CHEDM(1wt%) copolymer sample

Figure 3.74 Crystallization behavior for PET/CHEDM(1wt%) copolymer sample
Figure 3.75 Crystallization behavior for PET/CHEDM copolymer (from the glassy state)

Figure 3.76 Crystallization behavior for PET/CHEDM copolymer (cooling from the melt)
Tables 3.16 and 3.17 summarize the results of melting and crystallization behaviors for PET/CHEDM copolymers with 1wt% and 5wt% concentrations of CHEDM.

Table 3.16 Melting and crystallization behavior for PET/CHEDM copolymer samples

<table>
<thead>
<tr>
<th>Material</th>
<th>CHEDM content (wt%)</th>
<th>Catalyst content (ppm)</th>
<th>Melt IV</th>
<th>Heating from quench</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Melting</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T_g (°C)</td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>5</td>
<td>200</td>
<td>0.73</td>
<td>79</td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>1</td>
<td>400</td>
<td>0.57</td>
<td>77</td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>1</td>
<td>200</td>
<td>0.67</td>
<td>79</td>
</tr>
<tr>
<td>PET/CHEDM</td>
<td>5</td>
<td>400</td>
<td>0.56</td>
<td>78</td>
</tr>
</tbody>
</table>
Table 3.17 Crystallization behavior for PET/CHEDM copolymer samples

<table>
<thead>
<tr>
<th>Material</th>
<th>CHEDM content (wt%)</th>
<th>Catalyst content (ppm)</th>
<th>Melt IV</th>
<th>Cooling from the Melt, T_{cc} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/CHEDM 5</td>
<td></td>
<td>200</td>
<td>0.73</td>
<td>160</td>
</tr>
<tr>
<td>PET/CHEDM 1</td>
<td></td>
<td>400</td>
<td>0.57</td>
<td>164</td>
</tr>
<tr>
<td>PET/CHEDM 1</td>
<td></td>
<td>200</td>
<td>0.67</td>
<td>181</td>
</tr>
<tr>
<td>PET/CHEDM 1</td>
<td></td>
<td>400</td>
<td>0.56</td>
<td>188</td>
</tr>
</tbody>
</table>

3.16 Summary

In the previous two sections, the effects of the scavengers on thermal, rheological, and barrier properties of PET were evaluated. In this section, a technique was developed to determine the oxygen scavenging capacity of the scavengers experimentally and then it was compared with the theoretical value. The effect of cobalt octoate catalyst on thermal and rheological properties was also studied. The summary of this section has been discussed as follows:

- A technique was successfully developed to determine the oxygen scavenging capacity of the potential oxygen scavengers experimentally
The melt IV of PET/scavenger copolymer samples and WA314 PET was found to have decreased significantly with the addition of the cobalt octoate catalyst and thereby caused the crystallization faster for the PET/scavenger copolymers.

It was also observed that as the amount of cobalt octoate catalyst was increased from 200 ppm to 400 ppm, the melt IV of the PET/scavenger copolymers was further decreased and ultimately caused even faster crystallization.

3.17 A methodology to determine the scavenging capacity of potential oxygen scavengers

This section describes a methodology that was developed in order to determine the kinetics, scavenging capacity and effectiveness of potential oxygen scavengers. The oxidation kinetic parameters of the scavengers and the copolymers were determined by the following three methods: 1. Integral method; 2. Differential method; 3. Polymath nonlinear regression analysis. To evaluate the effectiveness of potential oxygen scavengers, we have calculated a dimensionless quantity called the “Thiele Modulus”.

3.17.1 Determination of the oxidation kinetics of pure MO and PET/MO copolymer

FTIR and NMR spectroscopy techniques were used to determine the oxidation kinetics of the pure scavengers and the PET/scavenger copolymers by studying changes in the unsaturated double bond peaks present in their spectra.
For Pure Monoolein

**FTIR data:**

The following steps were used to monitor the reaction progress quantitatively:

\[
\text{A (MO) + B (O}_2\text{) } \rightarrow \text{ products}
\]

1. Record time-dependent ATR spectra
2. Compute \( H(3010)/H1(1170) = R \) (where \( H \) is the absorbance height of the peak at a particular wave number)
3. Compute \( R/R(t_0) \)
4. Plot \( \ln(R/R(t_0)) \) versus time
5. Fit linear region \( \rightarrow \) pseudo–1\textsuperscript{st} order (**Integral method**)

Figure 3.77 shows the structure of pure MO compound.

![Figure 3.77 Structure of pure MO](image)

Figure 3.77 Structure of pure MO
Table 3.18 represents a few important IR band assignments which were observed for the IR spectrum of pure monoolein as shown in Figures 3.78 to 3.80:

Table 3.18 IR band assignments

<table>
<thead>
<tr>
<th>Wave number (cm⁻¹)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>723 m</td>
<td>Cis C=CH planar bend</td>
</tr>
<tr>
<td>1170 s</td>
<td>C(O)-C ester vibration</td>
</tr>
<tr>
<td>2855-2893 vs-sh</td>
<td>CH stretch (-CH₂- asymmetric and –CH₃ asymmetric)</td>
</tr>
<tr>
<td>2926-2955 vs-sh</td>
<td>CH stretch (-CH₂- symmetric and –CH₃ symmetric)</td>
</tr>
<tr>
<td>3010 w</td>
<td>Cis C=CH symmetric stretch</td>
</tr>
<tr>
<td>3451-3600 m (broad)</td>
<td>O-H stretch</td>
</tr>
</tbody>
</table>

* m = medium, s = strong, vs-sh = very strong-shoulder, w = weak

From Figures 3.78 and 3.79, it is clear that the height of double bond peak (CH=CH) at a wave number of 3010 cm⁻¹ decreases with time, because the oxidation of monoolein will occur at the double bond of CH=CH present in monoolein resulting in oxidation products such as aldehydes or ketones. The peak at a wave number of 1170 cm⁻¹ corresponds to ester vibration (C(O)-C). Since this peak does not change after oxidation of monoolein, it was taken as an internal reference.
Figure 3.78 FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C)
Figure 3.79 Expanded FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C)
Table 3.19 represents the data for change of height of double bond peak versus time for pure MO, when the sample was oxidized at 50°C.

Table 3.19 Height of double bond peak versus time of oxidation for pure MO using FTIR

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Height of double bond peak, H (3010 cm(^{-1}))</th>
<th>Reference peak height, H1 (1170 cm(^{-1}))</th>
<th>Normalized height of double bond peak, R = H/H1=C(_A)</th>
<th>ln(R/R(t(_0)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0314</td>
<td>0.0569</td>
<td>0.55</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.0279</td>
<td>0.0552</td>
<td>0.51</td>
<td>-0.0755</td>
</tr>
<tr>
<td>2</td>
<td>0.0266</td>
<td>0.0589</td>
<td>0.45</td>
<td>-0.2007</td>
</tr>
<tr>
<td>4</td>
<td>0.0235</td>
<td>0.0595</td>
<td>0.39</td>
<td>-0.3438</td>
</tr>
<tr>
<td>7</td>
<td>0.0185</td>
<td>0.0567</td>
<td>0.33</td>
<td>-0.5108</td>
</tr>
<tr>
<td>11</td>
<td>0.0171</td>
<td>0.0586</td>
<td>0.29</td>
<td>-0.6400</td>
</tr>
<tr>
<td>13</td>
<td>0.0146</td>
<td>0.0592</td>
<td>0.25</td>
<td>-0.7885</td>
</tr>
<tr>
<td>15</td>
<td>0.0132</td>
<td>0.0588</td>
<td>0.22</td>
<td>-0.9163</td>
</tr>
<tr>
<td>18</td>
<td>0.0105</td>
<td>0.0584</td>
<td>0.18</td>
<td>-1.117</td>
</tr>
<tr>
<td>21</td>
<td>0.0094</td>
<td>0.0587</td>
<td>0.16</td>
<td>-1.2347</td>
</tr>
</tbody>
</table>

The decrease of the cis C=C-H wagging peak at 723 cm\(^{-1}\) can also be easily seen for the time period of measurement as shown in Figure 3.80. The peak is becoming narrower as the scavenger is consumed by the oxygen.
Figure 3.80 Expanded FTIR spectrum of pure MO (before oxidation and after oxidation at 50°C)
After studying the unsaturated double bond peak as a function of time using FTIR spectroscopy, we determined the oxidation kinetic parameters from the data collected from the FTIR spectroscopy by using the following three different methods:

1. Integral method
2. Differential method
3. Polymath nonlinear regression analysis

The reason for using the above three methods is to compare the results of the oxidation kinetic parameters determined by these three different methods with each other and to validate these results.

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted concentration versus time curve with the experimental concentration versus time data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is used as follows:

1. Record time-dependent ATR spectra
2. Compute $H(3010)/H1(1170) = R$
3. Compute $R/R(t_0)$
4. Plot $\ln(R/R(t_0))$ versus time
5. Fit linear region $\rightarrow$ pseudo–1st order
According to the Integral method,

Let us assume that the reaction is first-order (or let us assume oxygen is in excess), then

\[-dC_A/dt = kC_A\]

With the limits \(C_A = C_{A0}\) at \(t = 0\) gives

\[\ln(C_A/C_{A0}) = -kt\]

or

\[\ln(R/R(t_0)) = -kt\]

Plot \(\ln(R/R(t_0))\) versus time, if it fits to a linear region, then the reaction is pseudo-1\(^{st}\) order and slope is equal to the rate constant of oxidation \((k)\) (as shown in Figure 3.81).

From Figure 3.81, it is clear that the data fits to a linear region, so

\[\text{Slope} = -k = -0.062\]

\[k = 0.062 \text{ day}^{-1}\]

Figure 3.81 Plot of \(\ln(R/R(t_0))\) versus time for pure monoolein
The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative \( \frac{dC_A}{dt} \), and testing the goodness of fit of the equation with the experimental data. The procedure is as follows:

1. Plot the \( C_A \) versus time data, and then draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.

2. Determine the slope of this curve at suitably selected concentration values. These slopes \( \frac{dC_A}{dt} = r_A \) are the rates of reaction at these compositions.

3. Now search for a rate expression to represent this \( r_A \) versus \( C_A \) data by testing an \( n \)th order form \( -r_A = kC_A^n \) by taking logarithms of the rate equation.

According to the Differential method,

\[
A \text{ (MO)} + B \text{ (O}_2\text{)} \text{Excess} \rightarrow \text{products}
\]

For an irreversible reaction, the rate law can be written as

\[
-r_A = kC_A^aC_B^b
\]

Using Method of excess, the rate can be written as

\[
-r_A = kC_A^a
\]

also

\[
-r_B = kC_B^b
\]

By combining mole balance and rate law, we obtain

\[
-dC_A/dt = kC_A^a
\]

After taking the natural logarithm of both sides, we get

\[
\ln(-dC_A/dt) = \ln(-\text{rate}) = \ln(k) + a \ln(C_A)
\]
The slope of a plot of ln(-dC_i/dt) versus ln(C_i) is the reaction order. To obtain the derivative (-dC_i/dt) used in this plot, we must differentiate the concentration-time data. The technique which we used to differentiate the data is first to fit the concentration-time data to a 2nd order polynomial (as shown in Figure 3.82):

\[ C_i = a_0 + a_1t + a_2t^2 \]

Where, \( a_i \)'s are the constants.

Now, \( \frac{dC_i}{dt} = a_1 + 2a_2t \)

The reaction order and rate constant can now be found from a plot of ln(-dC_i/dt) versus ln(C_i) (as shown in Figure 3.83).

From Figure 3.83,

\[
\begin{align*}
\text{Slope} &\quad = \quad 1.2 \\
\text{Intercept} &\quad = \quad \ln(k) \quad = \quad -2.6078 \\
\text{k} &\quad = \quad 0.074 \quad \text{day}^{-1}
\end{align*}
\]
Figure 3.82 Plot of normalized height of double bond peak versus time for pure MO

![Normalized height of double bond peak versus time](image1)

\[ y = 0.0007x^2 - 0.0311x + 0.5253 \]
\[ R^2 = 0.9799 \]

Figure 3.83 Plot of \( \ln(-\text{rate}) \) versus \( \ln(C_A) \) for pure MO

![\( \ln(-\text{rate}) \) versus \( \ln(C_A) \)](image2)

\[ y = 1.2312x + 2.6078 \]
\[ R^2 = 0.9681 \]
Polymath Nonlinear Regression analysis is also done because we want to find the kinetic parameter values (alpha, k) for which the sum of the squares of the differences, the measured parameter ($P_m$), and the calculated parameter ($P_c$) is a minimum [75].

$$\sigma^2 = \sum_{i=1}^{n} \frac{(P_{mi} - P_{ci})^2}{N - k}$$

That is we want $\sigma^2$ to be a minimum. This analysis is done by using software called “Polymath Nonlinear Regression”. For concentration-time data, the measured parameter P has concentration $C_A$. we can integrate the mole balance equation and rate law

$$\frac{dC_A}{dt} = -C_A^\alpha$$

to obtain

$$C_A = [C_{A0}^{1-\alpha} - (1-\alpha)kt]^{1/1-\alpha}$$

by rearranging this equation, we get

$$t = \frac{(C_{A0}^{1-\alpha} - C_A^{1-\alpha})}{k(1-\alpha)}$$

We now guess k and alpha and calculate each $C_{ACi}$ at different times and then compare it with the measured concentration by taking the difference and squaring it.

We then sum up the differences for all the data points:

$$S^2 = \sum_{i=1}^{N} (C_{Ami} - C_{AcI})^2 = \sum_{i=1}^{N} \left( C_{Ami} - \left[ C_{A0}^{1-\alpha} - (1-\alpha)kt_i \right]^{1/1-\alpha} \right)^2$$

We continue to guess k and alpha until we find the values of alpha and k which minimize $S^2$. 

173
According to Polymath Nonlinear Regression Analysis,

**POLYMATH Report**

Nonlinear Regression (L-M) 10-Oct-2008

**Model:** Time = ((CA0^(1-alpha))-(C^(1-alpha)))/(k*(1-alpha))

<table>
<thead>
<tr>
<th>Variable</th>
<th>Initial guess</th>
<th>Value</th>
<th>95% confidence</th>
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<td>0.5303393</td>
<td>0.0020003</td>
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<tr>
<td>alpha</td>
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<tr>
<td>k</td>
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<td>0.0004066</td>
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**Nonlinear regression settings**

Max # iterations = 64

**Precision**

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<td>Rmsd</td>
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<td>Variance</td>
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**General**

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<tr>
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<td>Indep vars</td>
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<td>Iterations</td>
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</table>
### Source data points and calculated data points

<table>
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<tr>
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<th>Delta Time</th>
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<td>5</td>
<td>0.36</td>
<td>5</td>
<td>6.009104</td>
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</tr>
<tr>
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<td>0.33</td>
<td>7</td>
<td>7.454685</td>
<td>-0.4546847</td>
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<tr>
<td>7</td>
<td>0.29</td>
<td>11</td>
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<td>1.329785</td>
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<td>11</td>
<td>0.16</td>
<td>21</td>
<td>21.01642</td>
<td>-0.0164185</td>
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</table>
Table 3.20 gives a comparison of the order of reaction and rate constant \( (k) \) values calculated by three different methods using FTIR data for pure monoolein. It is evident that the order of reaction and the rate constant values are very similar for all the three methods and \( R^2 \) value is also very good. This confirms that the order of the oxidation reaction for pure MO is 1 and the rate constant value is varying between 0.06-0.08 day\(^{-1}\) using FTIR data.

Table 3.20 Order of reaction and k values for pure MO using FTIR data

<table>
<thead>
<tr>
<th></th>
<th>Integral method</th>
<th>Differential method</th>
<th>Polymath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order (alpha)</td>
<td>1</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Rate constant (k), ( \text{day}^{-1} )</td>
<td>0.062</td>
<td>0.074</td>
<td>0.08</td>
</tr>
<tr>
<td>( R^2 ) value</td>
<td>0.98</td>
<td>0.97</td>
<td>0.99</td>
</tr>
</tbody>
</table>
**NMR data:**

In order to study the oxidation kinetics of pure MO using NMR spectroscopy, the samples were prepared by oxidizing pure MO at 50°C for 35 days. Figure 3.84 illustrates the $^1$H NMR spectrum for an unoxidized sample of pure MO. Figures 3.85 and 3.86 illustrate the $^1$H NMR spectra for pure MO oxidized at 50°C for different time periods. In the $^1$H NMR spectrum for an unoxidized sample of pure MO (as shown in Figure 3.84), the peak of protons of CH=CH at $\delta= 5.38$ ppm has an area under the peak of 1.88. In the $^1$H NMR spectrum of pure MO sample oxidized for 8 days at 50°C (as shown in Figure 3.85), the peak of protons of CH=CH at $\delta= 5.38$ ppm has an area under the peak of 1.34 and in the $^1$H NMR spectrum of pure monoolein oxidized for 21 days at 50°C (as shown in Figure 3.86), the peak of protons of CH=CH at $\delta= 5.39$ ppm has an area under the peak of 0.67.

It is evident that the number of protons of double bond of CH=CH, where the oxidation is occurring, are decreasing after the oxidation. Also, the area under the peak of highlighted protons of $\text{CH}_2\text{CH=CHCH}_2$ of the monoolein unit at $\delta= 2.04$ ppm is decreasing after oxidation. This decrease in area under the peak occurs because there is change in chemical environment around the double bond after oxidation.
Figure 3.84 $^1$H NMR spectrum of pure MO (before oxidation)

Figure 3.85 $^1$H NMR spectrum of pure MO (after oxidation for 8 days at 50°C)
Figure 3.86 $^1$H NMR spectrum of pure MO (after oxidation for 21 days at 50°C)

Table 3.21 gives examples of the data recorded for changes of area under the double bond peak ($A$) as a function of exposure time for pure MO oxidized at 50°C. It should also be noted that the area under the double bond peak is normalized with respect to the $\text{–CH}_3$ group peak which does not change at all after the oxidation reaction.

Table 3.21 Area under double bond peak ($A$) versus time for pure MO using NMR

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Area under double bond peak ($A$)</th>
<th>$A(t_0)$</th>
<th>$\ln(A/A(t_0))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.88</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1.34</td>
<td></td>
<td>-0.3386</td>
</tr>
<tr>
<td>14</td>
<td>1.02</td>
<td>1.88</td>
<td>-0.6115</td>
</tr>
<tr>
<td>21</td>
<td>0.67</td>
<td></td>
<td>-1.0318</td>
</tr>
<tr>
<td>35</td>
<td>0.36</td>
<td></td>
<td>-1.6529</td>
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</table>
After studying the unsaturated double bond peak for pure MO as a function of time using NMR spectroscopy, we determined the oxidation kinetic parameters for pure MO from the data collected from the NMR spectroscopy by using the following three methods:

1. Integral method

2. Differential method

3. Polymath nonlinear regression analysis

**According to the Integral method,**

Let us assume that the reaction is first-order (or let us assume oxygen is in excess), then

\[-dC_A/dt = kC_A\]

With the limits \(C_A = C_{A0}\) at \(t = 0\) gives

\[\ln(C_A/C_{A0}) = -kt\]

or

\[\ln(A/A_0) = -kt\]

Plot \(\ln(A/A_0)\) versus time, if it fits to a linear region, then the reaction is pseudo–1\(^{st}\) order and the slope is equal to the rate constant of oxidation (k) (as shown in Figure 3.87).

From Figure 3.87, it is clear that the data fits to a linear region, so

\[\text{Slope} = -k = -0.047\]

\[k = 0.047 \text{ day}^{-1}\]
The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative $\frac{dC_A}{dt}$, and testing the goodness of fit of the equation with experiment. The procedure is as follows:

1. Plot the $C_A$ versus time data, and then draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.

2. Determine the slope of this curve at suitably selected concentration values. These slopes $\frac{dC_A}{dt} = r_A$ are the rates of reaction at these compositions.

3. Now search for a rate expression to represent this $r_A$ versus $C_A$ data by testing an nth order form $-r_A = kC_A^n$ by taking logarithms of the rate equation.
According to the Differential method,

\[ A \text{ (MO)} + B \text{ (O}_2\text{)} \rightarrow \text{products} \]

For an irreversible reaction, the rate law can be written as

\[-r_A = kC_A^a C_B^b\]

Using Method of excess, the rate can be written as

\[-r_A = kC_A^a\]

also,

\[-r_A = kC_B^b\]

By combining mole balance and rate law, we obtain

\[-dC_A/dt = kC_A^a\]

After taking the natural logarithm of both sides, we get

\[\ln(-dC_A/dt) = \ln(-\text{rate}) = \ln(k) + a \ln(C_A)\]

The slope of a plot of \(\ln(-dC_A/dt)\) versus \(\ln(C_A)\) is the reaction order. To obtain the derivative \((-dC_A/dt)\) used in this plot, we must differentiate the concentration-time data. The technique which we used to differentiate the data is first to fit the concentration-time data to a 2nd order polynomial (as shown in Figure 3.88):

\[C_A = a_0 + a_1 t + a_2 t^2\]

where \(a_i\)'s are the constants.

Now,

\[dC_A/dt = a_1 + 2a_2 t\]

The reaction order and rate constant can now be found from a plot of \(\ln(-dC_A/dt)\) versus \(\ln(C_A)\) (from Figure 3.89).
From Figure 3.89,

\[
\text{Slope} = 1.1 \\
\text{Intercept} = \ln(k) = -3.1321 \\
k = 0.044 \text{ day}^{-1}
\]

Figure 3.88 Area under double bond peak versus time for pure MO using NMR data

Figure 3.89 $\ln(-\text{rate})$ versus $\ln(C_A)$ for pure MO using NMR data
According to Polymath nonlinear regression analysis,

**POLYMATH Report**

Nonlinear Regression (L-M) 10-Oct-2008

**Model:** Time = \((CA0^{(1-alpha)}-(C^{(1-alpha)})/(k*(1-alpha))\)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Initial guess</th>
<th>Value</th>
<th>95% confidence</th>
</tr>
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<tr>
<td>k</td>
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<td>0.0098541</td>
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**Nonlinear regression settings**
Max # iterations = 64

**Precision**

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<td>Rmsd</td>
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<tr>
<td>Variance</td>
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**General**

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<td>Indep vars</td>
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<td>Iterations</td>
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Source data points and calculated data points

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<th>C</th>
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<th>Delta Time</th>
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<td>2</td>
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<td>5</td>
<td>0.36</td>
<td>34.71784</td>
<td>0.2821638</td>
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</table>

Table 3.22 gives a comparison of the order of reaction and rate constant (k) values calculated by three different methods using NMR data for pure monoolein. It is evident that the order of reaction and the rate constant values are very similar for all the three methods and $R^2$ value is also very good. This confirms that the order of the oxidation reaction for pure MO is 1 and the rate constant value is varying between 0.04-0.05 day$^{-1}$ using NMR data.

Table 3.22 Order of reaction and k values for pure MO using NMR data

<table>
<thead>
<tr>
<th></th>
<th>Integral method</th>
<th>Differential method</th>
<th>Polymath</th>
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<tbody>
<tr>
<td>Order (alpha)</td>
<td>1</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>Rate constant (k), day$^{-1}$</td>
<td>0.05</td>
<td>0.044</td>
<td>0.05</td>
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<tr>
<td>$R^2$ value</td>
<td>1.0</td>
<td>0.93</td>
<td>1.0</td>
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It can be clearly seen that the values of the rate constant of oxidation ($k$) for pure MO calculated by using the FTIR data (as summarized in Table 3.21) and the NMR data (as summarized in Table 3.22) are not exactly the same. There could be two possibilities for this difference in $k$ value:

1. The two methods (i.e. FTIR and NMR) are completely different methods used to calculate the $k$ value because the sample conditions during oxygen exposure are different and the treatment of the samples during analysis is also different
2. The other possibility could be the diffusion effect of oxygen, because the thickness of the sample taken is different in the two methods

Correlation for the liquid diffusivity of small molecules is the empirical Wilke-Chang equation 76

To further evaluate the possibility 2 related to the diffusion effect of the oxygen through the sample (as mentioned above), the following correlation was used:

$$D_v = 7.4 \times 10^{-8} (\psi_B M_B)^{1/2} T/\mu V_A^{0.6}$$

(6)

Where

- $D_v$ = diffusivity, cm$^2$/s
- $T$ = absolute temperature, °K
- $\mu$ = viscosity of solution, cP
- $V_A$ = molar volume of O$_2$ as liquid at its normal boiling point, cm$^3$/g mol
- $\psi_B$ = association parameter
- $M_B$ = molecular weight
For pure monoolein

\[
\begin{align*}
\psi_B &= 1 \\
M_B &= 356.55 \text{ g/mol} \\
T &= 298^\circ\text{K} \\
V_A &= 25.6 \text{ cc/mol} \quad [77] \\
\mu &= 215 \text{ cP}
\end{align*}
\]

The viscosity was measured using ASTM D 1545-89 method (Bubble Time Method).

From equation 6,

\[
D_v = 2.77 \times 10^{-7} \text{ cm}^2/\text{s}
\]

For oxygen to diffuse through 85% of the thickness of the sample (thickness of the sample = 3 mm) (for slab),

\[
D_v \times t/L^2 = 0.68 \quad [77]
\]

Where

\[
\begin{align*}
t &= \text{time taken to diffuse through certain thickness of the sample} \\
L &= \text{half thickness of the sample}
\end{align*}
\]

\[
2.77 \times 10^{-7} \times t / (0.15)^2 = 0.68 \\
\therefore t = 0.64 \text{ day}
\]

Since the time taken to diffuse through 85% of the thickness of the sample is very short. We can say that the diffusion has very little effect on the differences in the k values determined by using the data of pure MO oxidation obtained through FTIR and NMR methods.
For PET/MO copolymer

**NMR data:**

The oxidation kinetics of PET/MO copolymer samples were studied in a manner similar to that described for the pure MO. In this case, copolymer samples were prepared for NMR spectroscopy by exposing them to temperature of 50°C for 39 days in the presence of air.

Figure 3.90 illustrates the $^1$H NMR spectrum for an unoxidized sample of PET/MO(5wt%) copolymer. Figures 3.91 and 3.92 illustrate the $^1$H NMR spectra for oxidized samples of PET/MO(5wt%) copolymer. In the $^1$H NMR spectrum of unoxidized sample of PET/MO(5wt%) copolymer (as shown in Figure 3.90), the peak of protons of CH=CH at $\delta=5.36$ ppm has an area under the peak of 1.73. In the $^1$H NMR spectrum of PET/MO(5wt%) copolymer sample oxidized for 15 days at 50°C, the peak of protons of CH=CH at $\delta=5.36$ ppm has an area under the peak of 1.10 (as shown in Figure 3.91) and in the $^1$H NMR spectrum of PET/MO(5wt%) copolymer sample oxidized for 39 days at 50°C, the peak of protons of CH=CH at $\delta=5.36$ ppm has an area under the peak of 0.40 (as shown in Figure 3.92). Therefore, it is clear that the number of protons of double bond of CH=CH are decreasing as a result of oxidation of the monoolein part of the copolymer.
Figure 3.90 $^1$H NMR spectrum of PET/MO copolymer sample (before oxidation)

Figure 3.91 $^1$H NMR spectrum of PET/MO copolymer (oxidized for 15 days at 50°C)
Figure 3.92 $^1$H NMR spectrum of PET/MO copolymer (oxidized for 39 days at 50°C)

Table 3.23 gives example of the data recorded for changes of area under the double bond peak (A) as a function of exposure time for PET/MO(5wt%) copolymer samples oxidized at 50°C. It should also be noted that the area under double bond peak is normalized with respect to the –CH$_3$ group peak which does not change at all after the oxidation reaction.

Table 3.23 Area under double bond peak versus time for PET/MO copolymer using NMR

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Area under double bond peak (A)</th>
<th>$A(t_0)$</th>
<th>$\ln(A/A(t_0))$</th>
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<tbody>
<tr>
<td>0</td>
<td>1.73</td>
<td></td>
<td>0</td>
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<tr>
<td>7</td>
<td>1.41</td>
<td>1.73</td>
<td>-0.2</td>
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<td>15</td>
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<td>1.73</td>
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<tr>
<td>24</td>
<td>0.76</td>
<td></td>
<td>-0.82</td>
</tr>
<tr>
<td>39</td>
<td>0.40</td>
<td></td>
<td>-1.46</td>
</tr>
</tbody>
</table>
After studying the unsaturated double bond peak for PET/MO copolymer as a function of time using NMR spectroscopy, we determined the oxidation kinetic parameters of PET/MO copolymer from the data collected from the NMR spectroscopy by using the following three methods:

1. Integral method

2. Differential method

3. Polymath nonlinear regression analysis

According to the Integral method,

Let us assume that the reaction is first-order (or let us assume oxygen is in excess), then

$$-\frac{dC_A}{dt} = kC_A$$

With the limits $C_A = C_{A0}$ at $t = 0$ gives

$$\ln(C_A/C_{A0}) = -kt$$

or

$$\ln(A/A_0) = -kt$$

Plot $\ln(A/A_0)$ versus time, if it fits to a linear region, then the reaction is pseudo–1$^{st}$ order and the slope is equal to the rate constant of oxidation ($k$) (as shown in Figure 3.93).

From Figure 3.93, it is clear that the data fits to a linear region, so

$$\text{Slope} = -k = -0.036$$

$$k = 0.036 \text{ day}^{-1}$$
According to the Differential method,

\[ A \text{ (MO)} + B \text{ (O}_2\text{)} \text{Excess} \rightarrow \text{products} \]

For an irreversible reaction, the rate law can be written as

\[-r_A = kC_A^a C_B^b\]

Using Method of excess, the rate can be written as

\[-r_A = kC_A^a\]

also

\[-r_A = kC_B^b\]

By combining mole balance and rate law, we obtain

\[-dC_A/dt = kC_A^a\]

After taking the natural logarithm of both sides, we get

\[\ln(-dC_A/dt) = \ln(-\text{rate}) = \ln(k) + a \ln(C_A)\]
The slope of a plot of ln(-dC_A/dt) versus ln(C_A) is the reaction order. To obtain the derivative (-dC_A/dt) used in this plot, we must differentiate the concentration-time data. The technique which we used to differentiate the data is first to fit the concentration-time data to a 2nd order polynomial (as shown in Figure 3.94):

\[ C_A = a_0 + a_1t + a_2t^2 \]

where a_i's are the constants.

Now,

\[ \frac{dC_A}{dt} = a_1 + 2a_2t \]

The reaction order and rate constant can now be found from a plot of ln(-dC_A/dt) versus ln(C_A) (as shown in Figure 3.95).

From Figure 3.95,

Slope = 0.7

Intercept = \ln(k) = -3.3735

\[ k = 0.034 \text{ day}^{-1} \]

Figure 3.94 Area under the double bond peak (A) versus time for PET/MO copolymer using NMR data
Figure 3.95 ln(-rate) versus ln(C_A) for PET/MO copolymer using NMR data

According to Polymath nonlinear regression analysis,

\begin{align*}
\text{Model: } \text{Time} &= \frac{(\text{CA}_0^{-(1-\alpha)} - (C^{-(1-\alpha)}))/k^{-(1-\alpha)}}{1}\nonumber
\end{align*}

<table>
<thead>
<tr>
<th>Variable</th>
<th>Initial guess</th>
<th>Value</th>
<th>95% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA0</td>
<td>1.73</td>
<td>1.738577</td>
<td>0.1027712</td>
</tr>
<tr>
<td>alpha</td>
<td>1.2</td>
<td>0.6212406</td>
<td>0.3460543</td>
</tr>
<tr>
<td>k</td>
<td>0.04</td>
<td>0.035741</td>
<td>0.0030571</td>
</tr>
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</table>

Nonlinear regression settings
Max # iterations = 64
Precision

<p>| | |</p>
<table>
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<tbody>
<tr>
<td>$R^2$</td>
<td>0.9994</td>
</tr>
<tr>
<td>$R^2_{adj}$</td>
<td>0.9987999</td>
</tr>
<tr>
<td>Rmsd</td>
<td>0.1490817</td>
</tr>
<tr>
<td>Variance</td>
<td>0.2778168</td>
</tr>
</tbody>
</table>

General

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample size</td>
<td>5</td>
</tr>
<tr>
<td>Model vars</td>
<td>3</td>
</tr>
<tr>
<td>Indep vars</td>
<td>1</td>
</tr>
<tr>
<td>Iterations</td>
<td>5</td>
</tr>
</tbody>
</table>

Source data points and calculated data points

<table>
<thead>
<tr>
<th>C</th>
<th>Time</th>
<th>Time calc</th>
<th>Delta Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.73</td>
<td>0.1704519</td>
<td>-0.1704519</td>
</tr>
<tr>
<td>2</td>
<td>1.41</td>
<td>6.947539</td>
<td>0.0524605</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>14.49903</td>
<td>0.5009712</td>
</tr>
<tr>
<td>4</td>
<td>0.76</td>
<td>24.50734</td>
<td>-0.507337</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>38.87564</td>
<td>0.1243572</td>
</tr>
</tbody>
</table>
Table 3.24 gives a comparison of the order of reaction and rate constant (k) values calculated by three different methods using the NMR data obtained for PET/MO copolymer samples oxidized at 50°C for times up to 39 days. It is evident that the order of the reaction and the rate constant values are very similar for all the three methods and $R^2$ value is also very good. This confirms that the order of the oxidation reaction for PET/MO copolymer sample is 1 and the rate constant value is varying between 0.034-0.036 day$^{-1}$ using NMR data.

Table 3.24 Order of reaction and k values for PET/MO copolymer using NMR data

<table>
<thead>
<tr>
<th></th>
<th>Integral method</th>
<th>Differential method</th>
<th>Polymath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order (alpha)</td>
<td>1</td>
<td>0.7</td>
<td>0.62</td>
</tr>
<tr>
<td>Rate constant (k), (day$^{-1}$)</td>
<td>0.036</td>
<td>0.034</td>
<td>0.036</td>
</tr>
<tr>
<td>$R^2$ value</td>
<td>0.99</td>
<td>0.99</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Calculation of Activation Energy for PET/MO copolymer

After determining the rate constant value for the oxidation reaction of PET/MO copolymer sample at 50°C, we oxidized PET/MO copolymer samples again at 60°C and 70°C and determined rate constant values at the additional temperatures. The objective was to determine the activation energy using Arrhenius equation given by equation 7.

\textbf{Equation 7: Arrhenius Equation}

\[ k = A \exp \left( -\frac{E_a}{RT} \right) \quad (7) \]

Where

- \( k \) = rate
- \( A \) = pre-exponential factor
- \( E_a \) = activation energy
- \( R \) = gas constant
- \( T \) = absolute temperature

Equation 8 shows the Arrhenius equation in its derived form.

\textbf{Equation 8: Determining Activation Energy}

\[ \ln (k) = \ln (A) - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) \quad (8) \]

This form allows the activation energy to be determined, by plotting the natural log of the rates versus the inverse of the temperatures (°K\(^{-1}\)). The slope of this plot is the activation energy divided by the gas constant, and y-intercept is the natural log of the pre-exponential factor (as shown in Figure 3.96).
From Figure 3.96,

\[
\text{Slope} = - \frac{E_a}{R} = -4488.7 \\
E_a = 4488.7 \times 1.99 \times 4.184 \text{ J/mol} \\
E_a = 8.9 \text{ kcal/mol}
\]

On extrapolation (from Figure 3.96),

\[
\text{at } T = 298^\circ \text{K} \\
k = 0.011 \text{ day}^{-1}
\]

Figure 3.96 $\ln(k)$ versus $1/T$
Table 3.25 gives the rate constant values and ln(k) values determined by using data obtained from the NMR method at three different oxidation temperatures of 323, 333, and 343 K.

Table 3.25 ln(k) versus 1/T

<table>
<thead>
<tr>
<th>k</th>
<th>temp</th>
<th>1/T</th>
<th>ln(k)</th>
<th>Ea (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.036</td>
<td>323</td>
<td>0.003096</td>
<td>-3.32424</td>
<td></td>
</tr>
<tr>
<td>0.053</td>
<td>333</td>
<td>0.003003</td>
<td>-2.93746</td>
<td>8.9</td>
</tr>
<tr>
<td>0.081</td>
<td>343</td>
<td>0.002915</td>
<td>-2.51331</td>
<td></td>
</tr>
</tbody>
</table>

3.17.2 Determination of the oxidation kinetics of the pure CHEDM and the PET/CHEDM copolymer

NMR data:

As in the case of pure MO, NMR spectroscopy was used to study the oxidation kinetics of the pure CHEDM compound. The samples were prepared by oxidizing pure CHEDM at 50°C for 19 days. Figure 3.97 shows the proposed oxidation mechanism of CHEDM compound. It can be clearly seen that the oxidation of CHEDM compound may lead to the formation of ketones or aldehydes. The aldehydes and ketones appear between δ= 9.5-10.0 ppm
In the $^1$H NMR spectrum of pure CHEDM compound oxidized for 4 days at 50°C with the addition of the catalyst (Figure 3.98), the peak of protons of oxidation byproduct at $\delta = 9.6$ ppm has an area under the peak of 0.21 and in the $^1$H NMR spectrum of pure CHEDM oxidized for 19 days at 50°C (Figure 3.102), the peak of protons of oxidation byproduct at $\delta = 9.6$ ppm has an area under the peak of 1.24. It is evident that the numbers of protons of oxidation byproduct peak are increasing after the oxidation (Figures 3.98 to 3.102).

Figure 3.97 Proposed oxidation mechanism of CHEDM compound

Ring opening but not dissociable from polymer backbone
Figure 3.98 pure CHEDM (oxidized for 4 days at 50°C)

Figure 3.99 pure CHEDM (oxidized for 7 days at 50°C)
Figure 3.100 pure CHEDM (oxidized for 10 days at 50°C)

Figure 3.101 pure CHEDM (oxidized for 14 days at 50°C)
Figure 3.102 pure CHEDM (oxidized for 19 days at 50°C)

Table 3.26 gives the data for the changes of relative area under oxidation byproduct peak (A) versus time for pure CHEDM samples oxidized at 50°C for times up to 19 days.

Table 3.26 Area under oxidation byproduct peak versus time for pure CHEDM using NMR

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Relative area under oxidation byproduct peak (C_p/C_A)</th>
<th>C_A0</th>
<th>C_A = C_A0/(1 + C_p/C_A)</th>
<th>ln(C_A/C_A0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.21</td>
<td>1.65</td>
<td>-0.1924</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.51</td>
<td>1.32</td>
<td>-0.4155</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.66</td>
<td>1.20</td>
<td>-0.5108</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.91</td>
<td>1.05</td>
<td>-0.6444</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1.24</td>
<td>0.89</td>
<td>-0.8097</td>
<td></td>
</tr>
</tbody>
</table>
After studying the oxidation byproduct peak for pure CHEDM compound as a function of time using NMR spectroscopy, we determined the oxidation kinetic parameters of pure CHEDM compound from the data collected from the NMR spectroscopy by using the following two methods:

1. Integral method

2. Differential method

**According to Integral method,**

Let us assume that the reaction is first-order (or let us assume oxygen is in excess), then

\[-\frac{dC_A}{dt} = kC_A\]

With the limits \(C_A = C_{A0}\) at \(t = 0\) gives

\[\ln \left( \frac{C_A}{C_{A0}} \right) = -kt\]

or

\[\ln \left( \frac{A}{A_0} \right) = -kt\]

where \(k = k_1C_B\)

where, \(k_1\) = rate constant of oxidation, and \(k\) = is proportional to rate of reaction

From NMR plot, we get

\[\frac{C_P}{C_A} = \text{Relative area under oxidation byproduct peak}\]

We know, \(C_{A0} - C_A = C_P\)

so,

\[\frac{C_{A0}}{C_A} - 1 = \frac{C_P}{C_A}\]

\[C_A = \frac{C_{A0}}{1 + \frac{C_P}{C_A}}\]
Plot $\ln(C/A_0)$ versus time, if it fits to a linear region, then the reaction is pseudo–1$^{st}$ order and slope give the value of ‘$k$’ (from Figure 3.103).

From Figure 3.103, it is clear that the data fits to a linear region, so

$$\text{Slope} = -k = -0.046$$

$$k = 0.046 \text{ day}^{-1}$$

![Figure 3.103 Plot of $\ln(C/A_0)$ versus time for pure CHEDM using NMR](image)

According to Differential method,

$$A \ (CHEDM) + B \ (O_2)_{\text{Excess}} \rightarrow \text{products (P)}$$

For an irreversible reaction, the rate law can be written as

$$-r_A = k_1 C_A^a C_B^b$$

Using Method of excess, the rate can be written as
\[-r_A = kC_A^a \quad \text{where } k = k_1C_B^b\]

also,

\[-r_A = kC_B^b\]

By combining mole balance and rate law, we obtain

\[-dC_A/dt = kC_A^a\]

After taking the natural logarithm of both sides, we get

\[\ln(-dC_A/dt) = \ln(-\text{rate}) = \ln(k) + a \ln(C_A)\]

The slope of a plot of \(\ln(-dC_A/dt)\) versus \(\ln(C_A)\) is the reaction order. To obtain the derivative \((-dC_A/dt)\) used in this plot, we must differentiate the concentration-time data. The technique which we used to differentiate the data is first to fit the concentration-time data to a 2nd order polynomial:

\[C_A = a_0 + a_1t + a_2t^2\]

where \(a_i\)'s are the constants.

Now,

\[dC_A/dt = a_1 + 2a_2t\]

The reaction order and ‘k’ value can now be found from a plot of \(\ln(-dC_A/dt)\) versus \(\ln(C_A)\) (from Figure 3.104).

From Figure 3.104,

\[
\begin{align*}
\text{Slope} & = 0.9 \\
\text{Intercept} & = \ln(k) = -3.4 \\
k & = 0.033 \text{ day}^{-1}
\end{align*}
\]
Figure 3.104 \( \ln(-\text{rate}) \) versus \( \ln(C_A) \) for pure CHEDM using NMR

For PET/CHEDM copolymer

**NMR data:**

To study the oxidation reaction of PET/CHEDM copolymer using NMR spectroscopy, the samples were prepared by oxidizing PET/CHEDM copolymer at 50°C.

In the \(^1\text{H} \) NMR spectrum of PET/CHEDM copolymer sample prepared without catalyst and oxidized for 7 days at 50°C, there is no peak representing protons of the oxidation byproduct at \( \delta = 9.56 \) ppm (as shown in Figure 3.105). Figure 3.106 gives an example of spectra obtained for PET/CHEDM copolymer prepared with 400 ppm catalyst and oxidized at 50°C. This sample was held at 50°C for 9 days. Similar results were obtained for other samples with increase in the peak area with increase in the exposure time at 50°C. The samples were oxidized for 16 days at 50°C.
Figure 3.105 $^1$H NMR spectrum of PET/CHEDM copolymer without catalyst (oxidized)

Figure 3.106 $^1$H NMR spectrum of PET/CHEDM copolymer with catalyst (oxidized for 9 days)
Table 3.27 gives the data for the changes of relative area under oxidation byproduct peak (A) versus time for PET/CHEDM copolymer samples oxidized at 50°C for times up to 16 days.

Table 3.27 Relative area under oxidation byproduct peak versus time for PET/CHEDM copolymer using NMR

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Relative area under oxidation byproduct peak (C_p/C_A)</th>
<th>C_A0</th>
<th>C_A = C_A0/(1 + C_p/C_A)</th>
<th>ln(C_A/C_A0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>2.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
<td>1.68</td>
<td>-0.174</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.50</td>
<td>1.33</td>
<td>-0.405</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.65</td>
<td>1.21</td>
<td>-0.50</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.88</td>
<td>1.06</td>
<td>-0.6313</td>
<td></td>
</tr>
</tbody>
</table>

After studying the oxidation byproduct peak for PET/CHEDM copolymer as a function of time using NMR spectroscopy, we determined the oxidation kinetic parameters of PET/CHEDM copolymer from the data collected from the NMR spectroscopy by using the following method:

- Integral method
According to Integral method,

Let us assume that the reaction is first-order (or let us assume oxygen is in excess), then

\[-\frac{dC_A}{dt} = kC_A\]

With the limits \(C_A = C_{A0}\) at \(t = 0\) gives

\[\ln\left(\frac{C_A}{C_{A0}}\right) = -kt\]

or

\[\ln\left(\frac{A}{A_0}\right) = -kt\]

where \(k = k_1C_B\)

where, \(k_1 = \) rate constant of oxidation, and \(k = \) is proportional to rate of reaction

From NMR plot, we get

\[\frac{C_P}{C_A} = \text{Relative area under oxidation byproduct peak}\]

We know, \(C_{A0} - C_A = C_P\)

so,

\[\frac{C_{A0}}{C_A} - 1 = \frac{C_P}{C_A}\]

\[C_A = \frac{C_{A0}}{1 + \frac{C_P}{C_A}}\]

Plot \(\ln(C_A/C_{A0})\) versus time, if it fits to a linear region, then the reaction is pseudo–1st order and slope give the value of ‘k’ (from Figure 3.107).

From Figure 3.107, it is clear that the data fits to a linear region, so

\[\text{Slope} = -k = 0.041\]

\[k = 0.041 \text{ day}^{-1}\]
3.17.3 Determination of the Thiele Modulus for the pure scavengers and the PET/scavenger copolymers

In order to determine if the k values calculated for pure MO, PET/MO copolymer samples, pure CHEDM, and PET/CHEDM copolymer samples are really low values (as discussed in sections 3.17.1 and 3.17.2) and also, to verify the previous result that the chemical reaction rate is small as compared to the diffusion reaction rate for PET/MO as well as for PET/CHEDM copolymer samples (as observed from the oxygen permeability data in section 3.11), we calculated a dimensionless quantity called “Thiele modulus”. In other words, in the following section, we have determined a quantity called “Thiele modulus” by using the data obtained from the FTIR and NMR methods and this quantity can further evaluate the effectiveness of the oxygen scavengers.
According to the analysis performed by Dr. Michael Cameron at the Polymer Institute [78], he developed a model to determine the shelf life of the active barrier packaging. He developed a model by taking two different approaches:

- Approach 1: Slow reaction kinetics
- Approach 2: Fast reaction kinetics

For an approach of slow reaction kinetics, he predicted that the Thiele modulus value should have a minimum value of 5 for an oxygen scavenger to be effective.

**Calculation of Thiele modulus**

Thiele modulus is given by the following equation

\[ \Phi^2 = \frac{k L^2}{D} \]  \hspace{1cm} (9) \hspace{1cm} [75]

Where

- \( \Phi \) = Thiele modulus
- \( D \) = Diffusivity of oxygen in scavenger or copolymers
- \( L \) = Thickness of the sample
- \( k \) = Rate constant of oxidation

The square root of the coefficient, \( \Phi \), is called the Thiele modulus. The quantity \( \Phi^2 \) is a measure of the ratio of a chemical reaction rate to a rate of diffusion.
\[ \Phi^2 = \frac{\text{chemical reaction rate}}{\text{diffusion rate}} \]

When the Thiele modulus is large, diffusion usually limits the overall rate of reaction; when \( \Phi \) is small, the chemical reaction is usually rate-limiting.

**For pure monoolein**

*FTIR data:*

\[
\begin{align*}
D & = 2.77 \times 10^{-7} \text{ cm}^2/\text{s} \quad [76] \\
k & = 0.062 \text{ day}^{-1} \\
L & = 0.2 \text{ mm}
\end{align*}
\]

From equation 9,

\[
\Phi^2 = \frac{0.062 \times (0.02)^2}{86400 \times 2.77 \times 10^{-7}} = 1.04 \times 10^{-3}
\]

\[ \Phi = 0.03 \]

i.e., \( \Phi = \text{reaction rate/diffusion rate} = 0.03 \)

Since, the Thiele modulus is small, the chemical reaction is the rate limiting step or in other words, we can say that the rate of diffusion is fast as compared to the rate of reaction.
**NMR data:**

\[
D = 2.77 \times 10^{-7} \text{ cm}^2/\text{s} \\
k = 0.047 \text{ day}^{-1} \\
L = 2 \text{ mm}
\]

From equation 9,

\[
\Phi^2 = 0.047 \times (0.2)^2 / 86400 \times 2.77 \times 10^{-7} \\
= 7.86 \times 10^{-2}
\]

\[
\Phi = 0.28
\]

i.e., \( \Phi \) = reaction rate/diffusion rate = 0.28

Again, we can say that the rate of diffusion is fast as compared to the rate of reaction.

After comparing my results with the results of Dr. Cameron’s work, it can be seen that the experimental value of the Thiele modulus for pure MO scavenger is very low as compared to the predicted value of the Thiele modulus for the scavengers. This implies that MO is not an effective oxygen scavenger.
For PET/MO(5wt%) copolymer

After determining the oxidation kinetic parameters and effectiveness of the pure MO scavenger, we determined the Thiele modulus and effectiveness of the PET/MO copolymer by using the data obtained from the NMR method. To make these determinations, we first need to evaluate the diffusivity of oxygen through the PET/MO copolymer at three oxidation temperatures of 323, 333, and 343°K. The following equation was used to determine the diffusivity.

Calculation of diffusivity of O₂ in the PET/MO copolymer at T = 323°K

For glassy polymers:

\[
\log D \approx \log D_o - \frac{E_D}{2.3RT} = -\frac{E_D(1/T - 1/\Theta_2)}{2.3R} - 4.0
\]  

(10) [79]

Where \( \Theta_2 = \frac{2500}{2.3R} = 545°K \)

Diameter of oxygen molecule, \( d = 3.47 \text{ Å} \) [79]

From the relationship between activation energy of diffusion, size of diffusing molecules and glass transition temperature of polymer [79],

At \( T = 323°K \) [Oxidation temperature]

\( R = 1.99 \text{ cal}^/\text{°K}^*\text{mol} \)

\( T_g = 345°K \) (For PET/MO(5wt %) copolymer)

\( E_D \approx 9392 \) [79]

From Equation 10,

\( D(323) = 2.5 \times 10^{-7} \text{ cm}^2/\text{sec} \)  

(11)
We have determined the diffusivity of oxygen through the PET/MO copolymer sample. This information can now be used to calculate the Thiele modulus.

**Calculation of Thiele Modulus**

*NMR data:*

\[
\begin{align*}
D &= 2.5 \times 10^{-7} \text{ cm}^2/\text{s} \quad \text{(from equation 11)} \\
k &= 0.036 \text{ day}^{-1} \\
L &= 0.2 \text{ mm}
\end{align*}
\]

From equation 9,

\[
\Phi^2 = \frac{0.036 \times (0.02)^2}{86400 \times 2.5 \times 10^{-7}} = 6.67 \times 10^{-4}
\]

\[
\Phi = \text{reaction rate/diffusion rate} = 0.026
\]

Since, the Thiele modulus is small, so the rate of reaction is the rate limiting step or in other words, we can say that diffusion is faster as compared to the chemical reaction.

**Calculation of diffusivity of O\textsubscript{2} in the PET/MO copolymer at T = 333\textdegree K**

At \( T = 333\textdegree K \) \ [Oxidation temperature]

\[
R = 1.99 \text{ cal/°K*mol}
\]

\[
T_g = 345\text{°K} \quad \text{(For PET/MO(5wt%) copolymer)}
\]

\[
E_D \approx 9392 \quad \text{[79]}
\]

From Equation 10, \( D(333) = 4.0 \times 10^{-7} \text{ cm}^2/\text{sec} \quad \text{(12)} \)
Calculation of Thiele Modulus

D = 4.0*10^{-7} \text{ cm}^2/\text{s} \quad \text{(from equation 12)}

k = 0.053 \text{ day}^{-1}

L = 0.2 \text{ mm}

From equation 9,

$$\Phi^2 = \frac{0.053*(0.02)^2}{86400*4.0*10^{-7}}$$

= 0.025

i.e., $\Phi = \frac{\text{reaction rate}}{\text{diffusion rate}} = 0.025$

Calculation of diffusivity of O$_2$ in the PET/MO copolymer at T = 343°C

At $T = 343°C \quad \text{[Oxidation temperature]}

R = 1.99 \text{ cal/°K*mol}

T_g = 345°C \quad \text{(For PET/MO(5wt%) copolymer)}

E_D \approx 9392 \quad \text{[79]}

From Equation 10,

$$D(343) = 6.1*10^{-7} \text{ cm}^2/\text{sec} \quad \text{(13)}$$

Calculation of Thiele Modulus

D = 6.1*10^{-7} \text{ cm}^2/\text{s} \quad \text{(from equation 13)}

k = 0.081 \text{ day}^{-1}

L = 0.2 \text{ mm}
From equation 9,
\[ \Phi^2 = \frac{0.081 \times (0.02)^2}{86400 \times 6.1 \times 10^{-7}} \]
\[ = 0.025 \]

i.e., \[ \Phi = \frac{\text{reaction rate}}{\text{diffusion rate}} = 0.025 \]

For PET/CHEDM(5wt%) copolymer

After determining the oxidation kinetic parameters of the pure CHEDM scavenger, we determined the Thiele modulus and effectiveness of the PET/CHEDM copolymer by using the data obtained from the NMR method. To make these determinations, we first need to evaluate the diffusivity of oxygen through the PET/CHEDM copolymer at the oxidation temperatures of 323°C. The following equation was used to determine the diffusivity.

Calculation of diffusivity of O$_2$ in the PET/CHEDM copolymer at T = 323°C

At T = 323°C [Oxidation temperature]

\[ R = 1.99 \text{ cal/°K*mol} \]

\[ T_g = 351^\circ \text{K} \quad \text{(For PET/CHEDM(5wt%) copolymer)} \]

\[ E_D \approx 9151 \quad \text{[79]} \]

From Equation 10,
\[ D(323) = 3.0 \times 10^{-7} \text{ cm}^2/\text{sec} \quad (14) \]
Calculation of Thiele modulus

NMR data:

\[ D = 3.0 \times 10^{-7} \text{ cm}^2/\text{s} \quad \text{(from equation 14)} \]
\[ k = 0.041 \text{ day}^{-1} \]
\[ L = 0.22 \text{ mm} \]

From equation 9,

\[ \Phi^2 = \frac{0.041 \times (0.022)^2}{86400 \times 3.0 \times 10^{-7}} \]
\[ = 7.66 \times 10^{-4} \]
\[ \Phi = 0.028 \]

i.e., \( \Phi = \frac{\text{reaction rate}}{\text{diffusion rate}} = 0.028 \)

Since, the Thiele modulus is small, so the rate of reaction is the rate limiting step or in other words, we can say that the rate of diffusion is fast as compared to the rate of reaction.

After comparing my results with the results of Dr. Cameron’s work, it can be seen that the experimental value of the Thiele modulus for PET/CHEDM copolymer is very low as compared to the predicted value of the Thiele modulus for the scavengers. This implies that CHEDM is not an effective oxygen scavenger.
3.18 Oxidation byproducts of the pure scavengers and PET/scavenger copolymers

During the oxidation kinetics of the PET/scavenger copolymers, small molecules of oxidation product can be released into the atmosphere. In order to completely understand this oxidation process, it is important to identify these oxidation products. One method that can be used for such analyses is as follows:

3.18.1 Analysis of the oxidation byproducts using GC-MS

In this research, we used gas chromatography-mass spectrometry (GC-MS) to identify the oxidation byproduct. The five GC sample bottles were put inside an oven to oxidize at 50°C for 12 days. After 12 days oxidation, a GC syringe was used to sample 5 microliters of gas from each oxidized sample. Each of the gas specimens was injected into Hewlett Packard (5890) GC-MS machine in order to obtain a GC-MS spectrum of their components. The spectrum of pure air is used as reference as shown in Figure 3.108. In this figure, the GC-MS spectrum is labeled with a series of numbers. Each of these numbers represents the m/z values corresponding to their respective peaks. Figures 3.109 to 3.112 show GC-MS spectra of pure MO, PET/MO copolymer, pure CHEDM, and PET/CHEDM copolymer respectively. There is a table on the right side of each figure. Each table describes the relative intensity of the peaks at their respective m/z values.
Table 3.108 GC-MS of pure Air

The spectra of pure MO compound (Figure 3.109) and PET/MO copolymer (Figure 3.110) shows three major gas compounds with molecular weights (i.e. m/z values) of 28, 32, and 44. The gas with molecular weight of 28 is nitrogen, the gas with molecular weight of 32 is oxygen, and the gas with molecular weight of 44 could be carbon dioxide or acetaldehyde.

The average carbon dioxide concentration in atmospheric air is 330 ppm. However, the intensity ratio of the unknown gas to that of nitrogen in the pure MO spectrum is 5 to 100 and the intensity ratio of the unknown gas to that of oxygen in the PET/MO copolymer spectrum is 5 to 100. The concentration of this unknown gas compound is unlikely to be carbon dioxide because of its high concentration.
Therefore, it can be concluded that the major volatile oxidation byproduct for the oxidation of the pure MO compound and the PET/MO copolymer is acetaldehyde.

Figure 3.109 GC-MS of pure Monoolein

Figure 3.110 GC-MS of PET/MO copolymer
The spectra of pure CHEDM compound (Figure 3.111) and PET/CHEDM copolymer (Figure 3.112) show two major gas compounds with molecular weights (i.e. m/z values) of 28 and 32. The gas with molecular weight of 28 is nitrogen, and the gas with molecular weight of 32 is oxygen.

The intensity ratio of the gas at m/z = 44 to that of oxygen in the pure CHEDM compound spectrum as well as in the PET/CHEDM copolymer spectrum is 0.5 to 100 and 0.3 to 100, respectively. The concentration of this gas compound is very close to the concentration of the same gas compound in pure air.

**Therefore, it can be concluded that there is no oxidation byproduct for the oxidation of the pure CHEDM compound and the PET/CHEDM copolymer.**

Also, from literature search [34], we have found that the oxidation of cycloalkenes should not result in low molecular weight products because it just causes rearrangement/bond migration or in other words, cycloalkene compound does not fragment as it oxidizes, thus avoiding the problem of imparting oxidation byproducts to the packaged material.
### Figure 3.111 GC-MS of pure CHEDM

<table>
<thead>
<tr>
<th>No.</th>
<th>m/z</th>
<th>RI(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.100</td>
<td>0.013</td>
</tr>
<tr>
<td>2</td>
<td>14.000</td>
<td>0.737</td>
</tr>
<tr>
<td>3</td>
<td>16.000</td>
<td>4.446</td>
</tr>
<tr>
<td>4</td>
<td>17.000</td>
<td>1.518</td>
</tr>
<tr>
<td>5</td>
<td>17.950</td>
<td>6.171</td>
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<td>27.950</td>
<td>28.243</td>
</tr>
<tr>
<td>7</td>
<td>28.900</td>
<td>0.252</td>
</tr>
<tr>
<td>8</td>
<td>31.900</td>
<td>100.000</td>
</tr>
<tr>
<td>9</td>
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<td>0.641</td>
</tr>
<tr>
<td>10</td>
<td>41.050</td>
<td>0.009</td>
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</tbody>
</table>

### Figure 3.112 GC-MS of PET/CHEDM copolymer

<table>
<thead>
<tr>
<th>No.</th>
<th>m/z</th>
<th>RI(%)</th>
</tr>
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<tbody>
<tr>
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</tr>
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<td>17.000</td>
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<td>17.950</td>
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</tr>
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<tr>
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<td>12</td>
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<td>13</td>
<td>72.850</td>
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</tr>
<tr>
<td>14</td>
<td>141.000</td>
<td>0.009</td>
</tr>
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</table>
3.18.2 Analysis of the oxidation byproducts using GC

In order to further evaluate the results of oxidation byproduct of pure scavengers (i.e., the peak at m/z = 44 correspond to acetaldehyde or CO₂) determined by using GC-MS, we analyzed the following two samples with the help of gas chromatograph:

1. Pure Acetaldehyde (AA)

2. Pure Monoolein

Figure 3.113 represents the gas chromatograph of pure acetaldehyde and it is clear that the peak at residence time = 2.25 min corresponds to AA.

Figure 3.113 Analysis of pure Acetaldehyde using GC

Figure 3.114 represents the gas chromatograph of pure MO sample oxidized for 5 days at 50°C and it can be clearly seen that there is a peak at residence time = 2.23 min. From Figure 3.113, we know that the peak at residence time = 2.25 min corresponds to
acetaldehyde. Therefore, it supports the previous results that the major volatile oxidation byproduct for the oxidation of the pure MO and the PET/MO copolymer is acetaldehyde.

Figure 3.114 Analysis of pure MO (oxidized for 7 days at 50°C) using GC
3.19 Summary

In the previous section, a technique was developed to determine the oxygen scavenging capacity of potential oxygen scavengers. In this section, the methodologies were developed in order to determine the oxidation kinetics of the scavengers and effectiveness of the potential oxygen scavengers using infrared FTIR and NMR spectroscopy techniques. The summary of this section has been discussed as follows:

- The height of double bond peak at a wave number of 3010 cm\(^{-1}\) in the FTIR spectra decreased as the times of oxidation were increased.
- Decrease of the cis C=CH wagging peak at a wave number of 723 cm\(^{-1}\) in the FTIR spectra were also observed as the times of oxidation were increased.
- The order of reaction for pure MO oxidation using FTIR data was determined to be 1 and the ‘k’ value was about 0.06-0.08 day\(^{-1}\).
- The areas under the double bond peak of CH=CH in the NMR spectra were also found to decrease as the times of oxidation were increased.
- The order of reaction for pure scavengers oxidation was determined to be 1 and the ‘k’ value was about 0.04-0.05 day\(^{-1}\) using NMR data.
- The order of reaction for the oxidation of PET/scavenger copolymer samples was also determined to be 1 and the ‘k’ value was about 0.04 day\(^{-1}\) using NMR data.
- Thiele modulus was small for pure scavengers as well as for the PET/scavenger copolymers which indicates that the rate of diffusion is fast as compared to the reaction of scavenger and oxygen.
- The major volatile oxidation by-product for the oxidation of pure MO and the PET/MO copolymer was found to be acetaldehyde, whereas, pure CHEDM...
compound and the PET/CHEDM copolymer do not fragment after reaction with oxygen and therefore, no oxidation by-products

- A methodology was successfully developed to determine the oxidation kinetic parameters of pure scavengers and the PET/scavenger copolymers using FTIR and NMR spectroscopy
Chapter 4

Conclusions and Recommendations

4.1 Conclusions

The objectives of this research have been to synthesize and characterize new active barrier copolymers of PET as well as to develop a methodology for determination of the oxygen scavenging capacities of potential oxygen scavengers. This methodology will ultimately help in efficiently designing the copolymers of PET and potential oxygen scavengers with better barrier properties. The specific copolymers of PET and oxygen scavengers for this work were synthesized through melt phase polymerization.

4.1.1 In situ polymerization

Two PET/scavenger copolymers were synthesized with two different scavengers each at different concentrations, at temperatures between 270-280°C using a batch scale melt polymerization system. The effects of the scavengers on thermal, rheological, and barrier properties of the PET copolymers were monitored in order to characterize the synthesized PET/scavenger copolymers.

- Scavengers were added in the early stage of the polycondensation reaction, the residence time of ~5 hours, at PET melt polymerization conditions. This shorter residence time reduced the loss in oxygen scavenging capacity of the scavengers in
comparison to a case in which it would have been added during the esterification reaction

- Polycondensation reaction was accelerated by ~20% due to the addition of 5wt% monoolein and it was accelerated by ~15% due to the addition of 5wt% 3-cyclohexene-1,1-dimethanol

- T_g and T_m of the PET/MO copolymers were decreased as the MO content was increased from 1wt% to 5wt%. This decrease was due to the higher contents of flexible parts provided by long side chain of MO in the copolymer. The T_g values of the PET/CHEDM copolymers did not change as the CHEDM content was increased from 1wt% to 5wt%; however, the melting peak temperatures (T_m) were found to decrease. The depression of melting temperature could be attributed to the transesterified CHEDM units which restrict PET crystallization, and reduce PET crystallite size. It may also be caused by the broadening of the interfacial region from the introduction of the CHEDM block

- Crystallization rates of the PET/MO copolymers were affected by the MO content. As the MO content in the copolymer was increased from 1wt% to 5wt%, it delayed the crystallization. Similar crystallization behavior was observed for the PET/CHEDM copolymers, as the CHEDM contents in the copolymer were increased from 1wt% to 5wt%, it delayed the crystallization

- Pure WA314 PET showed Newtonian behavior up to the measured values of shear rate, whereas, the copolymer samples of PET/MO(1wt%) showed Newtonian behavior up to the low values of shear rate; however, the copolymer sample of
PET/MO(5wt%) showed non-Newtonian behavior even at low shear rates. The reason for this behavior was that the branching occurs among the PET and MO chains.

- The copolymer samples of PET/CHEDM with three different compositions of CHEDM (1, 3, and 5wt%) showed Newtonian behavior up to the measured shear rate values in a manner similar to that of pure PET.

- There was an improvement of about 30 and 40% in oxygen permeability for the PET/MO and PET/CHEDM copolymer sample in comparison to that of WA314 PET.

- The average density values of the PET/MO(1wt%) and PET/CHEDM(1wt%) copolymer samples were similar to that of pure PET and the average specimen density was found to decrease as the scavenger concentration was increased from 1wt% to 5wt%.

- It was also observed that the average density of the PET/MO(5wt%) copolymer was lower than that of the PET/CHEDM(5wt%) copolymer sample. This occurred because PET/CHEDM copolymer packs well as compared to PET/MO copolymer because of the long side chain of MO unit. This outcome supported the previous result that the oxygen permeability of the PET/CHEDM copolymer was lower in comparison to that of the PET/MO copolymer.

4.1.2 Reaction between PET and scavengers

NMR spectroscopy was performed to confirm that interchange reactions between PET and the scavenger units had occurred. 2-D correlation spectroscopy (COSY) was also performed to further evaluate the experimental evidence to prove that reactions between PET and the scavenger had occurred.
• $^1$H NMR spectroscopy and 2-D COSY proved that there is an interchange reaction between PET and the MO and CHEDM scavenger units during melt phase polymerization leading to the formation of PET/scavenger copolymers

• $^1$H NMR spectroscopy also proved that in the case of physical blends of PET/scavenger, there is no interchange reaction between PET and the MO and CHEDM scavenger units

• $^1$H NMR spectroscopy proved that the reaction peaks were still present in the spectra of PET/scavenger copolymers extracted with chloroform. This indicated that the MO and CHEDM units were still bonded to the PET chains even after extraction with chloroform and ultimately proved that the reaction between PET and the MO and CHEDM scavenger units had occurred

4.1.3 Equilibrium melting point and isothermal crystallization behavior

The equilibrium melting points ($T_{m^0}$) of the PET/scavenger copolymer samples were determined by crystallizing the samples at various temperatures for one hour. The crystallization kinetic parameters were determined by using Avrami expressions and half time method.

• Three melting peaks were observed in the melting curves of isothermally crystallized samples. With increasing isothermal crystallization ($T_c$), the positions of $T_{m1}$ and $T_{m2}$ shifted to higher temperatures and the position of $T_{m3}$ did not change

• The equilibrium melting point ($T_{m^0}$) of the copolymers was found to be depressed with increasing MO and CHEDM contents in the copolymers
• With the increase of the MO content in the PET/MO copolymers, the crystallization half time was increased at the same degree of undercooling and therefore, the crystallization rate of the PET/MO copolymer was decreased. This isothermal crystallization behavior of the PET/MO copolymer was consistent with the non-isothermal crystallization behavior of the PET/MO copolymer

• With the increase of the CHEDM content in the PET/CHEDM copolymers, the crystallization half time was increased and therefore, the crystallization rate of the PET/CHEDM copolymer was decreased. This isothermal crystallization behavior of the PET/CHEDM copolymer was consistent with the non-isothermal crystallization behavior of the PET/CHEDM copolymer

• The crystallization kinetic parameters (n and k) determined by Avrami expression and half time method indicated that the crystallization mechanism was different for different copolymer samples with n values varying between 2 and 3

• WA314 PET and the copolymer samples of PET/MO and PET/CHEDM showed positive spherulites

• Spherulite radii increase as the crystallization time increases for WA314 PET, and the copolymer samples of PET/MO using small angle light scattering. However, we were not able to determine the average spherulite radius of the PET/CHEDM copolymer samples crystallized from the molten state, because it was difficult to obtain the data points in the linear growth region. This could be due to the large nucleation densities of the PET/CHEDM copolymer samples
4.1.4 Oxidation catalyst effect on thermal and rheological properties of the copolymers

Cobalt octoate catalyst was added to PET/scavenger copolymer pellets just before extruding the sheets in order to enhance oxygen uptake during permeation experiment.

- The melt IV of PET/scavenger copolymer samples and WA314 PET was found to have decreased significantly with the addition of the cobalt octoate catalyst and thereby caused the crystallization faster for the PET/scavenger copolymers
- It was also observed that as the amount of cobalt octoate catalyst was increased from 200 ppm to 400 ppm, the melt IV of the PET/scavenger copolymers was further decreased and ultimately caused even faster crystallization

4.1.5 Methodologies to determine the oxygen scavenging capacity of the scavengers

The methodologies were developed in order to determine the oxidation kinetics, scavenging capacity and effectiveness of the potential oxygen scavengers using infrared FTIR and NMR spectroscopy techniques. The oxidation kinetics of the pure scavengers and the PET/scavenger copolymers were determined by studying changes in the unsaturated double bond peaks present in their infrared FTIR and NMR spectra.

- The height of double bond peak at a wave number of 3010 cm\(^{-1}\) in the FTIR spectra decreased as the time of oxidation was increased
- Decrease of the cis C=CH wagging peak at a wave number of 723 cm\(^{-1}\) in the FTIR spectra were also observed as the times of oxidation were increased
- The order of reaction for pure MO oxidation using FTIR data was determined to be 1 and the ‘k’ value was about 0.06-0.08 day\(^{-1}\)
• The areas under the double bond peak of CH=CH in the NMR spectra were also found to decrease as the times of oxidation were increased

• The order of reaction for pure scavengers oxidation was determined to be 1 and the ‘k’ value was about 0.04-0.05 day\(^{-1}\) using NMR data

• The order of reaction for the oxidation of PET/scavenger copolymer samples was also determined to be 1 and the ‘k’ value was about 0.04 day\(^{-1}\) using NMR data

• Thiele modulus was small for pure scavengers as well as for the PET/scavenger copolymers which indicates that the rate of diffusion is fast as compared to the reaction of scavenger and oxygen

• The major volatile oxidation by-product for the oxidation of pure MO and the PET/MO copolymer was found to be acetaldehyde, whereas, pure CHEDM compound and the PET/CHEDM copolymer do not fragment after reaction with oxygen and therefore, no oxidation by-products

• A methodology was successfully developed to determine the oxidation kinetic parameters of pure scavengers and the PET/scavenger copolymers using FTIR and NMR spectroscopy

• A technique was successfully developed and established for use to determine the oxygen scavenging capacity of potential oxygen scavengers

4.2 Future Work/Recommendations

As a result of this research, it is recommended that this above developed methodology (which we have developed to determine the scavenging capacity of
potential oxygen scavengers at the Polymer Institute) should be applied to the unsaturated fatty acid compounds containing following types of bonds (as shown in Figure 4.1) to determine their oxygen scavenging capacity. According to the above developed methodology, compounds having conjugated double bonds and the compounds having a single methylene group between double bonds are expected to have higher oxidation rate in comparison to unsaturated compounds having just one double bond in their chain.

![Conjugated double bonds](image1)

![A single methylene group between double bonds](image2)

Figure 4.1 Potential oxygen scavengers
Chapter 5

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