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ABSTRACT

REACTIVE MELT MODIFICATION OF POLYETHYLENE TEREPHTHALATE

by Rahul Ramesh Dhavalikar

This work investigates the structural and chemorheological modification of polyethylene terephthalate in the melt phase with low molecular weight multifunctional glycidyl compounds as reactive additives. Polyethylene terephthalate undergoes chain extension and/or branching reactions with the additives that result in modified rheological properties suitable for certain polymer processing operations such as extrusion blow molding or extrusion foaming to low densities.

Among five different low MW difunctional and trifunctional epoxy compounds, triglycidyl isocyanurate is shown to be an efficient reactive melt modifier for commercially available polyethylene terephthalate polymers. Its stability at the polyethylene terephthalate melt temperatures is confirmed offline through thermogravimetric and FT-IR techniques. Melt modification of polyethylene terephthalate is followed in an intensive batch mixer by torque changes, analyzing the products for residual carboxyl content, insoluble content, and by dynamic mechanical analysis. The importance of undesirable melt degradation reactions occurring simultaneously with the branching/extension reactions is analyzed. Valuable information is obtained from the designed batch mixer experiments regarding the effects of various process parameters on the kinetics of the reactive modification. The melt-modification reaction products from the batch mixer are evaluated offline for melt viscoelastic properties using a dynamic mechanical analyzer. In addition to the indirect measurement of changes in melt viscosity in the batch mixer, chemorheological monitoring of the modification with triglycidyl isocyanurate in a dynamic mechanical analyzer provides insights into the evolution of molecular weight and molecular weight distribution of the polyester and its effect on the viscoelasticity behavior of the its melt.

The developed kinetic data are used to define the process requirements to carry out the reactive modification, continuously, in an extruder reactor. Monitoring of process conditions and product analysis indicate the formation of higher MW and broader MWD structures with predictable effects on their melt viscoelastic properties. Extrusion foaming experiments indicate that production of low-density foams by a process involving one-step reactive modification/gas injection foaming is feasible, at conditions not significantly different than those employed in the simple reactive modification of the polyethylene terephthalate resin.

REACTIVE MELT MODIFICATION OF POLYETHYLENE TEREPHTHALATE

By Rahul Ramesh Dhavalikar

A Dissertation Submitted to the Faculty of New Jersey Institute of Technology In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Chemical Engineering

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January 2003

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Dedicated to my mother, Chitra Dhavalikar and my father, Ramesh Dhavalikar.

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Chapter	Page
1 INTRODUCTION	. 1
1.1 Commercial Synthesis of PET	1
1.2 Applications and Limitations of Commercially Available PET	6
1.2.1 Applications	6
1.2.2 Limitations of PET	. 10
1.3 Chemical modification of PET	. 14
2 PURPOSE AND SCOPE	18
3 LITERATURE REVIEW	. 21
3.1 Modification Routes	. 21
3.1.1 Chemical Modification of PET – Traditional Approach	. 22
3.1.2 Chemical Modification of PET – Rheological Perspective	26
3.2 Choice of Chain Extenders for PET	. 34
3.2.1 Epoxides – Chemical nature	. 36
3.2.2 Reactions of Epoxy Resins	. 39
4 EXPERIMENTAL	46
4.1 Materials	. 46
4.1.1 Polyesters	46
4.1.2 Chain Extenders	. 47
4.1.3 Catalysts	49
4.1.4 Physical Blowing Agent	. 50

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

Chapter	Page
4.2 Processing and Characterization	51
4.2.1 Reactive Processing in Batch Mixer and Characterization	51
4.2.2 Reactive Processing – Rheometer	53
4.2.3 Spectroscopic Analysis – Melt Modification in a FT-IR Cell	56
4.2.4 Reactive Processing – Extruder	57
5 RESULTS AND DISCUSSION	59
5.1 Batch Mixer Processing and Characterization	59
5.1.1 Thermal Stability of the Modifiers	. 59
5.1.2 Process Stability of PET in a Batch Mixer	60
5.1.3 Reactions of Modifiers	64
5.1.4 Comparison of Epoxides	69
5.1.5 Reactions of TGIC with HPET and MPET	. 71
5.1.6 Estimation of Rate of HPET Modification by TGIC	76
5.1.7 Study on Role of Catalysts	. 79
5.1.8 Batch Mixer Summary	82
5.2 Offline Rheological Characterization of Batch Mixer Products	84
5.2.1 Typical Batch Mixing Runs	85
5.2.2 Rheological Characterization of Unmodified Processed HPET	86
5.2.3 Rheological Characterization of modified HPET	88

TABLE OF CONTENTS (Continued)

Chapter	
5.3 Real Time Spectroscopic Analysis of the PET/TGIC Reaction	96
5.4 Rheological Analysis of the HPET/TGIC Reaction	100
5.4.1 Effect of Temperature at Constant Frequency	. 101
5.4.2 Effects of Frequency at Constant Temperature	104
5.4.3 Effects of Method of Sample Preparation at Constant Temperature of Frequency	or 106
5.4.4 Effects of Time/Frequency Scans at Constant Temperature	108
5.4.5 Gel Structure Represented Through the Fractal Dimension	112
5.4.6 Summary of Chemorheological Study	113
5.5 Sequential Reactive Extrusion/Foaming	114
6 CONCLUSIONS AND RECOMMENDATIONS	119
REFERENCES	121

LIST OF TABLES

Table		Page
1.1	Intrinsic Viscosity Range of PET	. 5
4.1	Characteristics of Modifiers	50
5.1	HPET Degradation: First Order Rate Constants	63
5.2	First order rate constants for torque increase in the batch mixer at various reaction conditions of HPET with TGIC	5 78
5.3	Comparison of rate constants for the HPET/TGIC reaction	103
5.4	Extrusion data and Rheological Properties of Unmodified Vs. Modified RPET	l 116

LIST OF FIGURES

Figure		Page
1.1	Macromolecular formula of polyethylene terephthalate (PET)	2
1.2	PET synthesis from dimethyl terephthalate and ethylene glycol	. 3
1.3	Direct esterification by reaction of ethylene glycol with terephthalic acid for PET synthesis	. 4
1.4	Schematic of Injection Blow Molding	8
1.5	Schematic of Stretch Blow Molding	. 8
1.6	Schematic of Extrusion Blow Molding	. 11
1.7	Schematic of extrusion foaming with physical blowing agent	. 12
2.1	Phenomenological scheme of the research problem	. 18
3.1	PET thermal degradation reactions	22
3.2	Reactions of carboxylic groups with various electrophilic group	. 24
3.3	Suggested mechanism of the reaction of PET with pyromellitic dianhydride (PMDA)	. 30
3.4	Epoxy or Oxirane ring	. 37
3.5	Base catalyzed epoxide ring opening reaction	38
3.6	Reaction scheme of acid catalyzed epoxide reaction	39
3.7	Overall reaction between epichlorohydrin and bisphenol-A to produce epoxy resins	40
3.8	Primary amine – epoxy reaction	. 41
3.9	Anhydride – epoxy reaction	41
3.10	Acid – epoxy reaction	42

Figure	re P	
3.11	Base catalyzed carboxyl-glycidyl reaction	43
3.12	Base catalyzed hydroxyl-glycidyl reaction	43
4.1	Structure of diepoxides	47
4.2	Structure of triepoxides	48
4.3	Structure of tetraepoxide	49
5.1	Isothermal TGA data at 270°C of reactive modifiers	60
5.2	Torque evolution in an intensive batch mixer for HPET (Nominal I.V. 0.78) and MPET (Nominal I.V.= 0.58) at Chamber Temperature=270°C, 60rpm. Initial pellet carboxyl content (CC_0) and carboxyl content at 900s (CC_{15min}) are also shown	= er nd so 61
5.3	Blank HPET torque/time and temperature/time runs at 270°C, 285°C, an 300°C chamber set temperatures	nd 62
5.4	Carboxyl content vs. time data at 270°C(O), 285°C(△), and 300°C(□) for melt processed HPET. Data for unprocessed pellets, t=0s, (◊) are als shown	or so 64
5.5	Possible reactions between PET end groups and epoxy containing modifiers under operating conditions	ng 65
5.6	Effect of type of Diepoxide on torque vs. time curves for HPET at 270° and 60rpm. Stoichiometries of DGEBA and BGPM based on initia carboxyl content (CC _o) and carboxyl content at the time of modified addition (CC _{6min}) are shown.	C al er 68
5.7	Effect of Type of Triepoxide on torque vs. time curves for HPET a 270° C and 60rpm. Stoichiometries of TGG and TGIC based on initia carboxyl content (CC _o) and carboxyl content at the time of modified addition (CC _{6min}) are shown.	at al er 69
5.8	Effect of epoxide concentration on torque measured 6 minutes after epoxide addition	er 70

Figure		Page
5.9	Effect of TGIC concentration on torque/time curves for HPET at 60rpm and set chamber temperature = 300° C. Stoichiometries based of initial carboxyl content (CC _o) and carboxyl content at the time of modifier addition (CC _{6min}) are shown	n, m of 72
5.10	Effect of type of PET on torque/time curves obtained through the addition of 1X stoichiometric TGIC amount based on CC _o . So chamber temperature=270°C, 60rpm	ne et 72
5.11	Variation of CC of HPET measured after 15 min processing versu amount of TGIC added at different process temperature (Stoichiometry is based on initial pellet carboxyl content)	is es 74
5.12	Insoluble content of the HPET at the end of melt mixing for 15 minute at 60rpm and two chamber temperatures (270°C and 300°C) with an without TGIC. Data are compared to those of unprocesse pellets	es id ed 74
5.13	Insoluble content of the HPET at the end of melt mixing for 15 minute at 60rpm and two chamber temperatures (270°C and 300°C) with an without TGIC. Data are compared to those of unprocesse pellets	es id id 75
5.14	Rate constant versus temperature at various stoichiometries from the batch data	ie . 78
5.15	Effect of catalysts on PET-DGEBA reaction	80
5.16	Effect of addition of antimony oxide on HPET/1.5X TGIC me modification	lt 82
5.17	Torque (Nm) versus time (s) data during the reactive batch mixing	85
5.18	Effect of degradation on absolute value of complex viscosity $ \eta^* $ vs frequency ω	86
5.19	Modified Cole-Cole plots for unprocessed HPET pellets (♦), offline data of HPET processed at 270°C(■), offline data of HPET processed at 300°C(●)	ta at 87

Figure	Pa	ıge
5.20	Absolute value of complex viscosity $ \eta^* $ vs frequency ω for unmodified and modified HPET	88
5.21	Effect of reaction on the loss tangent vs frequency ω for modified and unmodified HPET	90
5.22	Modified Cole-Cole plots for unmodified and modified HPET samples	92
5.23	Relaxation spectra H (τ) vs relaxation time τ	94
5.24	TGIC stability at 270°C as monitored by FT-IR spectroscopy	96
5.25	HPET melt stability at 270°C as monitored by FT-IR spectroscopy	97
5.26	HPET + 10% TGIC at 270°C as monitored using spectroscopic analysis in comparison with control PET and TGIC samples at 270°C after 5min.	98
5.27	Changes in dynamic moduli (G', G") at a constant frequency of 10 rad/s and at 270°C and 300°C respectively	100
5.28	Evolution of storage modulus G' (Pa) versus reaction time (s) as a result of change in frequency (rad/s) at 270°C	105
5.29	Changes in storage moduli versus frequency at different reaction time intervals, and at 270°C	106
5.30	Comparison of method of sample preparation – solution casting from hexafluoroisopropanol versus powder mixing, to monitor the HPET/TGIC reaction 270°C and at a frequency of 1 rad/s	107
5.31	Frequency dependence of oscillatory shear modulus G' for HPET+1.5X TGIC at 270°C at various time intervals	108
5.32	Frequency dependence of $\tan \delta$ for HPET+1.5X TGIC at 270°C at various time intervals	109

Figure		Page
5.33	Relaxation Modulus <i>G(t)</i> for the HPET/TGIC system at 270°C obtained through real time frequency scans	1 110
5.34	Schematic of reactive modification of RPET with TGIC in a single screw extruder	, 115
5.35	Schematic of Sequential Reactive Extrusion Foaming of RPET+0.75X TGIC with Isobutane	X . 117
5.36	Foam cross section of TGIC modified PET	. 118

LIST OF SYMBOLS

Symbol	Description	Unit
A	Interfacial area during mixing	cm ²
CC	Carboxyl Content	eq./10 ⁶ g
CC _{6min}	Carboxyl Content at the end of 6 minutes in batch mixer	eq./10 ⁶ g
CCo	Initial Carboxyl Content	eq./10 ⁶ g
CC _p	Carboxyl Content of Pellets	eq./10 ⁶ g
CCt	Instantaneous Carboxyl Content	eq./10 ⁶ g
f	Functionality of the epoxide	-
D_{AB}	Mass Diffusivity	cm^2/s
G′	Storage Modulus	Ра
G″	Loss Modulus	Ра
G(t)	Relaxation Modulus	Pa
Η(λ)	Relaxation Spectrum	Ра
I.V.	Intrinsic Viscosity	dL/g
k	First Order Rate Constant	s ⁻¹
M _n	Number Average Molecular Weight	g/gmol
$M_{\rm w}$	Weight Average Molecular Weight	g/gmol
Mz	z-Average Molecular Weight	g/gmol
M.F.I.	Melt Flow Index	g/10 min.
n	Relaxation Exponent	-

r	Striation Thickness	cm
t	Time	S
t _d	Diffusion Time	S
t _r	Characteristic Reaction Time	S
Tg	Glass Transition Temperature	°C
T _m	Melt Temperature	°C
T _{cc}	Cold Crystallization Temperature	°C
tanδ	Loss Tangent	-
α	Thermal Diffusivity	cm ² /s
γ	Strain	-
η [*]	Absolute value of complex viscosity	Pa.s
[η]	Intrinsic Viscosity	dL/g
η _s	Solvent Viscosity	Pa.s
η_{sp}	Specific Viscosity	-
λ	Relaxation Time	S
λ_s	Time for the center of the sphere to reach melt temperature	S
λ_r	Characteristics Reaction Time	S
π	Geometric Constant	-
τ	Torque	Nm
ω	Frequency	rad/s

LIST OF ACRONYMS

BGPM	N, N'-bis [3(carbo-2', 3'epoxypropoxy) phenyl] pyromellitimide
------	----------------------------------------------------------------

- DGEBA diglycidyl ether of bisphenol A
- DMT dimethyl terephthalate
- EG ethylene glycol
- FTIR Fourier transform infrared spectrophotometer
- GMA glycidyl methacrylate
- GPC Gel Permeation Chromatography
- HFIP hexafluoroisopropanol
- HC hydroxyl content
- HPET high molecular weight poly (ethylene terephthalate)
- MCC modified Cole-Cole
- MPET medium molecular weight poly (ethylene terephthalate)
- MW molecular weight
- MWD molecular weight distribution
- PBT poly (butylene terephthalate)
- PET poly (ethylene terephthalate)
- PMDA pyromellitic dianhydride

R ₃ N	tertiary amine
TPA	terephthalic acid
TGA	thermogravimetric analysis
TGDDM	tetraglycidyl-4', 4"-diamino diphenyl methane
TGG	triglycidyl glycerol
TGIC	triglycidyl isocyanurate
X	times stoichiometric amount of epoxide added, followed by 0.5, 1 or 1.5

LIST OF TRADE NAMES

Trade Name	Company	Description
Araldite MY721	Ciba Specialty Chemicals Inc., Switzerland	Tetraglycidyl diamino diphenyl methane – a chain extender/branching agent
Armeen M2C	Akzo Nobel Inc., USA	Dicocomethylamine
Celpet	Sekisui Plastics Co. Ltd., Japan	Foams of poly (ethylene terephthalate)
Cobitech	Sinco Engineering, Italy, part of Gruppo Mossi and Ghisolfi, Italy	Foam grade pellets of poly (ethylene terephthalate)
Epon 828	Shell Chemical Company, USA	Diglycidyl ether of bisphenol A
Petlite	Shell Chemical Company, USA	Foamable poly (ethylene terephthalate) pellets
Plasticorder PL2000	C. W. Brabender Instruments Inc., USA	Intensive batch mixer
QA 50	TA Instruments, USA	Instrument for thermogravimetric
Rhopet	Rhodia-Ster SA, Brazil, now part of Gruppo Mossi and Ghisolfi, Italy	Bottle grade poly (ethylene terephthalate)
RMS-800	Rheometric Scientific Inc.	Parallel plate dynamic mechanical analyzer
Spectrum One	Perkin Elmer Inc.	Fourier transform infrared spectrophotometer

CHAPTER 1

INTRODUCTION

After its introduction as a suitable material for synthetic fibers, about fifty years ago, poly(ethylene terephthalate) (PET) has found new, interesting, and enduring applications, in many cases without any alternatives (Ludwig, 1971). The opportunities for PET applications are related to its properties, originating mostly from its structural characteristics (Fakirov, 2002). The high crystalline melting temperature (270°C) and stiff polymer chains of PET result in good mechanical properties up to 150-175°C, PET also offers good chemical, solvent, and hydrolytic resistance and is widely used in fiber, film, packaging, and insulation applications, in capacitors, and as an engineering plastic (Odian, 1991). In general, the range of applications is based on the typical set of properties offered by the material, which are a result of its chemical structure and its processing history. In other words, the chemistry during material synthesis and chemical changes during post reactor processing have an influence on the desired applications.

1.1 Commercial Synthesis of PET

From a classical polymer chemistry point of view, PET is commonly known as a condensation polyester characterized by the ester linkage (-COO-) with a combination of carboxyl and hydroxyl end group(s) depending on the manufacturing conditions (Maréchal, 2002). Figure 1.1 shows the macromolecular formula of PET produced from equimolar concentrations of diacid and glycol.



Figure 1.1 Macromolecular formula of polyethylene terephthalate (PET).

Various combinations of reactant(s) and process conditions are potentially available to synthesize polyesters (Goodman, 1988). Commercial scale production of PET most commonly involves two steps. PET is generally prepared by bulk or solution polymerization initially at around 150-210°C by transesterification (alcoholysis) from dimethyl terephthalate (DMT) and ethylene glycol (EG) or direct esterification from terephthalic acid (TPA) and EG, in the presence of catalysts, resulting in oligomers. In a second step, oligomers undergo melt polycondensation to produce high molecular weight PET resin.

In the case of reaction between DMT and EG, the methyl end groups of DMT are continuously replaced by ethyl end-groups of EG to produce bis (2-hydroxyethyl) terephthalate as shown in reaction (1) in Figure 1.2, along with small amounts of oligomers (Odian, 1991). In this process, EG is consumed while methanol is evaporated and re-collected to be returned to the DMT plant. The reactants are heated at temperatures increasingly from 150 to 210°C. Commonly used catalysts for ester transformation are oxides, carbonates, or acetates of calcium; manganese; cobalt; cadmium; lead or zinc (Sorenson et al., 2001). Typically, the amount of catalyst used is in the range of 0.05 to 0.1% by weight of the dimethyl terephthalate (Cimecioglu, 1986).

In the second-stage, the temperature is raised to 270-280°C and polymerization proceeds with the removal of ethylene glycol being facilitated by using a partial vacuum

of 0.5-1.00 mm Hg (Sorenson 2001). Antimony oxide (Sb_2O_3) is generally used as a second-stage catalyst. Sometimes germanium oxide (GeO_2) is added as a catalyst to the second stage also (Maréchal, 2001). Sb_2O_3 alone is known to be ineffective for the first stage reaction. The first stage catalyst is often deactivated by the addition of an alkyl or aryl phosphite or phosphate to reduce thermal degradation during the second stage. (Odian, 1991, Fakirov, 2002).



Figure 1.2 PET synthesis from dimethyl terephthalate and ethylene glycol.

The availability of terephthalic acid in higher purity than previously available has led to its use in a modification of a two-stage process (Odian, 1991). Terephthalic acid and an excess ethylene glycol (in the form of a paste) are used to produce the bis (2hydroxyethyl) terephthalate as shown in Figure 1.3. The reaction is carried out at a temperature of about 200°C at atmospheric pressure to eliminate water and form diolended polyester. This step is self-catalyzed by terephthalic acid. The second step consists of raising the temperature to about 280°C to effect transesterification, with elimination of ethylene glycol, using antimony oxide as catalyst (Maréchal, 2001). This is facilitated by carefully controlled agitation and progressive reduction of the pressure to about 1 mm Hg (Odian, 1991).



Figure 1.3 Direct esterification by reaction of ethylene glycol with terephthalic acid for PET synthesis.

A fundamental difference between the preparation of PET from DMT and EG, or from TPA and EG, consists in that TPA does not melt by itself at the temperatures used throughout the polymerization train, making its esterification by EG a prerequisite for the homogenization of the monomer mixture in the esterification reactor (Maréchal, 2001).

PET is produced into various grades, by slight variations in the general commercial synthesis procedures described above, for specific end-use applications. One of the important technological parameters in the choice of the grade of PET is the molecular weight, generally reported as intrinsic viscosity (I.V.) or limiting viscosity number ($[\eta]$). I.V. maybe obtained by an extrapolation procedure based on viscometric measurements made at several concentrations, or by an approximation from a single concentration measurement. Intrinsic viscosity is determined from the following Equation:

$$[\eta] = \lim_{c} \lim_{s \to 0} \left[\frac{\ln(\eta / \eta_{sp})}{c} \right]$$
(1.1)

where η is the solution viscosity, η_s is the solvent viscosity, c is the concentration, and η_{sp} is the specific viscosity that is calculated using the following equation:

$$\eta_{sp} = \frac{\eta}{\eta_s} - 1 \tag{1.2}$$

The relationship between $[\eta]$ and molecular weight (MW) depends upon the solvent system and the temperature used for the measurements. Standard solvent systems for PET I.V. measurements are 60/40 phenol/tetrachloroethane; other solvents include phenol/1,2-dichlorobenzene, o-chlorophenol (Japon et al.,1998, Khemani, 1998). Table 1 summarizes the I.V. range of commercial PET resins according to applications.

Application	Intrinsic Viscosity (dL/g)
Fiber grade	
* Textile	0.40-0.70
* Technical	0.72-0.98
Film Grade	
* Biaxially oriented film	0.60-0.70
* Sheet grade for thermoforming	0.70-1.00
Bottle grade	
* Water Bottle	0.70-0.78
* Carbonated soft drink grade	0.78-0.85

 Table 1.1 Intrinsic Viscosity Range of PET

To provide an approximate idea of I.V.-MW relationships, I.V. values of 0.43, 0.60, 0.72, and 1.00 dL/g correspond to number average molecular weights of 10000, 18000, 24000, and 40000 g/mol respectively (Gupta and Bashir, 2002).

1.2 Applications and Limitations of Commercially Available PET

1.2.1 Applications

Principal commercial products of PET are fibers, bottles, and films. Among them, commodity fibers have provided the largest outlet for its consumption (Rodriguez, 1996). The current growth rate for PET bottles is around 15% whereas for fibers it is less than 5%. Films have always been relatively small in production volume (about 10% of total PET), but they are used in high value added applications, such as audio and videotapes.

There is one noteworthy difference between the method PET filaments and fibers are produced and that used for producing PET sheets, films, or bottles (Gupta and Bashir, 2002). With filaments and fibers, direct shape forming is possible from the melt, while with films and bottles it is essential to first make an amorphous intermediate (sheet or preform) by quench cooling from the melt. Then the intermediate is softened by heating to a temperature ~20-30°C above the glass transition temperature - T_g, when it has enough strength to support itself but is pliable enough to be biaxially oriented. The combination of this two step process is called as injection-stretch-blow molding. Direct biaxial stretching of the melt is possible with polyolefins, but not with most of the PET resins because of their low melt elasticity/strength. Therefore, conventional film blowing and extrusion blow molding techniques, where biaxial stretching is applied to the melt, are not suitable for most of the commercially available PET resins (Dealy and Wissbrun, 1990).

In conventional forming processes, bottles could either be made using injection blow molding or stretch blow molding operations (Dealy and Wissbrun, 1990). As shown in the injection blow molding schematic in Figure 1.4 (b), a tube of molten polymer, the parison or preform produced by injection molding as per Figure 1.4 (a), is sealed at both ends and held in place while two halves of a hollow mold surround it (Rodriguez, 1996). Air is injected into the parison or preform, which blows in as if it were a rubber balloon. When the polymer surface meets the cold metal wall of the mold, it is cooled rapidly below T_g or T_m depending on whether the polymer is amorphous or crystalline. Once the product is dimensionally stable, the mold is opened, the bottle is ejected, a new parison is introduced, the mold is closed, and so on. In the case of stretch blow molding shown in Figure 1.5, in addition, to the above sequence, biaxial orientation in the bottle is increased by longitudinal stretching during radial blowing with the help of an internal rod (Rodriguez, 1996).

There are two crucial phenomena that are related to the blow molding process (Dealy and Wissbrun, 1990). The melt deformation that occurs in the die generates molecular orientation, which manifests itself at the die exit as 'parison swell'. Swell during blow molding is known to depend upon MW, the extent of branching, and/or molecular weight distribution (MWD). 'Sag' (drawdown), another important parameter, can cause large variations in thickness and diameter along the parison, and in an extreme case can cause the parison to break off. Sag is generally quantitatively related to the melt flow index of the polymer. PET in the melt state, cannot support its own weight long

enough for controlled biaxial stretching to take place which limits its melt processing applications. It should be noted that, in the case of PET filaments, despite the low melt strength, sagging does not arise because the filament is formed by accelerating the melt in the direction of gravity (Gupta and Bashir, 2002).



Figure 1.4 Schematic of Injection Blow Molding.

[Note: (a) Injection cycle - polymer melt supplied to mold halves from injection molding machine, product formed is preform or parison. (b) Heated preform inflated against cold mold wall halves.] (Rodriguez, 1996)



Figure 1.5 Schematic of Stretch Blow Molding.

[Note: Breakaway section showing blow mold with Stretch Blow Pin. A: Stretch-Blow Pin, B: Air Entrance, C: Mold Vents, D: Preform, E: Stretch Rod Extended, F: Cooling Channels.] (Rodriguez, 1996)

In the case of sheet applications, the amorphous PET sheet is made by extruding an appropriate molecular weight PET melt through a slit die and quenching over a chill roller (Dealy and Wissbrun, 1990). In thermoforming, the PET sheet is reheated or softened above T_g , but below the cold crystallization temperature T_{cc} , and cold molds are used to make clear cups, trays and blister packages for pharmaceutical tablets (Gupta and Bashir, 2002).

Biaxially oriented thin films (5-180µm) are made from PET in a sequential drawing process (Gupta and Bashir, 2002). In this process, PET is melt extruded through a slit die and quenched to form an amorphous precursor film. The quenched film is later drawn in the extrusion direction and the tangential direction. The films prepared under clean room conditions are used in applications such as video and magnetic tapes, floppy disks, photographic products, and capacitors. Biaxially oriented thick films (75-180µm) are used in photographic applications.

The PET resins produced by conventional synthetic routes are suitable for a variety of applications and end uses. However, their particular macromolecular structures may raise unique rheological concerns regarding their broader range of applications. For example, linear PET synthesized as described before in Section 1.1, if processed for applications involving extrusion foaming to low densities, extrusion blow molding, and thermoforming operations may present limitations mainly through its inadequate rheological properties for such operations.

1.2.2 Limitations of PET

Rheologically, PET, a linear polycondensation polymer, is usually considered as unsuitable for extrusion blow molding because it is nearly Newtonian above its melt temperature (Dealy and Wissbrun, 1990). Use of a multifunctional monomer such as 1,4cyclohexane dimethanol instead of ethylene glycol or tetraerythritol, or trimellitic anhydride which produce long chain branching and broadens the MWD can render PET the desirable processing and rheological properties for extrusion blow molding (Edelmen et al., 1979 and 1980). It is obvious that this option of varying the monomer functionality during commercial synthesis in compliance with different end use application(s) may be expensive from the point of view of bulk manufacturers. In order to understand the significance of the limitations of PET due to its properties, it is necessary at this point to define the process requirements, particularly for extrusion blow molding and extrusion foaming.

By contrast to the injection blow molding of PET, described earlier, the extrusion blow molding process would be faster on a time scale and more economical because of the fewer number of steps involved and time savings over cooling the parison. In the generalized extrusion blow molding process, shown in Figure 1.6, a tube or parison of melt is extruded from a die (Rodriguez, 1996). The mold halves then close around the parison to pinch it off at one end and if a bottle is to be made, to form a threaded neck at the other. Then the parison is inflated to conform to the shape of the mold. The extrusion can be intermittent, halting while the parison is pinched, inflated and cooled, or it can be continuous, by the use of two or more moving molds. In addition to parison swell and sag, 'shark skin' or 'melt fracture' is a parameter of concern in extrusion blow molding
operation (Dealy and Wissbrun, 1990). Shark skin is a distortion of the extrudate that can affect the surface finish of an extrusion blow molded container. Extrusion distortion is most severe in the case of polymers with narrow MWD (Dealy and Wissbrun, 1990).



Figure 1.6 Schematic of Extrusion Blow Molding (Rodriguez 1996).

There are certain rheological requirements for polymers used in the extrusion blow molding process, which are normally absent from linear PET resins in the melt state. "Die" or extrudate swell, a prime requirement, greatly varies from polymer to polymer, strongly affected by the degree of branching and the molecular weight distribution (Rosato and Rosato, 1989). Extrudate swell is used as a parameter for designing a die for blow molding operations. It is also useful in determining the stability of parison/preform of a polymer (Dealy and Wissbrun, 1990). For linear polymers such as PET, broadening of MWD generally results in higher extrudate swell. Extrudate swell is highly sensitive to the small amounts of high molecular weight material, which could be in the form of long chain branching (Rosato and Rosato, 1989). Raising the high molecular weight fraction increases the ultimate swell but decreases the rate of approach to the steady state value (Koopmans, 1988). Koopmans also found that highly branched polymers tend to swell more, but it is not possible to generalize when both branching and MWD are altered simultaneously. In summary, melt modification of PET by inducing long chain branching and/or widening of MWD may result in increased potential of using the material for extrusion blow molding.

Thermoplastic foams are prepared by various techniques. Among them, extrusion foaming by incorporating non-reacting physical blowing agents is of current interest. In a typical extrusion foaming to low densities, continuous gas phase (physical blowing agent) is injected into a continuous polymeric melt in the extruder at a high pressure (Xanthos et al. 2000a). As shown in Figure 1.7, a solution of a gas dissolved into polymer under pressure is extruded into a region of lower pressure, usually the atmosphere, where it becomes supersaturated (Xanthos, 1998). As the gas-laden melt emerges from the die it experiences a sudden pressure drop; this thermodynamic instability causes phase separation. The escaping gas leads to expansion within the fluid matrix in such a manner that individual bubbles merge into cells and through subsequent solidification, stable expanded structures are produced.



Figure 1.7 Schematic of extrusion foaming with physical blowing agent.

During the cell growth phase of extrusion foaming, the polymeric melt undergoes intense elongational deformations. These deformations are not sustained by the typically narrow MWD of most of the commercially available PET resins. Such PET resins are rheologically characterized by low values of melt viscosity, along with poor shear sensitivity, i.e., non-Newtonian behavior, and low melt elasticity usually expressed as melt strength and extrudate swell (Young et al., 1999, Xanthos et al., 2002). As a result, uncontrolled cell expansion and unstable growth of bubbles may occur resulting in poor foamability. In general, changes in melt strength and extrudate swell which are representations of changes in the melt elasticity of the polymer are required to improve foamability of PET. Changes in melt elasticity have also been correlated with changes in elongational viscosity. As discussed by Throne (Throne, 1996), melts with relatively low shear and elongational viscosity are needed during the initial foaming stage to allow rapid bubble growth. However, during the subsequent stages viscosity must increase, as for example by cooling or by strain hardening, to a level adequate for the stabilization of the growing bubbles. Strain-hardening behavior in the elongational viscosity, defined as the rapid increment of the elongational viscosity with elongational time or strain under a constant strain rate, is also required for other processes such as film processing, thermoforming, and blow molding (Yamaguchi, 2000). Most of the polymers without long chain branches, however, hardly show strain-hardening behavior in the elongational viscosity, whereas polymers with long-chain branches exhibit marked strain hardening (Meissner et al., 1981 and Meissner et al., 1994).

Additional general polymer requirements for enhanced foamability (Throne, 1996) are: moderately high elongational viscosity to allow biaxial stretching, high melt

strength/elasticity to resist membrane tearing (blow-out) and promote the formation of closed-cell structures, and if crystallizable, relatively rapid rate of crystallization.

Linear PET resins, in general, do not meet the above requirements and are characterized by a very narrow extrusion foaming window. Extrusion foaming to low densities is also affected by a slow rate of crystallization, and the possible interference of crystal nucleation with bubble nucleation. In addition, foaming characteristics of PET are challenged by its sensitivity towards hydrolytic, thermal and/or thermooxidative degradation which becomes particularly pronounced at the high melt temperatures (>270°C) involved during processing.

1.3 Chemical Modification of PET

Virgin and recycled grade PET resins offer favorable cost/performance characteristics, which may be extended to lower density foamed structures by chemical modification. Potential applications would take advantage of the combination of good mechanical properties, dimensional stability of the semicrystalline resin at temperatures up to 200°C, and recyclability (Odian, 1991). In addition to the food packaging industry where PET foams have already made advances, other applications would be intended for the construction/building, transportation and other industries currently utilizing rigid polyurethane, polystyrene or polyvinyl chloride foams.

In a broad sense, the chemical modification of single polymers may be accomplished with various reagents in the molten state, in solution, or on the surface of plastic parts/pellets. Recent advances in the technology and economics of the modification reactions for single polymers and polymer blends have demonstrated the suitability of extruders as continuous reactors, often operating in the complete absence of solvents (Xanthos, 2002).

It is well known that the improvement in the mechanical and chemical properties of PET, related to an increase in molecular weight, is also correlated with a decrease in the number of carboxylic end group(s) (Inata and Matsumura, 1985). Some of the property improvements are also the result of broadening the molecular weight distribution of the linear PET (Inokuchi et al., 1981). It is very difficult to obtain PET having a molecular weight represented by an intrinsic viscosity (I.V.) above 0.9 dL/g by the usual melt polycondensation synthesis (Aharoni, 2002). As the polycondensation proceeds, the reaction rate decreases and degradation of the terminal groups occurs leading to an increase in carboxyl content (CC). Thus, the rheological properties of PET differ from those of other common thermoplastic polymers, mainly addition polymers (Gupta and Bashir, 2002).

macromolecular To overcome the above structural limitations, postpolycondensation in the solid phase may be carried out, as reported by several authors (Aharoni, 2002, Inata and Matsumura, 1985). By 'solid stating' is meant that the polymer pellets remain in the solid state, below their melting temperature, during additional chain extension (Aharoni, 2002). In the first stage of the process, PET pellets are fed into crystallizers, in which they are exposed to low temperature. During crystallization, a high level of chain motion takes place, especially in the amorphous phase of the polymer allowing chain extension and transesterification. At the end of the pellets' residence time in the crystallizers, their surfaces are highly crystalline. The pellets are transferred to a vacuum dryer and stored at 160°C, which promotes chain extension and increase in MW.

After this stage, PET pellets are transferred to hopper reactors, maintained at a temperature of about 216°C and swept by a continuous stream of nitrogen under reduced pressure, resulting in increased MW at the end of the solid-stating. The disadvantages in this method are the very slow reaction rates, unfavorable economics, and the need for special equipment such as special heaters, hopper driers, hopper reactors for the large-scale operation (Aharoni, 2002).

Another method proposed to increase MW and broaden the MWD, particularly applicable to foaming and extrusion blow molding applications, is to use the so-called "chain extenders", these are able to react with a polymer end groups more effectively either during solid stating or, alternatively when added during a reactive extrusion process.

The production of extrusion foamable polyesters modified by solid state polyaddition with a premixed multifunctional modifier, e.g. pyromellitic dianhydride (PMDA) is discussed in a series of patents and publications from Sinco Engineering (Al Ghatta, 1993, Al Ghatta and Pizzetti, 1993, Al Ghatta et al., 1993). These resins are distinguished from non-foamable resins by increased MW, as measured by intrinsic viscosity I.V. (>0.9dL/g), increased melt strength, high extrudate swell, increased complex viscosity with higher shear sensitivity and increase in storage modulus. Postreactor modification by reactive extrusion of PET carried out using PMDA or other branching additives also results in significant increase in zero shear viscosity, increase in melt strength and die swell, increase in molecular weight and increase in polydispersity ratio M_z/M_n from about 4.5 up to 11. Property changes depend on the choice of process conditions and additive concentration and its type of carrier (Khemani et al., 1997, Khemani, 1998).

It is the latter process, i.e. the reactive melt modification of PET by multifunctional epoxy chain extenders, that is the topic of this thesis.

CHAPTER 2

PURPOSE AND SCOPE

This thesis focuses on understanding the structural modification of PET and its effect on the polymer rheological properties through a reactive melt processing approach using low MW multifunctional epoxides, for improving processability, particularly in extrusion foaming. Reactive processing, in this case, involves undesirable degradation reactions and desirable chain extension and branching reactions resulting in changes in MW and MWD of PET.



Figure 2.1 Phenomenological scheme of the research problem.

As sketched in Figure 2.1, extrusion foaming of PET to low densities is challenged by its low melt viscosity, melt strength, and melt elasticity. Researchers have correlated improvements in these and other rheological/processing properties with bubble stability and resistance to bubble coalescence during foaming. This thesis attempts to understand the effect of evolving branched polymeric structures, caused by reactions in a controlled environment, on the rheological properties of interest and their relation with foamability of the modified resin in extruders.

The experimental work involves first the selection of the PET resins and the epoxy modifiers combined with their full characterization. Specifically, for PET, parameters that were studied were (i) initial MW, MWD, (ii) end group content, and (iii) thermal stability. For epoxy modifiers, parameters that were studied were (i) structure, (ii) functionality, (iii) thermal stability, and (iv) concentration.

Melt modification was monitored and analyzed by carrying it out in three types of batch reactors: (1) intensive batch mixer, (2) dynamic mechanical analyzer (rheometry), (3) high temperature sodium chloride crystal cell for FT-IR, prior to proceeding with the reaction in continuous extruders.

During melt processing, PET may undergo undesirable thermal degradation. Thus, the role of such degradation reactions on the desirable chain/extension branching reactions was also evaluated. In order to understand the evolving and resultant macromolecular structure(s) and their particular rheological/processing properties, a combination of online, inline, and offline characterization methods were used. They include carboxyl content determination, insoluble content determination, and rheological analysis of the reaction products. The changes in the properties, which were monitored during melt modification, were analyzed to obtain the reaction kinetics information.

The developed kinetic data in association with the resultant reaction product properties were used to define the requirements for and extending the reaction in an extruder; this was followed by combining the reaction step with gas injection in a one step operation combining reactive extrusion/foaming.

This is the overall scheme followed in this thesis. The next chapter provides a review of literature pertinent to the present work.

CHAPTER 3

LITERATURE REVIEW

This chapter presents a review of the engineering and chemistry aspects of PET melt modification. The chapter is divided into two main sections. First, chemical modification of PET as reported by various authors is reviewed; it is then followed by a review of the specific published information that is pertinent to the experimental scheme of this thesis involving PET and multi-functional epoxide chain extenders.

3.1 Modification Routes

Literature on PET modification could be divided into four basic categories depending upon the end application: (i) controlled degradation, used to adjust molecular weight or to produce monomers/oligomers (solvolytic tertiary recycling); (ii) capping of carboxylic end groups, especially in fiber-forming polyesters; (iii) production of compatibilized blends with fine microstructure and enhanced properties by the addition of elastomers (for impact modification) or other thermoplastics; and (iv) chain extension/branching of the otherwise low MW and narrow MWD polyesters in order to produce materials with increased melt viscosity and melt strength for applications such as extrusion blow molding or low density extrusion foaming.

3.1.1 Chemical Modification of PET – Traditional Approach

PET may undergo undesirable thermal degradation through chain scission reactions in essentially air-free, moisture free environments. In thermal degradation, at first, random scission of PET chain takes place resulting in chain cleavage and the formation of carboxylic end groups and vinyl esters, aldehydes, carbon dioxide, and various crosslinked structures (Yoda et al., 1970).

Chain Cleavage Degradation



Figure 3.1 PET thermal degradation reactions (Yoda et al., 1970).

Figure 3.1 shows the thermal degradation reactions that are believed to occur during melt processing of PET. Thermomechanical degradation of PET melts in the

absence of modifiers is accompanied by decreases in intrinsic viscosity and melt viscosity. Yoda further suggested that vinyl esters accumulate to a certain concentration and then react with polyester chains resulting in extension/branching/crosslinking while forming polyene structures and promoting acetaldehyde generation. Through end-group degradation additional carboxyl groups may be formed. As reported by Yoda, Zimmerman and co-workers have summarized the reactions and suggested that thermal degradation of PET leads to branching and cross-linking while forming soft gel like material (Yoda et al., 1970). Transesterification reactions may also be important as well as subsequent reactions with the hydroxyl end groups of the polyester (Japon et al., 2001). In general, thermal degradation of PET results in an increase in carboxyl content and decrease in hydroxyl content (Bikiaris and Karayannidis, 1995, Bikiaris and Karayannidis, 1996, Japon et al., 1998). Thus, changes in the instantaneous concentration of PET end groups during melt processing and formation of cross-linked structures is anticipated; the melt effect of these complex degradation phenomena is an overall decrease in melt viscosity and reduction in molecular weight.

Controlling the properties and MW of PET resins through "controlled degradation" has been explored by many researchers particularly as a recycling option. The PET is hydrolyzed, often in the presence of catalyst, under neutral, acidic, or basic conditions to produce terephthalic acid and ethylene glycol; this method of tertiary recycling may also be categorized under 'controlled degradation' (Patel and Xanthos, 1994). Solvolytic reactions have also been used to lower MW and I.V. values in fiber production.

The majority of commercially available PET resins have nucleophilic end-groups (carboxylic and hydroxyl) that can form covalent bonds with suitable electrophilic functionality (Brown, 1992). Modifying PET by chemical means is not new. Brown summarizes detailed examples of polyester end-capping reactions with low molecular weight usually monofunctional additives (Brown, 1992). The capping agents are low or high MW reagents containing electrophilic groups such as anhydride, epoxide, oxazoline, isocyanate, or carbodimide. Figure 3.2 shows specific reactions of carboxylic acid terminal groups with some important electrophilic groups (Brown, 1992).



Figure 3.2 Reactions of carboxylic groups with various electrophilic groups (Brown, 1992).

The primary objective while modifying PET by this school of thought was mainly to improve thermal stability by end capping the chain ends of the polyester chain (measured by decreasing end group content) and thus restrict the corresponding degradation. Most of the available literature, emphasizes end capping reactions based on the carboxyl end groups since it has been established that lower carboxyl group content (CC) leads to better fiber hydrolytic stability and retention of strength under wet conditions. Accordingly, end-capping agents with preference towards carboxylic end groups have been described. Typical reactants are ethylene oxide, phenyl glycidyl ether (with lithium compounds as catalysts), N-glycidyl isocyanuric acid or other monofunctional epoxy compounds.

Liu and Huang have summarized the end group reactions of PET when blended with other high molecular weight polymers with complimentary functional groups (Liu and Huang, 2001). Work in the area of reactive blending of PET focussed on issues such as compatibility and properties such as microhardness, and transparency. Overall, achievement of the objectives was obviously supplemented by increase in the chain lengths/molecular weight (or viscosity) depending on the reaction chemistry, which also acted against the chain scission resulting from degradation reations. It is important to note that, the researchers mentioned so far, relied mainly on product characterization methods such as end group content, gel content, and solution viscosity using traditional wet chemistry techniques, as well as mechanical or thermal analysis, depending upon their objectives.

3.1.2 Chemical Modification of PET – Rheological Perspective

There exists a group of researchers who have investigated the modification of PET from a rheological perspective, towards applications requiring enhanced melt strength/melt elasticity; this is accompanied by increases in the average relaxation time and broadening of relaxation time distribution as a result of chain extension and long chain branching. The intended applications of resins with modified rheology were mainly extrusion foaming to low densities with physical blowing agents and extrusion blow molding. In order to understand the rheological effects of chain extension/branching, at this point, it is necessary to elaborate on the term "melt elasticity".

The term 'melt elasticity', although ill-defined, is widely used in polymer processing where complicating geometric effects and flow fields necessitate the use of linear viscoelastic functions or their non-linear counterparts (Han, 1981). Elastic recovery (recoil) has long been considered a useful parameter in determining fluid elasticity (Utracki, 1989). It is a measure of stored energy and may be characterized by quantities such as the 'steady-state shear compliance' or 'recoverable shear strain'. Changes in melt elasticity have been related to changes in the values of viscoelastic functions such as normal stress differences, storage modulus, and extrudate swell (Han, 1981, Utracki, 1989, Xanthos, 1997). Extrudate swell is considered to represent recovery of stored elastic energy (Dealy and Wissbrun, 1990). Changes in melt elasticity are also correlated to rheological properties such as extensional viscosity, melt strength, and storage modulus (Utracki, 1989, Xanthos, 1997, Japon, 1998). Prichard and Wissbrun have suggested that long chain branching is responsible for reduction in melt flow index (MFI) to certain extent and increase in extrudate swell (Prichard and Wissbrun, 1969). Polypropylene resins with high melt strength are reported to show increasing extensional viscosity at high extensional strains, known as strain hardening (Munstedt, 1981). Strain hardening behavior was found in resins of high polydispersity, also having higher melt strength and higher extrudate swell (Dealy and Wissbrun, 1990).

Yamaguchi and Suzuki studied the rheological properties and foam processability of blends of linear and crosslinked polyethylenes (Yamaguchi and Suzuki, 2001). They found that blending a small amount of crosslinked LLDPE enhanced strain hardening of the elongational viscosity, enhanced extrudate/die swell, and elastic modulus whereas it has little effect on the steady-state shear viscosity. The foams produced from these blends showed higher expansion ratio and more homogeneous cell size distribution. According to the studies by Yamaguchi and co-workers, the conditions, that a small amount of crosslinked polymer enhances the strain-hardening in elongational viscosity of a polymer, are: (1) the crosslinked polymer has a network chain with a low density of crosslink points; (2) the precursor of the crosslinked polymer is miscible with the linear polymer (Yamaguchi and Miyata, 2000, Yamaguchi and Suzuki, 2001, Abe and Yamaguchi, 2001). The origin of the resulting rheological properties has been suggested as a result of the chain stretching of network polymers via trapped entanglements with a linear polymer. Recent work has suggested that the presence of gel like structures in the amount of at least 70% are suitable for foaming resins with the resultant foams having minimal shrinkage (Abe and Yamaguchi, 2001, Yamaguchi and Suzuki, 2001). However, some of the patents suggest that formation of gel like structure in the amount of only 15% are needed for foamability (Okabe et al., 2001).

Yilmazer et al. studied the chain extension / branching of PET and reported that modified PET was characterized by low MFI, high extrudate/die swell, high viscosity, high shear sensitivity, high storage modulus, and pronounced non-Newtonian behavior (Yilmazer et al., 2000). The modified resins were suggested to have higher mean relaxation times and relaxation strengths than the unmodified ones.

Improved melt elasticity may also be correlated with improved foamability of PET resins (Japon et al., 2000). Long chain branching has also been suggested to enhance the "strain-hardening" behavior of the elongational viscosity because of the depression of chain contraction, which has been well recognized by theoretical approaches based on the Doi-Edwards "tube" model (Doi and Edwards, 1986, McLeish, 1998, Wagner, 2001).

In order to appreciate the rheological changes through chain extension/branching reactions of PET resins, it is necessary to look into the corresponding chemical changes. For the chemical melt modification of PET resins, by reacting end groups with multifunctional chain extenders, preferential reactivity towards carboxyl end groups seemed to dictate the choice of chain extenders (Inata et al., 1985, Japon et al., 1998). However, it is noteworthy that the hydroxyl end groups are predominant over the carboxyl end groups in the relatively low-molecular weight polyesters prepared by the usual melt polycondensation procedure (Inata et al., 1985). Thus, the selection of hydroxyl-reactive chain extenders would be more effective for polyesters of relatively low molecular weight.

Aharoni have explored the use of tertiary phosphites for the modification of PET and PBT (Aharoni and Masilamani, 1986). The chain extension of PET or other copolyesters with tertiary phosphites in a single screw extruder was suggested to involve initially the reaction with hydroxyl end-groups to give an alkyldiphenylphosphite ester which then reacts with carboxylic acid end groups to give a polyester with extended chain and increased intrinsic viscosity.

Due to inherent rheological and processing challenges, PET foaming was first reported in the early 80's, which was decades later since it was synthesized on a commercial scale (Lee et al., 2000). Significant developmental work has been conducted over the past twenty years by resin producers and converters to develop suitable resins and extrusion processes particularly for low density foaming, as evident from the large number of patents issued in this area. Since the early 1990s, Shell Chemical Co. (Petlite[™]) and Sekisui (Celpet[™]) have been among suppliers of PET foamed sheets with different bulk densities and low % crystallinity (Hayashi et al., 1991, Xanthos et al., 2000b). Since Engineering was among the recent suppliers of foam grade pellets (Cobitech[™]) (Al Ghatta et al., 1993, Al Ghatta, 1993). Foams with densities of 0.2 g/mL were obtained by injecting hydrogenated chlorofluorocarbons in the primary extruder of a tandem line (Khemani, 1997). In another patent on PET foaming by Hayashi and coworkers (Havashi et al., 1991), isopentane was injected into the molten blend of PET and pyromellitic dianhydride (PMDA) to produce rod-shaped foams. The expansion of the extrudate was proportional to the amount of PMDA added (up to 0.4% by weight); the density values for the PMDA modified foams ranged from 0.35-0.13 g/mL versus 0.7 g/mL when no PMDA was used.



Figure 3.3 Suggested mechanism of the reaction of PET with pyromellitic dianhydride (PMDA) (Khemani 1998).

with catalysts reported produce Dianhydrides metallic are also to hydrocarbon/inert gas extrusion foamable PET by substantially increasing its shear viscosity and melt strength (Hirai et al., 1993). Combinations of PMDA/pentaerylthritol /Lewis acid catalyst have also been used to produce resins with modified rheology, as summarized elsewhere (Xanthos, 2002). A suggested mechanism of the reaction with PMDA involves as a first step linear extension through reaction of the terminal polyester hydroxyl end-groups with the anhydride functionalities and the formation of two carboxyl groups per incorporated PMDA moiety (Khemani, 1997, Khemani, 1998). As shown in Figure 3.3, subsequent reactions may involve all functionalities of the PMDA molecule through esterification and transreactions to yield branched or even crosslinked structures.

Among epoxy modifiers, low MW multifunctional epoxides, used at concentrations less than 1% by weight include diglycidyl terephthalate, diglycidyl tetrahydrophthalate, tetraglycidyl-4', 4"-diamino diphenyl methane (TGDDM), bisphenol

A diglycidyl ether, often in the presence of metal catalysts (Hayashi et al., 1991, Khemani, 1997, Inokuchi et al., 1991, Guo et al., 1998). The tetrafunctional epoxide, TGDDM, was chosen among others for evaluation in the present study. High MW modifiers include ethylene terpolymers containing glycidyl methacrylate (GMA) in the presence of stannous octaoate, hydrated zinc acetate (Deyrup et al., 1990) or zinc ionomers (Howe, 1992), or styrene-GMA copolymers at high concentrations up to 20% by weight (Shiwaku et al., 1996).

Biakiaris et al. have reported the use of N-N'bis glycidyl imides of pyromellitic acid (diepoxides) for the chain extension and/or branching of PET as well as PBT by post polymerization melt modification (Bikiaris et al., 1995 and 1996). Higher concentrations of diepoxide resulted in gel formation. Overall, they reported that, hydroxyl content was increased and carboxyl content was decreased upon melt modification. They also reported that the I.V. was increased from 0.6 to 1.16; this is in the range suitable for extrusion foaming and extrusion blow molding applications. MW and gel content were found to depend upon type and concentration of diepoxide, and reaction time. One of the diepoxides mentioned in the above study is also evaluated in the present work.

Melt modification of PET for extrusion blow molding using polyepoxides has been the topic of exploration for last three decades. Kodama et al. have disclosed melt viscosity improvements by reacting with an isocyanuric acid ester – triglycidyl isocyanurate (TGIC) (Kodama et al., 1979). Endo has described the reaction of poly (ether ester) elastomers with TGIC to produce a material having desirable blow molding properties (Endo, 1981). Similar treatment of PBT is described by Aoyama et al. (Aoyama et al., 1975). It was believed that, branched structures were formed by reaction of the carboxylic acid end groups of the polyester with each of the epoxy groups. By reason of this branching, the modified polymer displays low viscosity during extrusion through a die and high viscosity in parison or shaped form, i.e. high shear sensitivity. These are precisely the properties desired for extrusion blow molding operations.

For optimum branching by the use of TGIC, proportions up to about 2 parts by weight per 100 parts of polyester were generally employed for melt blending (Yol et al., 1987). Such concentrations of TGIC produced gel like structures, which were difficult to process into shapes. Brown et al. thought that such blending methods have certain disadvantages for applications of interest such as extrusion blow molding, profile extrusion, and thermoforming (Brown et al., 1988). In the first place, TGIC is supplied in the form of powder, which may agglomerate into coarse particles. Brown et al. claimed that the particles are difficult to mix uniformly with the polyester during extrusion, and may result in regions of gel formation, which produce flaw sites in the formed article. To avoid these difficulties, modification of the polyester in a two step process was suggested (Brown et al., 1988). As a first step, a masterbatch or reactive concentrate from TGIC and polyester was formed, which resulted in end-capped polyester with two epoxide functionalized end groups. The concentrate was then mixed with PBT resin in a second step. The method was claimed to produce homogeneous blends free from potential flaw sites. It was also suggested that it minimized the proportion of polyepoxide, which must be used to provide the desired melt viscosity properties. The second step was the reaction of the concentrate with the polyester - PET or PBT containing a measurable proportion of carboxylic acid end groups.

Characterizing the products of the melt modification of PET has been shown to be a difficult technical challenge. At this point, it is necessary to note some of the common traits that some of the literature shares from the perspective of limitations on the characterization methods used. Some researchers have reported assessment of the evaluation of the melt modification reactions by determining MFI of the modified PET before ensuring that the reaction is complete (Guo and Chan, 1998, Khemani, 1998). If the reaction is incomplete and still continues during measurement of MFI, it may give false results. Approaching the gel point (state of infinite viscosity) as a result of melt modification reaction overlapped and at times was confused with the concept of formation of critical gel like structures (Brown et al., 1998, Yilmazer et al., 2000).

Many researchers have characterized the melt modified PET using intrinsic viscosity determination of the reaction products (Bikiaris and Karayannidis, 1995, Japon et al., 1998, Haralabakopoulos et al., 1999). In some cases, products contained gel-like structures, which may have changed the flow characteristics in the capillary during the measurements unless removed. When the dilute polymer solutions were filtered, before viscometry, the gel like structures were screened out and, thus, high MW products were unaccounted for.

In most of the patent literature, the amount of modifier was added at orders of magnitude higher than that required by the stoichiometry and the excess presumably remained in the polymer ready for further reaction (Yol et al., 1987, Deyrup et al., 1990, Brown et al., 1988, Al Ghatta, 1993). Melt modification measurements reported were single point measurements with few exceptions (Harabakopoulos, 1999, Abe and Yamaguchi, 2001).

Melt modification of PET has been reported on a batch scale or using an extruder by developing reaction kinetics information (Japon et al., 1998, Xanthos et al., 2001). Melt modification carried out in an extruder is subject to variable shear rates, which may influence reaction kinetics. The undesirable thermal degradation of PET is a well-known phenomenon; however, the formation of gel like structures during degradation or crosslinking with excess modifiers and its relevance to foamability has not been explored.

Thus, it is obvious that fundamental information is still lacking on understanding the melt modification of PET to improve foamability is still lacking. This thesis documents an attempt to fill this gap.

3.2 Choice of Chain Extenders for PET

It is well known that reactive extrusion is one of the most effective means for modifying the structural and rheological properties of PET at short processing times corresponding to extruder residence times of the order of few minutes (Xanthos, 2001). Considering the extrusion processing conditions, the choice of the chain extenders for PET in this work was driven by the following factors:

- 1. High reactivity.
- 2. Availability.
- Thermal stability and low volatility at process temperatures near the melting temperature of PET (~270°C).
- 4. No generation of by-products preferable.

- 5. Ease of mixing in the polymer melt. Insufficient mixing may result into product inhomogeneity and/or formation of gel regions.
- 6. Formation of chemical linkages formed after modification that are stable to subsequent thermomechanical processing.
- For multi-functional modifiers, reaction of one of the functional groups should not hinder the reactivity of the other unreacted group(s).

These constraints, even though favorable for developing a robust melt modification process, limit many of the potential compounds/modifiers, which are capable of reacting with PET end groups. Limitations on by-product formation also limits the chain extenders, to addition-type. Thus, the main chain extenders of this type are anhydrides, isocyanate, and epoxides. Bikiaris et al. has suggested that some of the compounds such as epoxides may cause undesirable branching or introduce gel like structures in the polymer (Bikiaris et al., 1995). Recently, it has been suggested that foams having insufficient gel fractions were thermally unstable and exhibited cell collapse (Hong et al., 2001). However, the gel fraction of the materials studied in the latter work never exceeded 50%. On the other hand, Abe and Yamaguchi were able to form poly (ethylene-co-hexane) foams containing at least 70% gel content (Abe and Yamaguchi, 2001).

For the melt modification of PET aimed at extrusion foaming to low densities, PMDA has been one of the highly explored low cost chain-extender/modifier. However, its use accompanies some of the crucial challenges (Khemani, 1998). PMDA easily sublimes, is a highly reactive molecule, which makes it vulnerable to hydrolysis (even by atmospheric moisture) and other nucleophilic attacks resulting in structures which have a diminished reactivity towards the hydroxyl end groups of PET. Another possible concern with PMDA is that it needs to be added to a minimum concentration of 0.5% by weight in order to make PET melt foamable. Below this concentration, the modified melt is not foamable. PET modified by PMDA may contains traces of unreacted PMDA at levels <50ppm. This may be important for food packaging applications, where any free PMDA could be extracted into food items. Japon et al. have suggested that reactive melt modification of recycled PET resins using PMDA is difficult due to polycondensation and auto-accelerated degradation due to the impurities in PET (Japon et al., 1998).

Therefore, considering the technical constraints posed (rather than cost), epoxide has been suggested as one of the most suitable functionalities to react with both end groups present in PET at process conditions typical of reactive extrusion (Xanthos, 2001). The strong polarization of the hydroxyl bond of carboxylic acids ensures fast reaction between epoxy/carboxyl groups, although epoxy/hydroxyl reactions are possible, perhaps at slower rates.

Before discussing the reactions involved in the melt modification of PET by epoxides, it is useful to briefly survey the reactivity of epoxides, towards functional groups containing active hydrogen, including those present in PET.

3.2.1 Epoxides – Chemical Nature

Epoxides are compounds containing a three membered ring as shown in Figure 3.4, commonly known as the oxirane ring. Classically, epoxides are ethers, but with unusual properties.



Figure 3.4 Epoxy or Oxirane ring.

Epoxides owe their importance to their high reactivity, which is due to the ease of opening the highly strained three-membered ring containing C-O polar bond. The bond angles of the ring, which average 60°, are considerably less than the normal tetrahedral carbon angle 109.5° or divalent oxygen angle of 110° for open chain ethers (Morrison and Boyd, 1987). Since the atoms can not be located to permit maximum overlap of orbitals, the bonds are weaker compared to an ordinary ether making the ring less stable and susceptible to reaction. When epoxides undergo ring-opening reactions by cleavage of the C-O bond, the products have normal tetrahedral angles, so they are not strained. As a result, the energy barrier for cleavage of a C-O bond of an epoxide is smaller than for other ethers, and the rate of cleavage is more rapid.

Epoxides undergo ring-opening reactions by both acid and base catalysis (Morrison and Boyd, 1987). Ring-opening reactions of symmetrical epoxides yield the same product under acidic and basic conditions. However, ring-opening reactions of unsymmetrical epoxides could yield two isomeric products. Under basic conditions, the reaction is regioselective and the major product results from attack of the nucleophile at the less substituted carbon atom. In an acid-catalyzed reaction, the regioselectivity is different. The major product results from attack of the nucleophile at the more substituted carbon atom. These generalizations are illustrated by comparing the base-catalyzed reaction with methanol.

Figure 3.5 shows the ring opening by CH_3O^{Θ} in methanol when epoxy ring is cleaved under basic conditions (Ege, 1999). Base catalyzed reactions of epoxides are characteristic of S_N2 attack by nucleophiles. In base catalyzed cleavage, the nucleophile attacks the less hindered carbon, just as one would expect from an S_N2 attack. (1°>2°>3°). That is, it attacks the primary rather than the secondary carbon atom of 2methyloxirane in the rate-determining step. This intermediate alkoxide ion then abstracts a proton from the solvent in a faster second step, regenerating the methoxide base.



Figure 3.5 Base catalyzed epoxide ring opening reaction (Ege, 1999).

Acid catalyzed reactions of epoxides are possible in acidic solution, in which the oxygen of an epoxide is protonated reversibly. A protonated epoxide can be attacked by weak nucleophiles such as water, alcohols, or halide ions, at the more hindered carbon in the epoxide ring. Figure 3.6 shows an example of the reaction (Ege, 1999). Protonated epoxide has a fair amount of carbocation character. Carbocation stability increases in the order of $3^{\circ}>2^{\circ}>1^{\circ}$. Therefore, subsequent nucleophilic attack is favored at the more positive carbon having lower energy barrier even though it is more hindered. This

carbocation stability overrides the effect of steric hindrance that disfavors attack at the tertiary center. Protonated epoxide reacts with the nucleophile methanol in the rate-determining step. Subsequently, the protonated product reversibly transfers a proton to the solvent.



Figure 3.6 Reaction scheme of acid catalyzed epoxide reaction (Ege, 1999).

3.2.2 Reactions of Epoxy Resins

Typical epoxy resins are the products of the reaction between bisphenol-A and epichlorohydrin in the presence of NaOH as shown in Figure 3.7. An excess of the epoxide monomer is used so that an epoxy group is left at each end of the pre-polymer chain. They are highly viscous liquids and solids containing epoxy functionality and residual hydroxyl groups (Gowariker, 1998).



Figure 3.7 Overall reaction between epichlorohydrin and bisphenol-A to produce epoxy resins.

Epoxy resins undergo crosslinking (curing) reactions through the oxirane ring with a large variety of compounds containing active hydrogen. Among them, the three most important classes of commercial curing agents are (1) aliphatic and aromatic amines, (2) acid anhydrides, and (3) latent curing agents or catalysts. Other types of curing agents used in significant quantities in commercial applications are phenols, carboxylic acids, ureas, inorganic acids and bases, and mercaptans, essentially, compounds with characteristic active hydrogen. The section below shows examples of reactions of epoxy resins with emphasis on compounds with carboxyl/hydroxyl functionalities that are also present in PET.

A typical reaction between an epoxy group and a primary amine is shown in Figure 3.8 (Dowd, 1968). As shown, the primary amine is fast converted to a secondary amine and eventually a tertiary amine; both steps are accompanied by the formation of hydroxyl groups that may further react with the epoxy group. 1. Attack of primary amine on oxirane ring



Figure 3.8 Primary amine – epoxy reaction (Dowd, 1968).



Figure 3.9 Anhydride – epoxy reaction (Dowd, 1968).

With respect to the reaction between epoxy/anhydride, it is noteworthy that little or no reaction occurs between the pure epoxide and the pure anhydride. The mechanism of anhydride curing is complex as shown in Figure 3.9 (Dowd, 1968). It is believed that the anhydride ring is opened by an alcoholic hydroxyl group (or salt or water). These might be the hydroxyl groups attached to the epoxy resin. The carboxylic acid portion of the halfester then can react with an epoxy group to form an ester linkage and a hydroxyl. These hydroxyls are susceptible for reaction with a new epoxy ring. It has also been found that unless a basic catalyst is used, etherification reactions occur through the hydroxyl group.

Polyesters may be formed by the reaction of epoxy ring with the carboxylic groups as shown in Figure 3.10 (Dowd, 1968). Both the epoxide and the secondary hydroxyl groups of the glycidyl ether resins react, each epoxide group having the potential of being converted into two ester linkages. Esterification reactions are often catalyzed by the presence of basic catalysts. Unless a basic catalyst is employed, the etherification reaction is favored, resulting in the intermolecular reaction between epoxide groups with the secondary hydroxyl groups to form higher molecular weight materials; this may cause premature gelation in the resulting polyesters.



Figure 3.10 Acid – epoxy reaction (Dowd, 1968).

Lewis bases are those compounds containing an atom with an unshared electron pair in its outer orbital. They are attracted to areas of reduced electron density in the molecule with which they react. The organic bases such as tertiary amines (R_3N :) are representation of Lewis bases in the form of catalysts suitable for ring opening reaction of epoxides, by contrast to primary and secondary amines containing a transferable proton.



Figure 3.11 Base catalyzed carboxyl-glycidyl reaction (Schechter and Wynstra, 1956).



Figure 3.12 Base catalyzed hydroxyl-glycidyl reaction (Schechter and Wynstra, 1956).

Schechter and Wynstra have suggested a reaction sequence with tertiary amines as external catalyst in the epoxy – alcohol and epoxy –carboxyl reaction mixture from the observed increased reaction rates (Schechter and Wynstra, 1956). Their proposed carboxyl-glycidyl reaction mechanism and the hydroxyl-glycidyl reaction mechanism is shown in Figure 3.11 and 3.12 respectively. The tertiary amine used in their experimental study was benzyldimethylamine. For the carboxyl, reaction is controlled by the decomposition of the acid salt formed between the carboxyl group and the base catalyst. Blank et al. have summarized that, the reaction mechanism between carboxyl and epoxy groups can also be influenced by catalysts other than tertiary amines (Blank et al., 2002). Lewis Acids may act as cationic catalysts. Many inorganic salts such as halides of Al, B, Be, Fe(III), Sb(V), Sn, Ti, Zr, and Zn are included in the category of active catalysts. Blank and coworkers have claimed that metal chelates act as catalysts for the epoxy-carboxyl reaction with advantages such as hydrolytic and thermal stability.

Pappas et al. (Pappas, 1991) have suggested that the tertiary amine catalysts for epoxy/carboxyl reaction containing an amide linkage (-CO-NH-), may behave differently than the tertiary alkyl amines. The carbonyl group may weaken the tertiary nitrogen, by withdrawing electrons from the nitrogen atom towards the carbonyl group. In certain cases, amic acid may be formed which would liberate tertiary nitrogen to catalyze the carboxyl-epoxy reaction.

With respect to the carboxyl and hydroxyl end groups present in PET, there are many factors that may affect their reaction with the glycidyl group(s). Reactions may be catalyzed by a variety of compounds including Lewis acids and quaternary ammonium salts (Brown, 1992), and antimony oxide or remnants of catalysts used during the polyester preparation, particularly antimony and gallium (Stewart et al., 1993). Stewart et al. investigated the effect of catalysts generally used during PET synthesis, on the postpolymerization modification of PET by ethylene glycidyl methacrylate (EGMA) copolymer (Stewart et al., 1993). They reported that, catalysts used in amounts of even 200 ppm could catalyze the melt modification of PET as suggested by the increased torque upon mixing in the intensive batch mixer. They have reported that the catalytic activity to enhance the PET-epoxide reaction decreases in the order: antimony > gallium > tin=titanium > germanium.

The next chapter details on materials, experimental processes, and analytical characterization techniques used in this study.

CHAPTER 4

EXPERIMENTAL

4.1 Materials

4.1.1 Polyesters

Four types of polyester resins were chosen for the experimental study. A generic structure of PET is shown earlier in Figure 1.1. The high MW PET resins are:

- HPET Virgin bottle grade PET (Rhopet S78) with nominal I.V. 0.78 and reported hydroxyl content = 62 eq./10⁶g and carboxyl content = 13.4 eq./ 10⁶g (Xanthos et al. 2001) was obtained from Rhodia-Ster, SA (Brazil). This material was used for the batch study, FT-IR study and chemorheological evaluation.
- MPET Medium Molecular weight PET resin with nominal I.V. 0.58 (Scientific Polymer Products). MPET has been used in the batch mixer study.
- RPET Post-consumer bottle grade pelletized resin PET (Wellman, Inc) with nominal I.V. of 0.71, carboxyl content = 27.9 eq. /10⁶ g, hydroxyl content = 89 eq/10⁶g (Xanthos et al. 2001). This material was used in the continuous melt modification by reactive extrusion and in the reactive extrusion foaming process.

In few exploratory experiments, saturated polyester in oligomeric form was also used. The material used was poly [di(ethylene glycol) adipate], with reported boiling point higher than 300°C, melting point less than -14°C and a number average molecular weight of 2500. (Sigma-Aldrich Catalog 2001)
4.1.2 Chain Extenders

The structures of the low molecular weight multi-functional modifiers and a summary of their important physical properties are shown below and the accompanying Table 4.1.

• Diepoxides:

-Diglycidyl ether of bisphenol A - DGEBA (EPON 828[®]); CAS No. 25068-38-6, (Sigma Aldrich).

-N, N'-bis [3(carbo-2', 3'epoxypropoxy) phenyl] pyromellitimide (BGPM) laboratory synthesized (Bikiaris and Karayannidis 1995, 1996).

Both diepoxides were used in the batch study and their structures are shown in Fig. 4.1.

Diglycidyl ether of bisphenol A (DGEBA) -



N, N'-bis [3(carbo-2', 3'epoxypropoxy) phenyl] pyromellitimide (BGPM)-



Fig. 4.1 Structure of diepoxides.

• Triepoxides:

-Triglycidyl Glycerol (TGG); CAS No. 25038-04-4 (Polysciences Inc.).

-Triglycidyl isocyanurate (TGIC); CAS No. 2451-62-9 (Sigma-Aldrich).

Both the triepoxides were used in the batch study. TGIC was also used in rheometry, spectroscopic study and in continuous extruder for melt modification and foaming. The structures of the triepoxides are shown in Fig. 4.2.

Triglycidyl glycerol (TGG)-



Triglycidyl isocyanurate (TGIC) –



Fig. 4.2 Structure of triepoxides.

• Tetraepoxide:

- Tetraglycidyl diamino diphenyl methane (TGDDM) – CAS No. 28768-32-3 (Araldite[®] MY 721 Ciba-Geigy).

TGDDM was used in the batch mixer study and its structure is shown in Fig. 4.3. With the exception of the diepoxide (BGPM), all other modifiers were commercially available materials.

Tetraglycidyl diamino diphenyl methane (TGDDM) -



Fig. 4.3 Structure of tetraepoxide.

Table 4.1 summarizes the important physical properties of the modifiers.

4.1.3 Catalysts

The following catalysts were evaluated.

- Benzyltrimethyl ammonium bromide, CAS No. 5350-41-4, melting point =230-232°C.
- Dicocomethylamine. CAS No. 61788-62-3. Boiling Point =120-125°C (Akzo Nobel Armeen M2C).

• Antimony Oxide (Sb₂O₃), CAS No. 1309-64-4, melting point = 655° C.

Modifier	Molecular	Physical form	Functionality	Reported
	Weight (MW)	at room		M.P./B.P (°C)*
		temperature		
DGEBA	348 (average)	Colorless	di-	283-286
(diepoxide)		viscous liquid		
BGPM	569	Yellow powder	di-	270
(diepoxide)				
TGG	260	Clear brown	Tri-	Not available
(triepoxide)		liquid		
TGIC	297	White powder	Tri-	100
(triepoxide)				
TGDDM	422	Clear brown	Tetra-	Not available
(tetraepoxide)		liquid		

 Table 4.1
 Characteristics of Modifiers

* supplier data

4.1.4 Physical Blowing Agent

Isobutane gas was used as a physical-blowing agent during extrusion foaming experiments.

Isobutane gas, CAS No. 75-28-5, boiling point =-12°C. (S. O. S. Gases, Kearny, NJ)

In this work, four types of reactors are used. (1) Intensive Batch Mixer, (2) Parallel plate – dynamic mechanical analyzer, (3) high temperature FT-IR cell, and (4) single screw extruder. The reactions were analyzed by inline, online, and offline characterization methods.

4.2.1 Reactive Processing in Batch Mixer and Characterization

Melt modification of the PET resin was carried out in an intensive batch mixer (Brabender Plasticorder PL2000[®]) on predried materials under nitrogen blanket, in order to minimize the possibility of hydrolytic and/or thermo-oxidative degradation. In a typical experiment, approximately 56.3 g of PET pellets, dried overnight to less than 0.01 wt% moisture content at 120°C were first added in the intensive mixer heated at a preset chamber temperature and approximately 6 minutes later, when melting was assumed complete, the modifier was added at a predetermined stoichiometric amount. Temperature and torque were monitored during the experiments. Reactive mixing continued for an additional period of 9 minutes. The effects of temperature and concentration of TGIC on the overall rate of modification were investigated by setting the chamber temperature at 270°C and 300°C and by varying the amount of additive from 0.5X (~800ppm) to 1.5X (~2000ppm) (X= times stoichiometric amount) based on the initial carboxyl content (CC_0), while maintaining a constant rate of mixing at 60rpm. Due to the exothermic nature of the reactions and as a result of viscous dissipation, melt temperatures during processing increased by approximately 5-7%. Stoichiometric amount calculations are elaborated in the forthcoming section.

Considering the difficulties arising from the high temperatures involved and the limited hydrolytic and thermal stability of PET melt under process conditions, particular care was taken to ensure reproducibility of the experimental data and minimization of errors. Thus, PET pellets were pre-dried to very low moisture content, the same protocol of addition of modifier was used in all experiments, bowl temperature and temperature off-shoot during processing were kept within narrow limits and a consistent procedure for specimen preparation for rheological characterization was adopted.

<u>Carboxyl Content (CC)</u> of the PET resins before and after processing in the batch mixer was determined according to Pohl's method (Pohl 1954) by titrating a solution of the resin in benzyl alcohol/chloroform with standard NaOH in benzyl alcohol in the presence of phenol red as an indicator.

Insoluble content of the reacted and control samples was determined by dissolving the samples in hexafluoroisopropanol (HFIP) at room temperature. After 24 hours, the solution was filtered using 1 μ m filter and the residue was washed with the solvent and then dried under vacuum for 48 hours at room temperature. Differences in weight measurements were used to determine the insoluble content.

<u>Isothermal Thermogravimetric Analysis (TGA)</u> of the modifiers was carried out using Model QA 50 (TA Instruments) in a non-pressurized system under nitrogen blanket for a total time of approximately 19 minutes; an initial heating ramp of 4 min from room temperature to 270°C was followed by isothermal heating for 15 min at 270°C, during which weight percentage losses were monitored.

<u>Rheological properties</u> such as absolute value of complex shear viscosity $|\eta^*|$, storage modulus G', and loss modulus G' data of predried unreacted pellets and reacted specimens as a function of frequency were collected at 285°C using a Rheometrics Mechanical Spectrometer RMS-800 in a parallel plate mode under nitrogen. Specimens were discs of 2.5cm dia. and 0.5cm in thickness, prepared by compression molding at 285°C, with 1-min melting/holding time, 5-min cooling time. The discs were stored under vacuum at room temperature to avoid possible hydrolytic degradation during testing. The RMS-800 system was programmed to perform frequency sweeps within the range of 0.1 to 100 rad/s at 285°C. In order to avoid thermal degradation, measurements were not conducted at frequencies below 0.1 rad/s thereby limiting the effect of time on degradative and other reactions. Except for the "as received" pellets, all other specimens were melt processed in the intensive batch mixer for 15 minutes.

4.2.2 Reactive Processing – Rheometer

The rheological data reported in this section correspond to the real time monitoring of the melt modification of PET by TGIC. Melt shear viscosity $|\eta^*|$, storage modulus G', and loss modulus G' data of reacting specimens as a function of frequency or time were collected, based on the type of experiment, using a Rheometrics Mechanical Spectrometer RMS-800. Samples for the rheological testing were prepared by powder sintering or film casting below the transition temperatures of the components/polymer(s) since at higher temperatures changes in the peak heights of the functional groups detected by FTIR indicated the onset of reactions. Samples were prepared by the following methods:

<u>Powder Cake Method:</u> A typical sample preparation protocol for the analysis began with size reduction of PET pellets. A grinder was used to crush the pellets to granules in the presence of dry ice. The resultant PET powder (particle diameter = 0.89 ± 0.37 mm) was vacuum dried at 150° C for 4 hours and dry blended with 2000 ppm TGIC powder (average particle diameter = 0.15 ± 0.16 mm) in a Crescent reciprocatory shaker. TGIC powder was also stored in the desiccator in order to minimize the effect of moisture.

Powder dry blends were shaped into discs of 2.5cm dia. and 0.5cm in thickness by compression molding at room temperature and 28 MPa. The sintered discs were prepared immediately before the rheological experiments, which were carried out under nitrogen atmosphere to minimize the effects of thermo-oxidative degradation under the measurement conditions.

Solution Casting Method: A method similar to the method suggested by Yang and Lin was adopted for sample preparation as an alternative to the "Powder Cake" Method (Yang and Lin 2002). A predried powder blend of predetermined amount of PET containing 2000 ppm TGIC was dissolved in few drops of hexafluoroisopropanol (HFIP) in order to cast a thin film of approximately 2.5cm dia. that was subsequently vacuum dried at room temperature for 48 hours to evaporate the solvent. In total, 10 films were stacked together to form a layered disc like structure of approximately 0.5 cm thickness. Films of PET and TGIC controls were prepared similarly.

During the measurements, the compressed discs prepared by the "Powder Cake" method and the stack of discs prepared by the "Solution Casting" method were inserted between the parallel plates of the RMS, which were preheated to 270°C under nitrogen. It took approximately 300s for the samples to reach 246°C, the temperature at which the mixture began to melt partially (as monitored by the changes in the stress sensor attached

to the parallel plates). An additional time of 30s was required by the apparatus to reach and stabilize at the set temperature of 270°C, at which it was assumed that the gap between the parallel plates was completely filled with the melt phase. It is believed that the reaction did not start before melting of the PET in the powder or the films, as confirmed by the negligible apparatus response monitored before melting. It is recognized that in the case of the "Powder Cake" method, uniformity of dispersion of particles in the dry-blended sample and uniformity of compaction during sintering would dictate variations in localized melting within the sample, which would reflect on the chain extension/branching reactions. It is also possible that even at these mild experimental conditions, the samples could be susceptible to thermal as well as shear degradation, as shown earlier in batch mixer experiments.

The small amplitude oscillatory shear measurements included the following sets of experiments:

(i) Effect of temperature changes on the PET/TGIC reaction was investigated by measuring changes in dynamic moduli with respect to time at a constant frequency of 10rad/s, applied strain of 0.3. Experiments were performed at two different temperatures *i.e.* 270° C and 300° C.

(ii) Effect of frequency changes on the PET/TGIC reaction was investigated by measuring changes in dynamic moduli with respect to time at a constant temperature of 270°C, applied strain of 0.1-0.3. Experiments were carried out at three different frequencies – 0.1 rad/s, 1 rad/s, and 10 rad/s. A sample prepared by the "Solution Casting" method was tested under a similar set of conditions, but only at a frequency of 1 rad/s.

(iii) From experiments in (ii) above, the 1 rad/s experimental run was broken down at different reaction times to carry out intermittent frequency scans from 1 to 100 rad/s. Thus, this experiment was a composite of time scans and frequency scans.

4.2.3 Spectroscopic Analysis – Melt Modification in a FT-IR Cell

The PET/TGIC powder dryblends were prepared in a similar way as discussed in the section 4.2.2 for the rheological analysis except in this case, TGIC was used in significant excess (10% by wt.).

A predetermined amount of PET/TGIC dry blend was dissolved in few drops of hexafluoroisopropanol (HFIP) in order to cast a film that was subsequently vacuum dried at room temperature for 48 hours to evaporate the solvent. Films of PET and TGIC controls were similarly prepared.

A background spectrum was recorded with 4 scans and a resolution of 4 cm⁻¹, within the spectral region 4000 to 700 wavenumbers with two dry sodium chloride crystals of 3mm thickness each using Spectrum One (Perkin-Elmer) FTIR spectrophotometer. The film was then sandwiched between the crystals. Teflon tape was used to seal the crystal sandwich with the film in between, before inserting in the high temperature cell (temperature range 25°C-350°C), which was mounted in the spectrophotometer. The cell was heated from room temperature to 270°C (the set temperature) within 5 minutes and held at this temperature during measurements.

Recording of spectra was initiated at room temperature as soon as the sample was inserted and was carried forward as a function of time under the same conditions as the background spectrum. It took approximately 40 seconds to record an individual set of data.

4.2.4 Reactive Processing – Extruder

The TGIC was dry blended at appropriate amounts with PET pellets (predried overnight at 120°C) and fed through a volumetric feeder at 1.45kg/hr in the hopper of a 40:1 L: D, 32 mm segmented Killion extruder equipped with a 2.2 mm circular die and operating at 15 rpm. Screw configuration involved conveying sections separated by mixing elements. Barrel settings were 204-290-260°C.

The average diameter (D_{aver}) of free falling extrudates was measured as they exited the die of diameter $D_{d,}$ in order to calculate extrudate swell (die swell) as D_{aver} / D_{d} . The D_{aver} was measured on cooled extrudates by using a vernier caliper over three different directions across the cross section.

The extrudates were characterized by melt flow index in a Tinius-Olsen plastometer (285°C/2.16kg) and for melt strength by an empirical/relative method. Melt strength was measured by pulling a strand extruded from the die (25.4 mm long, 0.762 mm dia., entrance angle $\pi/2$) of a capillary rheometer operating at 285°C by a set of winding rolls. The transverse force at the largest draw ratio at which a given strand did not break was taken as melt strength.

<u>One-step reactive extrusion/foaming.</u> The same 32 mm dia., 40 L/D Killion segmented single screw extruder equipped with gas injection port was used to produce foamed rods from hopper fed mixtures of PET/modifier at the same feeding rate (1.45 kg/hr) and the same temperature profile as before. In a typical experiment with 0.75X TGIC modifier,

isobutane was injected at 19D length at 2-3 phr concentrations and mixed into the PET melt. The residence time was estimated by adding few colored pellets in the hopper at steady state conditions and noting the time required to change the color of the extrudate.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter is divided into five major sections. The first section discusses reaction monitoring in a batch mixer and corresponding online characterization for the reactive systems consisting of PET and multifunctional epoxides. The second section discusses the offline rheological characterization of the batch mixer products. The third section presents the PET/TGIC system that was monitored in a high temperature cell by FTIR analysis. The fourth section elaborates the chemorheological study of the system and the fifth section presents the melt modification in an extruder followed by foaming.

5.1 Batch Mixer Processing and Characterization

5.1.1 Thermal Stability of the Modifiers

Before using the multifunctional epoxides as modifiers, their thermal stability was evaluated at the experimental reaction/melt temperatures (270-300°C). These temperatures are equal to or higher than the known melt temperatures of the five modifiers listed in Table 4.1. TGA of the five additives at a typical process temperature (270°C) showed significant differences in their thermal characteristics (Figure 5.1). The results indicated very high weight retention for the high molecular weight Diepoxide-BGPM, and lower weight retention for the Triepoxide-TGG, Diepoxide-DGEBA and Triepoxide-TGIC. It is not clear at this point whether the excessive weight losses for TGG, DGEBA and especially TGIC after about 4-5 minutes of heating time are due to

chemical degradation, which could cause possible changes in their reactivity, or simply due to their partial evaporation/sublimation. It should be noted that caution is required in any direct extrapolation of the TGA data to processing equipment such as extruders or batch mixers, which represent closed or pressurized reactors with variable residence times.



Figure 5.1 Isothermal TGA data at 270° C of reactive modifiers. (Total time of the test 19 minutes = initial heating ramp of 4min from room temperature to 270° C + heating under nitrogen blanket for 15min.)

5.1.2 Process Stability of PET in a Batch Mixer

In order to obtain the baseline for the torque/time curve in the batch mixer that would quantify the effect of addition of a modifier, HPET and MPET were processed in the absence of any modifier at 270°C as shown in Figure 5.2. After an initial melting period, torque decreased noticeably for HPET as a result of degradation reactions. Differences in torque levels in HPET and MPET could be due to the comparatively lower initial

molecular weight of MPET as also confirmed by their respective intrinsic viscosities, or the effects of different comonomers or stabilizers present in the commercial resins. The rate of torque decrease suggesting enhanced degradation in HPET was also confirmed by an increase in the CC as time progressed. CC almost doubled for HPET after 15 min compared to a 40% increase for MPET.

In general, thermal degradation of PET results in an increase in carboxyl content and decrease in hydroxyl content (Japon et al. 1998, Xanthos et al. 2001). Thus, changes in the instantaneous concentration of PET end groups available for reaction with the present modifiers is anticipated; the complex degradation phenomena also shown in Figure 3.1, lead to an overall decrease in melt viscosity and a corresponding reduction in molecular weight.



Figure 5.2 Torque evolution in an intensive batch mixer for HPET (Nominal I.V. = 0.78) and MPET (Nominal I.V.= 0.58) at Chamber Temperature= 270° C, 60rpm. Initial pellet carboxyl content (CC_o) and carboxyl content at 900s (CC_{15min}) are also shown.

Most of the work presented in this section was carried out using HPET. Figure 5.3 shows the evolution of torque versus time curves for HPET at different temperatures without modifiers. It is evident that as the chamber temperature increases, the viscosity decreases as shown by the location of the torque curves (300°C<285°C<270°C). Corresponding temperature curves are also shown in the upper half of the figure. Figure 5.3 suggests that about six minutes are required for the chamber temperature to attain thermal equilibrium and the melt to attain an approximately constant torque value; this time was chosen as the point of addition of the modifier as will be shown below.



Figure 5.3 Blank HPET torque/time and temperature/time runs at 270°C, 285°C, and 300°C chamber set temperatures.

The kinetics of the degradation reactions of PET were analyzed by treating the initial torque/time data (between six min and 10.5 min) from Figure 5.3, in the form of

rate expressions analogous to those derived in Chemical Kinetics. The first order rate equation:

$$-\frac{d\tau}{dt} = k\tau \tag{5.1}$$

where τ is the torque (Nm) proportional to melt viscosity and consequently molecular weight, t is time (s), and k is the rate constant (Nm.s⁻¹) was found to fit the torque decay with a least error as compared to second and third order fits. The overall first order rate constants determined by regression analysis and shown in Table 5.1 indicate the expected effect of temperature on rate of MW reduction.

Temperature (°C)	First order rate constant (Nm.s ⁻¹)
270	0.0007
285	0.0009
300	0.0013

Table 5.1 HPET Degradation: First Order Rate Constants

(Note: Batch Mixer processing at 60rpm, at various chamber temperatures during HPET control runs)

For the rate study, the experiments were stopped at the end of a residence time of 15 min., the time corresponding to severe degradation becoming visible through the yellowish shade of the cooled melt from the mixer (Edge at al., 1996). As also reported earlier, degradation was accompanied by an overall real time increase in the carboxyl content (Japon et al., 1998, Japon et al., 2000, Xanthos et al., 2001). Data for three time intervals and three temperatures are shown in Figure 5.4. As anticipated, an increase in the melt mixing temperature resulted in the formation of higher number of carboxyl

groups at the same time intervals. It should be noted that the products of some of the blank runs contained gel like material, up to 20% (see below), which could hinder during titration the access of the neutralizing species to the entrapped carboxyl groups and, thus, result in incorrect experimental CC values.



Figure 5.4 Carboxyl content vs. time data at $270^{\circ}C(O)$, $285^{\circ}C(\Delta)$, and $300^{\circ}C(\Box)$ for melt processed HPET. Data for unprocessed pellets, t=0s, (\diamond) are also shown.

5.1.3 Reactions of Modifiers

Figure 5.5 shows the two main chain reactions suggested for the glycidyl groups of the modifiers with the initially present terminal carboxyl and/or hydroxyl groups of high MW PET (Xanthos et al., 2001). Additional reactions of the modifiers may involve the newly formed carboxyl or hydroxyl groups as a result of thermal degradation of the PET shown earlier and also the secondary hydroxyl groups formed in the etherification step of the Figure 5.5.



Figure 5.5 Possible reactions between PET end groups and epoxy containing modifiers under operating conditions.

During the experiments, it is assumed that, at least initially, the glycidyl groups react preferentially with the carboxyl rather than the hydroxyl groups at elevated temperatures, given the relatively short residence times in a batch mixer or extruders (Japon et al. 1998, Xanthos et al. 2001). Based on this assumption, the theoretical modifier amount for the reaction was calculated from (Xanthos et al. 2001):

$$Wt\% = \frac{MW \times CC}{f \times 10^4}$$
(5.2)

In Equation (5.2), MW is the molecular weight of the modifier, CC the initial (CC_o) or instantaneous (CC_t) carboxyl content of the polyesters in eq/10⁶g and f is the functionality of the epoxide. It has to be noted that the real time formation of CC as a result of degradation would unbalance Equation (5.2). Thus, theoretically, an amount of modifier in excess of stoichiometry (based on CC_o) should be added for the complete conversion of all carboxyl and hydroxyl groups. As modification would proceed, depending on the functionality, stoichiometry, and reactivity of the epoxide and the relative concentration of carboxyl/hydroxyl end groups in the PET resin, a variety of linear, branched or cross-linked structures may be formed.

At this point, it is necessary to consider some of the parameters related to mixing in the batch mixer. The time required by the center of the TGIC particle (average particle diameter = 0.15 ± 0.16 mm), to equilibrate thermally with the PET melt environment by conductive heating would be:

$$\lambda_s = \frac{1}{\alpha} \left(\frac{d}{2}\right)^2 \approx 0.05s \tag{5.3}$$

where α is the thermal Diffusivity assumed to be equal to 10^{-3} cm²/s (Gogos, 2003). Taking into consideration that the TGIC thermal equilibration is additionally

taking place by the convective; not conductive heat transfer and that the change of phase is taking place at 100°C, λ_s could be assumed larger, in the range of 0.1 –1s. If λ_r is the characteristic reaction time (1/k(T,C)) for first order reaction kinetics, ~200s), for a uniform reaction in the batch mixer, λ_s/λ_r should be less than 1. This is indeed the case, $\lambda_s/\lambda_r = 5 \times 10^{-3}$. Hence, the reaction takes place in a uniform temperature environment.

In a laminar shear mixing, the quality of the mixture and the mixing process can be well characterized by the striation thickness (Tadmor and Gogos, 1979). The laminar mixing process proceeds by reducing the striation thickness to any desired value upto the molecular level. The striation thickness, r, is inversely proportional to the interfacial area, i.e., $r \propto 1/A \propto 1/\gamma$, where γ is the product of shear rate and time. Most of the batch mixer experiments were carried out at 60 rpm, at an estimated shear rate of 20 s⁻¹. Therefore, as the time TGIC spends within the PET melt environment from say 10s, 20s, 30s etc. after addition, total strains applied are 200, 400, 600, respectively. At the time of melting of TGIC, the striation thickness is about 5×10^{-2} cm. The time needed for diffusional mixing would be: $t_d = r^2/D_{AB} = 225$ seconds, assuming $D_{AB} = 10^{-6}$ cm²/s, giving $t_d/t_r \sim 1$. Five seconds later, $r = (1.5 \times 10^{-2})/100 = 1.5 \times 10^{-4}$ and hence $t_d = 2.25 \times 10^{-8}/10^{-6} \sim 10^{-2}$ yielding $t_d/t_r << 1$, suggesting uniform mixing condition for the reaction.

Runs in Figure 5.6 and Figure 5.7 compare the torque/time data after the addition, at 6 min, of the nitrogen containing epoxide modifiers namely BGPM (di-) and TGIC (tri-) against DGEBA (di-) and TGG (tri-) respectively. Stoichiometric amounts calculated from Equation (5.2), based on the initial pellet carboxyl group content (CC_o), actually corresponded to 0.8X stoichiometry if the calculations were based on CC_{6min} value. DGEBA and TGG showed little or no effect on the torque level compared to BGPM and TGIC. This enhanced reactivity may be attributed to the presence of tetiary amine functionality as an in-built catalyst in the vicinity of glycidyl group in the structure of epoxides. Tertiary amines are known catalysts for the epoxy/carboxyl or epoxy/hydroxyl reactions (Shechter and Wynstra, 1956, Tanaka and Kakiuchi, 1964, Inata and Matsumura, 1986). Please note that the trifunctional epoxide (TGIC) results in an increase in the evolution of torque up to 900s, whereas for the difunctional modifier (BGPM), torque reaches a maximum at about 600s, decreasing thereafter, possibly due to degradation (Japon et al., 1998). It is of interest that the anticipated "curing" reaction of DGEBA with the PET endgroups, containing active hydrogen was not evident at the elevated processing temperatures possibly marked by competing reactions. For example, Huang et al. who studied mixtures of DGEBA and PET in the absence of a catalyst by differential scanning calorimetry, suggested the possibility of interchange reactions as shown by increase in glass transition temperature, (Huang et al., 1999).



Figure 5.6 Effect of type of Diepoxide on torque vs. time curves for HPET at 270° C and 60rpm. Stoichiometries of DGEBA and BGPM based on initial carboxyl content (CC_o) and carboxyl content at the time of modifier addition (CC_{6min}) are shown.



Figure 5.7 Effect of Type of Triepoxide on torque vs. time curves for HPET at 270° C and 60rpm. Stoichiometries of TGG and TGIC based on initial carboxyl content (CC_o) and carboxyl content at the time of modifier addition (CC_{6min}) are shown.

5.1.4 Comparison of Epoxides

Figure 5.8 shows the percentage increase in torque when di-, tri-, and tetra- epoxides (BGPM, TGIC, and TGDDM respectively) were added in the PET melt at 270° C at different stoichiometric amounts. Torque curve of the PET melt in the batch mixer was allowed to stabilize and at the end of about 6 minutes, the modifier was added to the melt. In this Figure, increase in torque was calculated 6 minutes after epoxide addition. At concentration equal to the stoichiometric amount, it seems that as the functionality of the epoxide increases, percentage increase in torque also increases. BGPM shows significant increase in torque with increasing concentration. TGDDM shows minimal increase in torque from 1X to 1.5X stoichiometries, which could fall within the range of experimental error resulting from metering the small amount of epoxides involved in the

calculations of Equation (5.2). It is clear that TGIC gives the maximum amount of increase in torque at 1.5X stoichiometry compared to other compounds.



Figure 5.8 Effect of epoxide concentration on torque measured 6 minutes after epoxide addition.

On a comparative basis, it could be suggested that, the modifier possessing the bulkier spacers, as in the case of diepoxide and tetraepoxide, limit their reactivity resulting from molecular stiffness and the resulting limitations on mobility. Whereas in the case of triepoxide, the short spacer possibly renders the molecule relatively mobile while diffusing in the PET melt, which increases the possibility of its reaction with more carboxyl end groups. Based on the results, TGIC emerged as a suitable option for further study.

5.1.5 Reactions of TGIC with HPET and MPET

The Figure 5.9 shows HPET/TGIC torque-time data at different stoichiometries, at 60rpm and a chamber temperature of 300°C. The experiments were stopped when the chamber temperature was increased by more than 3% from the set temperature due to frictional effects and the exothermic nature of the reaction. Stoichiometric amounts were based on CC_o and CC_{6min} . The lowest decreasing torque curve in the Figure, suggesting degradation, represents the blank run (or the baseline) of HPET without modifier addition. With the addition of increasing amounts of TGIC, the torque curves are shifted upwards suggesting increasing reaction rates and increased molecular weight as a result of chain extension/branching reactions. As anticipated, the percentage increases in torque from the baseline were increasing functions of concentration of the epoxide added and the melt temperature. When the amount of modifier is increased to 1.5 times, the stoichiometric amount based on CC_o , material processability became extremely difficult. Hence, 1.5X approximately defines an upper bound for retaining a limited degree of thermoplasticity.

In Figure 5.10, two types of PET, namely, HPET and MPET are compared for the same (stoichiometric) concentration of TGIC based on CC_o . Differences in the rate of torque increase and the maximum torque values reveal the role of the type of PET in these modification reactions. Higher percentage increase in torque in the case of HPET after TGIC addition may be explained by considering the availability of a higher number of carboxyl end groups as a result of its lower process stability (Figure 3.1). Differences in initial hydroxyl/carboxyl content ratios of the PET resins could also play a role by affecting the pathway of the degradation reactions shown in Figure3.1.



Figure 5.9 Effect of TGIC concentration on torque/time curves for HPET at 60rpm, and set chamber temperature = 300° C. Stoichiometries based on initial carboxyl content (CC_o) and carboxyl content at the time of modifier addition (CC_{omin}) are shown.



Figure 5.10 Effect of type of PET on torque/time curves obtained through the addition of 1X stoichiometric TGIC amount based on CC_o . Set chamber temperature=270°C, 60rpm.

Figure 5.11 shows the variation of CC of HPET processed for 15 minutes at 270°C, 285°C and 300°C chamber temperatures versus the amount of TGIC added. The data show that the CCs of the reacted products, at all concentrations of the modifier, are always lower than the respective CCs of the controls at a given reaction temperature. This indicates that the modification reactions dominate over the competing degradation reactions resulting in a net decrease of carboxyl groups. The data for 1X and 1.5X at 285°C and 300°C show discrepancies in terms of the trend observed for 270°C and lower (0.5X) modifier concentration. Errors in the titration procedure as a result of the presence of insoluble gel formed at higher temperatures and stoichiometries are entirely possible.

An estimate of the insoluble content of pellets and melt processed samples of HPET was determined by dissolving in HFIP at room temperature and then filtering with 1µm size filter is shown in Figure 5.12. The data should be viewed as only relative, reflecting the particular solvent and dissolution conditions. Unprocessed PET pellets did not contain any insoluble content whereas processed PET, even in the absence of modifier, contained a certain amount of insolubles as a result of branching/crosslinking as shown in Figure 3.1. As anticipated, for TGIC modified PET an increase in reaction temperature as well as an increase in the stoichiometric amount added resulted in an increase in the insoluble content.

Figure 5.12 confirms that at 1.5X and 300°C, an almost insoluble crosslinked network was formed as a result of the modification. Inaccessible carboxyl groups for neutralization surrounded by the branched gel-like structure, remain a possibility resulting in possible errors in the CC determination of Figure 5.11.



Figure 5.11 Variation of CC of HPET measured after 15 min processing versus amount of TGIC added at different process temperatures (Stoichiometry is based on initial pellet carboxyl content).



Figure 5.12 Insoluble content of the HPET at the end of melt mixing for 15 minutes at 60rpm and two chamber temperatures (270°C and 300°C) with and without TGIC. Data are compared to those of unprocessed pellets.

Figure 5.13 shows the effect of mixing speed on the torque development of HPET after TGIC was added at about 360s. It is noticed that at 40 rpm, the torque is increasing continuously with time indicating unfinished modification up to 900s. In this case, it is apparent that chain extension/branching reactions are the dominating mechanism. In the case of 60rpm, the torque reached a plateau at about 900s suggesting equilibrium between degradation reactions and chain extension/branching reactions. At 80 rpm, torque increases rapidly, reaches a maximum and later decreases, possibly as a result of degradation reactions becoming the dominating mechanism in the post plateau period. During the post modifier addition period (after 360s), the torque/time slope increased with increasing rpm. From the mixing mechanism viewpoint, increasing the speed from 40 rpm to 80 rpm This suggests that enhanced mixing resulted in higher probability of accessibility of the reactive end groups and a higher rate of the chain extension/branching reactions.



Figure 5.13 Effect of rpm on torque/time curves of HPET reacted with TGIC at set chamber temperature=270°C, 0.26wt% of TGIC, CC_p - 1X, CC_{6min} - 0.8X.

Increase in shear rate for the same time interval will result in reduced striation thickness, suggesting improved mixing. The 80 rpm curve from Figure 5.13 exhibits three reaction stages, namely, modification dominance, a single peak, and the degradation prone zone. Although not directly comparable, it is of interest to note the results obtained by Japon et al. (Japon et al., 1998) on PET-TGDDM (Tetraglycidyl diamino diphenyl dimethane) modification where two different peaks were reported. The first peak was claimed to be due to reaction between carboxyl and glycidyl groups and the second higher peak to reaction between hydroxyl and glycidyl groups. Due to the complexity associated with hydroxyl groups determination (Xanthos et al., 2001), no attempt was made in this work to verify the extent of reaction between hydroxyl end groups or secondary hydroxyl groups and the epoxy functionalities.

5.1.6 Estimation of Rate of HPET Modification by TGIC

In the present study, accounting for the effect of the concentration of the reacting species on the overall rate of modification is difficult. A quantitative description of the process requires the construction of a rather rigorous kinetic model involving parallel (and opposite) degradation and chain extension/ branching reactions. As the glycidyl groups react with the carboxyl groups, the torque would increase with an increase in the molecular weight of PET. As the modification proceeds while increasing the degree of branching, insoluble gel like material starts to appear in the reaction medium. This may diminish the mobility of various functional groups and their accessibility for the reaction. Therefore, it is inadequate to model the PET modification only by monitoring the concentration of one or more species or functionalities (e.g. carboxyl groups) with respect to time. In a general sense, the HPET-TGIC system may be analyzed by treating the experimental torque versus time data with rate expressions analogous to those derived in Chemical Kinetics. The initial torque/time data (recorded between 360s and 630s) obtained at different temperatures and stoichiometries were also found to follow the first order rate Equation:

$$\frac{d\tau}{dt} = k\tau \tag{5.4}$$

where τ is the torque (Nm), t is time (s), and k is the rate constant (Nm.s⁻¹). Torque increase in this particular case represents viscosity increase that results in overall increase in MW due to chain extension/branching and changes in the concentration of the reacting species. Increase in chain extension/branching resulted in broader MWD as shown by Japon and coworkers (Japon et al., 2001). The authors have used an elaborate Gel Permeation Chromatography (GPC) apparatus modified with multiple detectors with dichloromethane/HFIP/tetra ethyl ammonium chloride as an eluent system. In the present study, quantitative assessment of chain extension/branching by GPC was not attempted owing to the complexity of the required modified apparatus and the toxicity, high price and incompatibility of PET solvents with the stationary phase.

From Table 5.2 and Fig. 5.14, it is evident that the calculated rate constants (k) increase with increasing temperature and amounts of TGIC, although some scatter is observed from the trends. From the Table 5.2, the k value for 300° C averaged over three concentrations is $0.0087 \pm 0.0027 \text{ s}^{-1}$. The k value for 270° C, averaged over three concentrations is $0.0023 \pm 0.0006 \text{ s}^{-1}$. The calculated reaction half-life based on these extreme k values are 310s and 86s, respectively. Thus, time equivalent to approximately seven half-lives would be needed to reach 99% conversion based on first order kinetics.

These calculations provide a design parameter for continuous modification in extrusion equipment resulting to an estimated a total residence time ranging from 36 to 10 minutes depending upon temperature profile.

 Table 5.2 First order rate constants for torque increase in the batch mixer at various

 reaction conditions of HPET with TGIC

Stoich. amt. of TGIC	Reaction Temp.	Reaction Temp.	Reaction Temp.
added (based on	$= 270^{\circ}C$	= 285°C	$= 300^{\circ}C$
CC _{6min})	(Nm.s ⁻¹)	(Nm.s ⁻¹)	(Nm.s ⁻¹)
0.5X	0.0018	0.0018	0.0058
1X	0.0022	0.0040	0.0112
111	0.0022	0.0040	0.0112
1.5X	0.0030	0.0066	0.0090



Figure 5.14 Rate Constant versus temperature at various stoichiometries from the batch data.

5.1.7 Study on Role of Catalysts

As discussed in Sections 3.2.2 and 5.1.3, the considerable increases in torque levels shown in Figure 5.6 and Figure 5.7 for BGPM and TGIC addition, may be attributed to the presence of a tetiary amine functionality as an in-built catalyst in the vicinity of the glycidyl group. In order to understand the effect of tertiary amines on the PET/epoxide systems, separate experiments were carried out involving DGEBA and TGG with conventional "epoxy curing" tertiary amine catalysts that are normally used at lower temperatures.

Note that, as shown in Figure 5.6 and Figure 5.7, DGEBA and TGG did not produce any appreciable torque increase, as compared to BGPM or TGIC. In Figure5.15, 0.25 phr of a solid quaternary ammonium salt and a liquid tertiary amine were added in the HPET melt at 270°C, 6 minutes after the addition of 0.5 phr of DGEBA. It is clear that, addition of the catalysts contrary to what is suggested by other authors (Inata and Matsumura, 1985, Blank et al., 2002), does not facilitate the chain extension/branching reaction of PET by DGEBA, under the reaction conditions. On the contrary, the decrease in torque for both catalysts suggest further degradation reaction taking place in the PET melt, possibly also related to the instability of the catalysts at the relatively higher temperature of 270°C. Experiments with TGG and the two catalysts produced similar results.



Figure 5.15 Effect of potential catalysts on the HPET-DGEBA reaction.

In order to confirm that the high temperature of melt mixing was the reason behind the unsuccessful attempts, a low molecular weight carboxyl terminated polyester $(M_n=2500)$, was mixed with 5 wt% of DGEBA and TGG at room temperature and about 0.5 wt% of the catalysts discussed above were mixed. Upon overnight stirring, it was observed that the viscosity of the mixture increased, indicating possible chain extension/branching reaction. Further stirring of the mixture for more than 48 hours at room temperature, resulted in the formation of gel.

The epoxides (BGPM and TGIC) that have been shown in this work to perform at melt temperatures $> 270^{\circ}$ C contain the tertiary nitrogen adjacent to the carbonyl groups, forming, thus, a tertiary amide linkage. The catalytic effect of tertiary amide linkage on reaction between carboxyl and epoxy groups has been suggested by different authors (Myers and McKinstry, 1996, Malhotra, 2001). Pappas has suggested that the carbonyl

groups adjacent to the tertiary amines impart an electron withdrawing effect, making the tertiary nitrogen weakly basic (Pappas et al., 1991).

As noted in the Section 1.1, antimony oxide is often used as a catalyst in melt polycondensation reactions during the PET commercial synthesis process. Stewart et al. suggested that Sb₂O₃ from catalyst remnants has a catalytic effect on the chain extension/branching of PET, with OH/COOH ratios ranging from 0.07-300, with epoxides based on ethylene/GMA copolymers that did not contain tertiary nitrogen in their structures (Stewart et al., 1993). Chemistry analysis of the HPET used in this work indicated the presence of 188ppm of Sb, a sufficient quantity as shown by Stewart et al. (Stewart et al., 1993) to catalyze the reaction of PET containing carboxyl and hydroxyl groups with high concentration (>5wt%) of ethylene/GMA copolymers. To investigate the effect of the presence of Sb on the reaction of HPET and TGIC, an additional 1000ppm of Sb₂O₃ was added in the Brabender Batch Mixer at 270°C, 60rpm, as shown in Figure 5.16. The absence of any additional reaction confirms the hypothesis that the reactivity of TGIC is the result of its tertiary nitrogen containing structures.



Figure 5.16 Effect of addition of antimony oxide on HPET/1.5X TGIC melt modification.

5.1.8 Batch Mixer Data Summary

Process stability of PET and hence the instantaneous changes in the end group content play a crucial role in determining stoichiometries of modifiers for chain extension/branching. Among four different difunctional and trifunctional compounds, TGIC and BGPM are efficient reactive melt modifiers for commercially available PET. Application of chemical kinetics methodology suggests that the TGIC reaction with the higher MW PET is fast enough to be carried out in continuous compounding equipment. The required amounts of epoxide for this reaction can be calculated based on initial carboxyl content or time dependent carboxyl content as a result of PET thermal degradation. At equivalent stoichiometries and functionalities, tertiary amine containing structures of epoxy modifiers show significantly higher reactivity with PET. PET melt modification by TGIC is sensitive to changes in stoichiometry, temperature, and rate of shear and the chemical composition of the polyester resin. The lower MW PET shows
overall less activity towards TGIC, possibly due to differences in changes in end group contents as a result of degradation. Overall, depending on type and concentration of modifier and the choice of process conditions, products with different degrees of chain extension, branching and/or crosslinking may be obtained.

5.2 Offline Rheological Characterization of Batch Mixer Products

During chain extension/branching in the melt phase with multifunctional additives, PET may undergo very rapid changes in its molecular structure and properties. The chains grow in size and degree of branching to an extreme of forming an infinite cluster. This occurs at the gel point, which marks the transition from the liquid state to the solid state and the material at the gel point is also termed as 'critical gel' (Winter and Chambon, 1986). Gelation has been defined as the conversion of a liquid to a disordered solid by formation of a network of chemical or physical bonds between the molecules (Larson, 1999). The liquid precursor is called 'sol' and the solid formed is called 'gel' (Winter and Chambon, 1986, Larson, 1999). Crucial to the formation of such chemical gels is branching or multifunctionality (Winter and Chambon, 1986). Prior to the gel point, all polymeric chains are finite in size, able to flow and can be dissolved completely in an appropriate solvent (Winter and Chambon, 1986). After gelation, an infinite molecule is formed, which is insoluble and unable to flow. During the process of extensive long chain branching, the molecules on the verge of forming a gel are expected to coexist within the reaction medium composed of widely distributed sized polymeric chains of finite lengths (Begishev and Malkin, 1999).

Rheological changes are a direct representation of the modifications induced in the molecular structure (Gupta, 2000) during the complex degradation and chain extension/branching reactions in the system under investigation. The rheological results obtained and the calculated relaxation spectrum over a wide time range were used to provide further information related to long chain branching, changes in molecular weight, and molecular weight distribution.

5.2.1 Typical Batch Mixing Runs

Products from four different batch mixer runs were chosen for further rheological characterization. Specifically, Figure 5.17 shows the effect of stoichiometry and processing temperature on the torque development of HPET after TGIC addition at about 360s, compared to HPET without modification. It is noted that at 270°C and 0.5X and, 270°C and 1.5X the torque is increasing continuously with time, indicating incomplete modification up to 900s. Thus, at a processing temperature of 270°C, it is apparent that chain extension/branching reactions dominate over degradation. In the cases of 300°C/0.5X and 300°C/1.5X the torque increased from 360s indicating dominance of the chain extension/branching reaction, reached a plateau between 750s to 800s suggesting equilibrium between degradation and chain extension/branching reactions and later decreases, possibly as a result of further degradation reactions becoming the dominating mechanism in the post plateau period.



Figure 5.17 Torque (Nm) versus time (s) data during the reactive batch mixing. (270°C-blank (♦), 300°C-blank (■). TGIC was added at about 360s at different stoichiometric amounts. 270°C-0.5X(◊), 270°C-1.5X(O), 300°C-0.5X(□), 300°C-1.5X(Δ), X= times stoichiometric amount.)

The modified as well as the blank HPET samples from Figure 5.17 at the end of the processing runs were offline characterized for rheological properties as discussed below.

5.2.2 Rheological Characterization of Unmodified Processed HPET

Figure 5.18 shows the frequency dependence of the absolute value of complex viscosity $|\eta^*|$ for unprocessed HPET pellets and HPET processed at 270°C and 300°C for 15min. Variation of $|\eta^*|$ versus frequency suggests an almost Newtonian behavior at frequencies below 100 rad/s for all three samples, typical of linear structures (Ferry, 1980, Menard, 1999). The blank curve (270°C) lies lower than that of the unprocessed HPET, representing decrease in molecular weight due to degradation during processing (Ferry, 1980).



Figure 5.18 Effect of degradation on absolute value of complex viscosity $|\eta^*|$ vs frequency ω .

(unprocessed HPET pellets (\diamond), offline data of processed HPET at 270°C(\blacksquare), offline data of processed HPET at 300°C(\bullet).)

It appears that the higher process temperature (300°C) may have caused branching (Figure 3.1) and hence increase somewhat the molecular weight compared to the 270°C run. Overall, Figure 5.18 indicates that shear viscosity does not change significantly under the experimental conditions.

Figure 5.19 shows the modified Cole-Cole (MCC) plots for the same samples as in Figure 5.17. The blank data located away from the 45° equilibrium modulus line, demonstrating narrowing of relaxation time distribution and, hence, narrower molecular weight distribution (Yilmazer et al., 2000, Nakajima and Harell, 1987), suggest that chain scission dominates over the cross-linking reaction. It appears that the degradation reactions during processing result in dominance of viscous over elastic mechanisms in the flow behavior.



Figure 5.19 Modified Cole-Cole plots for unprocessed HPET pellets (\blacklozenge), offline data of PET processed at 270°C(\blacksquare), offline data of HPET processed at 300°C(\blacklozenge).

5.2.3 Rheological Characterization of modified HPET

5.2.3.1 Dynamic Properties. Figure 5.20 shows comparative plots of $|\eta^*|$ vs ω for: HPET pellets; HPET+0.5X TGIC at 270°C; HPET+1.5X TGIC at 270°C; HPET+0.5X TGIC at 300°C; HPET+1.5X TGIC at 300°C. Reactions with TGIC significantly modify the low frequency viscosity region and the Newtonian characteristics of the unprocessed/unmodified HPET. The data suggest broadening of the relaxation time distribution i.e., more high molecular weight fraction and long chain branches as well as short chain molecules are generated.





($|\eta^*|$ Vs ω for unprocessed HPET pellets (\blacklozenge), HPET+ 0.5X TGIC at 270°C(\blacksquare), HPET+1.5X TGIC at 270°C(\Box), HPET+0.5X TGIC at 300°C (\blacktriangle), HPET+1.5X TGIC at 300°C (\bigtriangleup).

The rheological curves obtained at 1.5X stoichiometry are characterized by the highest complex viscosity at low shear rates, high shear sensitivity, and pronounced non-Newtonian behavior, as a result of long chain branching. Such behavior has been correlated with better processability in blow molding and extrusion foaming by gas

injection (Dealy and Wissbrun, 1990). Enhanced shear sensitivity of the complex viscosity or more pronounced power law behavior may be correlated with broader molecular weight distribution (Larson, 1990, Menard, 1999, Gupta, 2000). It has been shown that several thermoplastics after reactive modification by chain extension exhibit more enhanced shear thinning behavior in the lower shear rate region; this is attributed to a long time relaxation mechanism, such as entanglement couplings between high molecular weight fraction and those associated with long chain branches. On the other hand, broadening the relaxation time distribution is also responsible for the weak level of shear thinning in the higher shear rate region (Yilmazer et al., 2000). The modified HPET produced in this work will be consisting of gel particles dispersed in a polymeric melt, as demonstrated by the data in Figure 5.12. For such structures the presence of gel in appropriate form, i.e. miscible with the linear polymer and with low density of crosslink points, drastically enhances the strain hardening behavior of the elongational viscosity (Yamaguchi and Suzuki, 2001) and improves elastic properties; both effects can be related to higher melt strength and extrudate swell (Yamaguchi, 2000).

The Fig 5.21 shows the variation of tano versus frequency for the modified HPET resins. It is observed that with increasing temperature and TGIC concentration, the material behavior turns from liquid-like into solid-like. This result is in agreement with the gel content data of Figure 5.12 showing that, for the modified HPET, an increase in reaction temperature as well as an increase in the TGIC concentration resulted in higher insoluble content. Furthermore, Figure 5.12 confirms that at 1.5X and 300°C, an almost insoluble crosslinked network was formed as a result of the modification.



Figure 5.21 Effect of reaction on the loss tangent vs frequency ω for modified and unmodified HPET. (unprocessed HPET pellets (\bullet), offline data of HPET+0.5X TGIC at 270°C (\blacksquare), offline data of HPET+1.5X TGIC at 270°C (\Box), offline data of HPET+0.5X TGIC at 300°C (\bullet), offline data of HPET+1.5X TGIC at 300°C (\circ).)

At 1.5X stoichiometric addition, tan δ is approximately constant representing rheological behavior near the sol-gel transition, as discussed in detail by Winter and Chambon who considered the fractal structure of a critical gel. During the evolution of tan $\delta(\omega)$ for 1.5X stoichiometric addition, at first the slope is negative; later it becomes positive resulting in a slight shoulder (Winter and Chambon, 1986). This maximum at lower frequencies may be associated with the losses involved in entanglement slippage (Ferry, 1980). In addition, theoretically, these data suggest that the reacted samples contain a gel like structure while maintaining their processability or fluidity. Moreover, the presence of a gel like structure in the HPET melt matrix affects relaxation modes at all length scales and, thus, can be observed within the relatively small frequency window of the dynamic mechanical experiments performed. It should be noted that tan δ is larger than 1, i.e., G">G' for all samples employed; this corresponds to the characteristic rheological power scaling law for gel like material suggesting formation of weak gels (Winter and Chambon, 1986, Valles et al., 1990):

$$G' < G'' \propto \omega^n \tag{5.5}$$

In his classical book, de Gennes also defines a weak gelation process as the reactive system in which the crosslinks (bonds) formed lack stability because of the presence of debonding mechanisms (de Gennes, 1979). In the current study, reaction with TGIC could be termed as the bonding mechanism whereas degradation reactions could correspond to the debonding mechanisms. It should be noted that our reacted samples might be considered as weak gel-like structures while maintaining significant processability/fluidity.

The Figure 5.22 shows MCC plots for the unmodified and TGIC modified HPET samples under similar experimental conditions. The position of the data with respect to the equi-moduli line G'=G'' is a measure of the degree of melt elasticity. It has been shown in earlier work with dianhydride and diepoxides as reactive modifiers (Yilmazer et al., 2000), that branched polymers with higher MWD and higher G' values have MCC plots that lie lower in comparison to polymers that are linear with narrower MWD (Nakajima et al., 1987). The present data with 1.5X triepoxide approach the 45° line at all frequencies, whereas the 0.5X data approach the 45° line only at high frequencies. The changes in the rheological properties indicative of higher melt elasticity are in the direction of increasing TGIC concentration. It is understood, however, that excess modification may create problems with processability.



Figure 5.22 Modified Cole-Cole plots for unmodified and modified HPET samples. (G' vs G" for unprocessed PET pellets (\blacktriangle), PET+ 0.5X TGIC at 270°C(\blacksquare), PET+1.5X TGIC at 270°C(\bullet).)

5.2.3.2 Relaxation Spectrum. The enhanced storage modulus for the modified HPET in Figure 5.22 suggests that the modified resins have structures representing long relaxation times. For a better understanding of the viscoelastic properties in the long time region, the relaxation spectrum, H (λ) were calculated from the oscillatory moduli data using the Tschoegl equations (Tschoegl, 1971):

$$H(\lambda) = \frac{dG'}{d\ln\omega} - \frac{1}{2} \frac{d}{d\ln\omega} \Big|_{1/\omega = \tau/\sqrt{2}}$$
(5.6)

and

$$H(\lambda) = \frac{2}{\pi} \left[G'' - \frac{4}{3} \left(\frac{dG''}{d \ln \omega} \right) + \frac{1}{3} \left(\frac{d G''}{d \ln \omega} \right) \right]_{1/\omega = \tau/\sqrt{5}}$$
(5.7)

In the calculations, the frequencies used in the experiments determine the range of relaxation times irrespective of the relaxation spectra of the specimens. In other words, relaxation spectra of polymeric samples are, usually, truncated at the same relaxation time as long as the experimental frequency range is fixed. However, it should be noted that not all tested samples have necessarily the same longest relaxation time, depending on the degree of modification of their chemical structure. It is observed that the relaxation spectra determined from the curves of G' agree well with those determined from G". Therefore, for clarity, only the data calculated from G" of each reacted/processed specimen are shown in Figure 5.23.

From the overall spectral representation, it is observed that at short relaxation times, the materials have a rubbery response (Ferry, 1980). The differences in the chemical structure and molecular weights become pronounced at increased relaxation times. The relaxation spectra of the products of the blank runs are shifted downwards compared to those of pellets due to degradation during processing accompanied by decreased molecular weight; this indicates that the longest relaxation mechanism of the material could be entanglement slippage of linear chains (Ferry, 1980, Yamaguchi et al., 1997). For the modified resins, the H (λ) curves do not drop suggesting a longer relaxation time due to the presence of long chain branches which are also responsible for improved melt elasticity. Elastic polymers have long chain branches with longer relaxation times and take longer to yield before they start to flow (Ferry, 1980). Viscous fluids flow sooner than solids under imposed stress. Thus, the curves for HPET pellets and the blank runs suggest shorter branches or absence of long chain branching. When the branches are long compared to the entanglement spacing, the relaxation spectrum is broadened, and the longest relaxation mechanism appears in the long time region (Dossin and Graessley, 1979). Polymers with long chain branches can not relax by simple reptation like linear chains, since one end of each arm of the branched molecule is anchored to a cross-link point (de Gennes, 1979, Graessley, 1982). The arm therefore relaxes by primitive-path fluctuations that are assumed to be slower compared to other typical relaxation mechanisms (Larson, 1999).



Figure 5.22 Relaxation spectra H (λ) vs relaxation time λ . (unprocessed HPET pellets (+), Blank HPET at 270°C (**•**), Blank HPET at 300°C (**▲**), HPET+0.5X TGIC at 270°C (×), HPET+1.5X TGIC at 270°C (□), HPET+0.5XTGIC at 300°C (**★**), HPET+1.5X TGIC at 300°C (**△**).

Although H (λ) of the 0.5X TGIC system at longest relaxation times in Figure 5.22 is larger than H (λ) of the 1.5X TGIC, the order could be changed in a longer relaxation time region corresponding to frequencies less than 0.1 rad/s. As discussed in Figure 5.21, the modified HPET behaves like a critical gel in this experimental region. As a result, log H (λ) decreases linearly with increasing relaxation time, i.e., $H(\lambda) \propto \lambda^{-n}$,

whereas $H(\lambda)$ of the unmodified HPET falls off as a liquid. Furthermore, the 1.5X TGIC product shows quite a smaller slope than the 0.5X TGIC, indicating a higher density of crosslink or branch points. It is possible that the 1.5X TGIC product may have a plateau modulus in a very long time region although it is quite difficult to discuss the implications of this behavior on actual processability based on linear viscoelastic properties. It has been suggested that (Xanthos et al., 2000a, Xanthos and Dey, 2000b) an increase in the storage modulus of chemically modified PET could be related to the improvement in melt elasticity in spite of the non-linear region corresponding to actual processing conditions.

5.2.3.3 Summary of Offline Rheological Characterization of Batch Products. Polyethylene terephthalate when melt processed in the absence of epoxide modifier, oxygen and moisture, undergoes scission/crosslinking reactions which result into a net decrease in the overall molecular weight and narrowing of molecular weight distribution, as suggested by rheological data. By contrast, reactive modification with TGIC results in an increase in relaxation time and broadening of relaxation time distribution and their corresponding effects on molecular weight and molecular weight distribution, as suggested by changes in melt viscosity and elasticity, and shear sensitivity of complex viscosity. Even small amounts (~800ppm) of TGIC can modify a linear PET polymer to a power law fluid through long chain branching and with a polymeric melt containing sparsely distributed weak gel-like structures. It is suggested that the sol-gel transition of the reactive system is dictated by the concentration of the epoxide added, under the experimental conditions. By contrast to the 0.5X modified HPET, addition of 1.5X (~2000ppm) stoichiometric amount of TGIC results in a structure characteristic of power

scaling law model. It is suggested that certain modified resins have rheological properties suitable for process operations such as extrusion foaming, blow molding, and thermoforming.

5.3 Real Time Spectroscopic Analysis of the PET/TGIC Reaction

From Figure 5.24, it is observed that the structural stability of TGIC was noticeably decaying for the first five minutes after it reached the set temperature of 270°C. Significant changes in the 910-950 cm⁻¹ region at about four minutes after reaching at 270°C, suggest disintegration of the epoxide ring which should be accompanied by loss of reactivity as a function of time.



Figure 5.24 TGIC stability at 270°C as monitored by FT-IR spectroscopy. (Sample was prepared by the solution casting method.)

However, the disintegration of the TGIC structure, may also have accompanied the formation of hydroxyl groups, as evident by the broad peak near 3300 cm^{-1} (Skoog and Leary, 1992). These hydroxyls may be participating in chain extension/branching reactions by reacting with carboxyl groups under the experimental conditions.



Figure 5.25 HPET melt stability at 270°C as monitored by FT-IR spectroscopy. (Sample was prepared by the solution casting method.

Figure 5.25 shows the spectral monitoring of HPET held at 270°C as a function of time. HPET is found to be relatively stable with some changes in the 1700-1000 cm⁻¹ region. Increase in peak height at 1725.7 cm⁻¹, 1255.5 cm⁻¹, and 1091.81 cm⁻¹ may be assigned to the formation of aldehyde carbonyl (C=O) in the aldehyde (Silverstein and Webster, 1997), C=O in plane vibration in ester and/or ether (Pearce et al., 1983), and C-O asymmetrical stretching in ester functionality, respectively (Pearce et al., 1983). The ester referred in this particular context is terephthalate type carboxylic acid ester and/or aromatic type carboxylic acid ester. The appearance of these broad peaks could be due to

overlapping bands arising from several different carbonyl degradation species including products of transesterification reactions (Pearce et al., 1983). It is interesting to note that the broad C-O and C=O may also be due to the carboxylic end groups generated as a result of melt degradation, which has been quantified earlier in the Section 5.1.2.

It is as evident from Figure 5.24 and Figure 5.25 that the epoxide region at 910-950 cm⁻¹ is crowded with overlapping peaks from PET as well as TGIC, making quantitative monitoring of the reaction through the disappearance of the oxirane peak a tedious task.



Figure 5.26 HPET + 10% TGIC at 270°C as monitored using spectroscopic analysis in comparison with control PET and TGIC samples at 270°C after 5min. (Sample was prepared by the solution casting method.)

Initial attempts to follow the reaction with 2000 ppm TGIC in the heated cell at 270°C were unsuccessful. To enhance the sensitivity of the technique an excess of 10 wt% of TGIC was added to the PET powder as detailed in the experimental procedure in

the Section 4.1.3. As evident from Figure 5.26, a peak at 870.3 cm⁻¹ is prominent again in the PET+10% TGIC mixture as with the PET control, which may be assigned to the aromatic C-H bending vibration arising from PET (Pearce et al., 1983). In the region, 1000-800 cm⁻¹, the carbonyl (ester) and epoxy ring have characteristic peaks. In addition, the characteristic peak due to the oxirane ring from TGIC in the mixture is not strong enough to be useful as a basis for monitoring the extent of reaction.

Even at 10% TGIC addition, it is clear that, monitoring the reaction by changes in the peak heights of the epoxide is difficult as shown in Figure 5.26 and, hence, limits the use of this technique for the analysis. However, the spectroscopic analysis provides some interesting clues about the possible reaction mechanisms. It is noteworthy that the PET/TGIC mixture does not show changes in the relative peak heights at around 1200 cm⁻¹ and 1600 cm⁻¹, which corresponds to C-N and C=N respectively, as the reaction proceeds with time (Silverstein and Webster, 1997). For the first 4-5 minutes, the TGIC structure is also stable as confirmed before by TGA and FT-IR analysis. Changes in C-N and C=N peak heights would suggest an additional different reaction involving esterification through the TGIC carbonyl groups (Pappas et al., 1991, Myers and McKinstry, 1996). Additional information about the reactions could be obtained by subtracting the spectra obtained with real time monitoring from the spectra at t=0 in attempting to identify other peaks rather than that of the extremely weak oxirane ring. However, in this preliminary study, this more detailed analysis was not carried out.

5.4 Rheological Analysis of the PET/TGIC Reaction

The PET-epoxide system represents a complex set of concurrent reactions (melt degradation and chain extension/branching) that may often lead to poorly defined structural and rheological properties of the reaction products. Quantitative description of such a complex reaction process by a classical kinetic model requires knowledge of instantaneous concentrations of all the reacting species along with the individual reaction constants of the competing reactions. This is not always feasible and as a result the use of various physical methods for monitoring chemical changes in a reactive polymeric system has become widespread (Begishev and Malkin, 1999). Such methods for quantitative modeling are based on real time monitoring of a given property of the reacting species. Among the most widely used methods are thermal (or calorimetric), rheological, and spectroscopic methods (Begishev and Malkin, 1999).

Among the above-mentioned analytical techniques, thermal and spectroscopic methods cannot accommodate variable shear rates. Initial experiments with the PET/TGIC reactive system revealed that changes in thermal properties during reaction are beyond the sensitivity range of a typical differential scanning calorimeter. Details of real time FTIR spectroscopic analysis for the PET/TGIC reaction discussed in Section 5.3 indicate that this method is also inadequate to follow the evolution of the modification reaction. However, rheological properties at different shear rates or frequencies such as dynamic moduli and complex viscosity are very sensitive to the variations in molecular structure and phase transitions occurring in reactive polymeric systems (Valles et al., 1990, Cai and Solvay, 2001). As a result, the PET/TGIC reactive system was studied in this work by focusing on the use of a dynamic mechanical analyzer in order to relate the

changes in dynamic moduli and melt viscosity as a function of temperature and frequency with the development of long chain branches and gel like structures in the reacting specimens. Oscillatory measurements are ideal for evaluating the development of material structure, since minimal damage occurs to the structure, by contrast to batch mixers operating under higher and often variable shear rates.

5.4.1 Effect of Temperature at Constant Frequency

The dynamic moduli as a function of reaction time are shown in Figure 5.27 for samples prepared by the "powder cake" method at two different reaction temperatures, 270°C and 300°C, and 10rad/s. Initially, both the dynamic moduli increase in the order of 270°C<300°C as a result of reactions leading to an increase in degree of branching and overall increase in the molecular weight of the system (Cai and Salovey, 2001). The initial rate of increase in the extent of reaction in the range of 0 to 700s, represented by an increase in moduli, is higher at 300°C than at 270°C, which confirms similar observations from batch mixer data. In the batch mixer experiments, the reaction between HPET and 50% excess stoichiometric amount of TGIC was also evaluated at 270°C and 300°C but at an estimated shear rate of 220 s⁻¹ (Brabender Batch Mixer Manual, 2002) with TGIC added in the mixer six minutes after the PET pellets. Assuming first order kinetics for the initial part of the reaction, the first order rate constants obtained from the batch mixer data and the rheological testing are compared in Table 5.3. Considering the differences in the experimental conditions, it is of interest to note that the calculated rate constants are of the same order of magnitude and agree well for the low temperature data.



Figure 5.27 Changes in dynamic moduli (G', G") at a constant frequency of 10 rad/s and at 270°C and 300°C respectively. $((\bullet)270^{\circ}C-G', (\bullet)270^{\circ}C-G', (\bullet)300^{\circ}C-G', (\Box)300^{\circ}C-G''$. Samples were prepared by the powder cake

 $((\bullet)270$ C-G, $(\bullet)270$ C-G, $(\bullet)300$ C-G, $(\Box)300$ C-G. Samples were prepared by the powder cake method.)

 Table 5.3 Comparison of rate constants for the HPET/TGIC reaction

Reaction Temperature	k (s ⁻¹) (batch mixer, shear	k (s ⁻¹) (oscillatory
(°C)	rate of approx. 220s ⁻¹)	experiments at 10 rad/s
		frequency)*
270	0.003	0.0035
300	0.0095	0.0057

* Samples were prepared by the powder cake method.

(By modeling the torque evolution versus time in a batch mixer and G' evolution versus time in a dynamic mechanical analyzer, as an analog of a first order reaction.)

Variations in the 300°C data may be related to the lower shear rates and less uniform TGIC dispersion during the oscillatory measurements as well as the potential for increased reactivity in the batch mixer due to thermomechanical degradation and corresponding increase in the available carboxyl groups (Xanthos et al. 2001).

In the case of 270°C, the moduli increased continuously over the duration of the experiment as shown in Figure 5.27. It has been suggested that increase in storage modulus is a measure of 'chemical' degree of transformation during chain extension/branching reactions resulting in an enhanced elastic behavior (Begishev and Malkin, 1999). During chain extension/branching in the melt phase with multifunctional additives, PET may undergo very rapid changes in its molecular structure and properties. During the process of extensive long chain branching, the macromolecules on the verge of forming a gel are expected to coexist in a reaction medium composed of chains with widely distributed sizes. The chains grow in size and degree of branching to an extreme of forming an infinite gel like structure. At 270°C, at about 1000s, a crossover between the G' and G" curves is observed which suggests a transition from an initial liquid like behavior (G' \leq G") to the solid-like behavior (G' \geq G") (Begishev and Malkin, 1999). A similar crossover is observed for the 300°C data at about 500s. The crossover has been approximated as the gel point, where the crosslinks have progressed to form an 'infinite' network of chains across the specimen (Winter, 1987, Heise et al., 1990). Therefore, the time limits, namely 1000s and 500s, may be considered as the "gel time(s)" for the respective systems. It is obvious that, for the PET-TGIC reactive system, the "gel time" depends on the temperature of the reaction at the particular constant frequency.

Earlier it has been shown that the high torque values reached during reactive modification decrease with continuing shearing at high temperatures, presumably as a result of thermomechanical degradation of the reaction product. As shown in Figure 5.27 for the 270°C time sweep, the storage modulus increases steadily with time while the loss modulus keeps increasing at a much lower rate. Whereas, in the case of the 300°C time

sweep, initially both the storage as well as loss moduli increase, suggesting a dominance of the chain extension/branching reactions, reach a plateau suggesting equilibrium between the opposing degradation and chain extension/branching and later decrease suggesting reduced average molecular weight, as the chain scission reactions become the dominant mechanism. The time for reaching the plateau could be considered as representing the maximum allowable residence time in a typical continuous polymer processing equipment under the corresponding operating variables of shear rate and temperature.

5.4.2 Effects of Frequency at Constant Temperature

The effect of frequency on the overall rate of the HPET/TGIC reaction for the "powder cake" samples was investigated by monitoring the evolution of storage modulus G' (Pa) versus time (s) at 270° C. As shown in Figure 5.28, it is clear that the system is shear sensitive. It is apparent that, at 270° C, irrespective of frequency of measurement, chain extension/branching is the dominant reaction mechanism over degradation even at the longest residence times attained within the experimental limits. As the frequency decreases, G' increases at a faster rate (at least initially); this is evident from Figure 5.29 where G' is plotted versus frequency at various reaction times. Figure 5.29 also suggests that lower frequencies (0.1 and 1 rad/s) result in higher percentage increase in the storage moduli by allowing sufficient time for the macromolecular chains in the reaction medium to attain favorable conformations, thus, rendering higher exposure to the reactive groups.

It should be noted that in the PET-epoxide reactive system, as the melt modification reaction progresses the formation of gel particles might diminish the accessibility of unreacted groups for reaction by steric hindrance. Thus, changes in the testing frequency may offer clues about the rates of increase of the size of polymer chains and the evolution of branched structures.



Figure 5.28 Evolution of storage modulus G' (Pa) versus reaction time (s) as a result of change in frequency (rad/s) at 270°C. (Samples were prepared by the powder cake method.)

As observed from the data in Figure 5.8, it is evident that the onset of reaction is different for the different sets of frequencies which may be attributed to diffusional mixing taking place in the powder cake sample. During heating of the powder, TGIC would melt first at 100°C and form a layer around the HPET granules which would melt later. Theoretically, the time required by TGIC to diffuse to the center of the PET granules could be estimated from:

$$t_{diff} = \frac{\left(\frac{d}{2}\right)^2}{D_{AB}}$$
(5.8)

Assuming $D_{AB}=10^{-6}$ cm²/s (Gogos, 2003) and for PET using d =0.089 cm (Section 4.2.2), t_{diff}=2000s or 34 minutes. This time is larger than the estimated residence time for the reaction of 12-13 minutes (Section 5.1.6). Therefore, it could be said that the reaction in the powder cake method is a segregated or non-uniform reaction, diffusion controlled (t_{diff}/t_{rxn}>1). It is noteworthy that, after the initial flat growth of the storage modulus versus time, the slope of the curves start increasing, which is an indirect representation of miscibility of TGIC into the PET melt.



Figure 5.29 Changes in storage moduli versus frequency at different reaction time intervals, and at 270°C.

(Samples were prepared by the powder cake method.)

5.4.3 Effects of Method of Sample Preparation at Constant Temperature/Frequency

Figure 5.30 shows the comparative time scans at 270°C and at a frequency of 1 rad/s for samples prepared by the "powder cake" method and the "solution casting" methods. As discussed in the earlier section, powder cake method experiments are characterized by diffusional mixing mechanism. The samples prepared by the solution casting method are

believed to be characterized by a molecular mixing mechanism. Therefore, after around 100 seconds, a period during which time, local temperatures, and composition variations are still believed to exist, the "powder cake" method sample shows a more prominent increase in G' and G" values than the "solution casting" samples. However, the values for G' tend to cross each other near about 650s and the G" values at about 550s. After that time, both type of samples follow a rising trend in a similar way, although the differences between them become less pronounced. Thus, it appears that the final gel like structure formed during the PET/TGIC reaction is independent of the method of sample preparation. In summary, the three reactor systems used in the study, i.e., intesive batch mixer, rheometer-powder cake, rheometer-solution casting are characterized by laminar shear mixing, diffusion controlled/segregated reaction, and molecular mixing/uniform reaction, respectively.



Figure 5.30 Comparison of method of sample preparation - solution casting from hexafluoroisopropanol versus powder mixing, to monitor the HPET/TGIC reaction at 270° C and a frequency of 1 rad/s.

5.4.4 Effects of Time/Frequency Scans at Constant Temperature

The knowledge of factors that control a phase transition of a polymer melt as a result of gelation provides information on the rheological changes from liquid-like into solid-like behavior and is important from a processability point of view. Monitoring the variations in the G' and $tan\delta$ versus frequency as a function of reaction time may provide insights in the evolution of chain lengths, degree of branching, and the set of processing conditions associated with the PET melt phase transition. In the following analysis, an attempt is made to interpret our experimental observations by applying the theory of critical gel formation due to crosslinking.



Figure 5.31 Frequency dependence of oscillatory shear modulus G' for HPET+1.5X TGIC at 270°C at various time intervals. (Samples were prepared by the powder cake method.)

Figure 5.31 shows the frequency dependence of oscillatory shear/storage modulus G' and Figure 5.32 shows the frequency dependence of loss tangent $tan\delta$ at 270°C for the PET/TGIC reactive system at progressive time intervals. It was observed that G' increases monotonically and $tan\delta$ decreases with time. Increase in G' is due to an

increase in the melt elasticity resulting from increases in the average relaxation time and relaxation time distribution or molecular weight and molecular weight distribution, respectively. As discussed in Section 3.1.2, according to the Doi-Edwards tube model, branched polymers have long relaxation time due to contour length fluctuation because simple reptation is impossible. In other words, branched structures with long chains offer increased resistance to flow as a result of entanglement couplings associated with the branches. It is also to be noted that due to chain extension, in addition to branching reactions sketched in Figure 5.5 chain lengths with molecular weight greater than the entanglement molecular weight will be formed during the modification. It is to be noted that G' versus frequency data do not show a plateau behavior, which is evidence of entanglement behavior in the observable frequency window.



Fig 5.32 Frequency dependence of $\tan \delta$ for HPET+1.5X TGIC at 270°C at various time intervals.

(Samples were prepared by the powder cake method.)

In order to study the effect of the PET/TGIC reaction on the increase of the degree of branching or widening of the molecular weight distribution, the relaxation modulus G(t) plotted in Figure 5.33 versus time was calculated from the relation proposed by (Schwarzl, 1975) involving the measured oscillatory shear moduli data:

$$G(t) = G'(\omega) - 0.56G''\left(\frac{\omega}{2}\right) + 0.2G''(\omega)\Big|_{\omega = \frac{1}{t}}$$
(5.9)

From Figure 5.33, it is clear that, G(t) falls off rapidly for the unmodified PET suggesting liquid like behavior whereas it relaxes with a constant slope on a log-log plot for the modified samples. Formation of long chain branches during the reaction widens the relaxation time distribution with increasing residence time for reaction. As the degree of branching increases, the relaxation modulus increases for the same relaxation times, which is clear from Figure 5.33.



Figure 5.33 Relaxation Modulus G(t) for the PET/TGIC system at 270°C obtained through real time frequency scans.

(The values for the system were calculated by using Equation 5.7).

In general, for crosslinked systems, linear viscoelastic properties, such as relaxation modulus G(t), in the wider vicinity of the gel point is governed by the scaling law $G(t) \sim t^{-n}$, where t is time (s) and n is the relaxation exponent; this could also be represented by the following relations proposed by (Winter and Chambon, 1986):

$$G' \propto G'' \propto \omega^n \tag{5.10}$$

Hence,
$$\tan \delta = \tan\left(\frac{n\pi}{2}\right)$$
 (5.11)

And
$$G(t) = St^{-n}$$
 $0 < n < 1$ (5.12)

where ω is frequency (rad/s) and S (Pa.sⁿ) is the gel strength. Power law mechanical behavior modeled through Equation 5.10 is an expression of a self-similarity of structure that evolves during gelation; it was confirmed by numerical curve fitting techniques that the present PET/TGIC reactive system follows the above relations. Equation 5.8 is also said to represent fractal time behavior that is a feature of processes that do not have a characteristic time scale.

It is apparent that the oscillatory shear moduli (Figure 5.31), loss tangent (Figure 5.32), and the relaxation modulus (Figure 5.33) obey Equations 5.10-5.12 in the experimental time or frequency region in the wider vicinity of the gel point. At higher time intervals in Figure 5.32, $tan\delta$ remains at a constant value of 0.8 independent of frequency, suggesting the presence of a critical gel like structure or gel point (Winter and Chambon, 1986, Valles et al., 1990). Substituting $tan \delta = 0.8$ in Equation 5.9 yields n = 0.46. This value of n normally lies between 0 and 1, and is within the theoretical limits predicted by the correction to the Muthukumar's theory for polydispersity of critical gels (Muthukumar and Winter, 1986, Muthukumar, 1989). The calculated n value confirms

the applicability of Equation 5.8 in calculating G(t). Furthermore, application of this analysis to actual residence time in processing equipment suggests that the maximum allowable times should not reach the values at which the critical gel is formed or the conditions for the material to obey Equations 5.8-5.10.

5.4.5 Gel Structure Represented Through the Fractal Dimension

This section discusses one of the unique characteristics of the polymeric melt near the sol-gel transition. Fractal dimension is meaningful for objects, which exhibit scaling behavior (Falconer, 1990). The statistical similarity of polymer undergoing self-similarity is quantified by a fractal dimension, d_{f} , which essentially relates the polymer average molecular weight, M, to its average size, its radius of gyration R_g by $R_g \propto M^{1/d_f}$. Muthukumar has developed a model in which it is assumed that variation in the chain length should enhance the excluded volume effect (Muthukumar and Winter, 1986, Muthukumar, 1989). To account for this effect, it was suggested that if the excluded volume effect was fully screened, the relaxation exponent n for a polydisperse system could be related as follows:

$$n = \frac{d(d+2-2d_f)}{2(d+2-d_f)}$$
(5.13)

In the framework of the above equation, all values of the relaxation exponent $0 \le n \le 1$ are possible for a fractal in the physically possible domain $1 \le d_f \le 3$. Substituting the earlier defined n=0.46 and assuming a space dimension d=3 in Equation 5.11, $d_f=2.2$. Adolf and Martin have suggested that the fractal dimension for chemically crosslinked gels from percolation theory ranges between 2.5 and 2.0 as determined experimentally for the crosslinked gels in swelling equilibrium (Adolf and Martin, 1991). The fractal dimension of 2.2 falls well within this range.

5.4.6 Summary of Chemorheological Study

An attempt was made to develop insights on the evolution of the molecular architecture resulting from the melt modification of polyethylene terephthalate (PET) with TGIC through real time monitoring of rheology under controlled conditions.

From rheological analysis, melt modification of PET was found to be a function of temperature and rate of shear at constant TGIC concentration. Chain extension/ branching of PET by the selected triepoxide results in formation of critical gel like structures followed by solid like viscoelastic behavior. Gel time varies as a function of reaction temperature as well as the rate of shear or frequency in this case. Changes in rheological properties resulting from chain extension/branching reactions were detected at low frequencies or shear rates, which are non-typical for a typical processing operation in an extruder.

The value of fractal dimension calculated from the model of Muthukumar, considering the screening of excluded volume interactions, suggests increasing crosslinking density and real time formation of "tight" network structure.

5.5 Sequential Reactive Extrusion/Foaming

A methodology described in the literature to define the reactive extrusion process conditions from reaction fundamentals could be applicable to the PET-TGIC system of this research (Xanthos, 1992). Important steps are:

(a) <u>Understanding of overall chemistry and main reactions</u>. The suggested reaction chemistry is reviewed and summarized in Chapter 3 as well as in Section 5.1.3 involving undesirable melt degradation and desirable chain extension/branching reactions.

(b) <u>Selection of reactants with known material properties and the correct</u> <u>stoichiometry</u>: Confirming to the above guidelines, TGIC was the choice for the reactive modification of HPET among the five different modifiers selected in the beginning of this work as discussed in Sections 5.1.3 and 5.1.4. Stoichiometric amounts of modifiers to be added are also elaborated in Section 5.1.3.

(c) <u>Development of reaction kinetic data from batch mixer experiments</u>: These are summarized in Section 5.1.6.

(d) <u>Assessment of reaction rates from batch data and application to continuous</u> <u>reactor throughput rates along with estimation of residence time:</u> Assessment based on the initial reaction rates for first order reaction from the batch mixer data (Table 5.2) resulted in an estimated half-life of about 1 to 1.5 min. Time equivalent to approximately seven half-lives would be needed to reach the completion of reaction based on first order kinetics.

(e) <u>Consideration of byproducts and assessment of need for devolatilization</u>: Since, epoxides were selected as the reactive modifiers; there was no need to consider the formation of epoxy/PET reaction byproducts and therefore, introduce devolatilization step. However, formation of decomposition products from unreacted TGIC after about 6 minutes (see TGA data in Section 5.1.1) and acetaldehyde from thermal degradation of PET should not be ruled out, although, such products could be removed at the extruder die. The PET has been dried to less than 0.01 wt% prior to extrusion and therefore, no need for further moisture removal was considered.

(f) <u>Outline and selection of options for sequence of addition of reactants in an</u> <u>extruder</u>: In this work, only one option was considered towards the sequence of addition of reactants in the extruder, i.e. hopper feeding of dryblend of predetermined stoichiometric amount of TGIC and RPET.

(g) <u>Off-line and in-line characterization of the reaction product to meet required</u> <u>properties:</u> With respect to batch data, carboxyl content analysis, insoluble content determination, rheological characterization, and FT-IR analysis were carried out (Section 5.1-5.4). Data from extrusion experiments are shown in Table 5.4 below.



Figure 5.34 Schematic of reactive modification of RPET with TGIC in a single screw extruder.

With this background, an exploratory reactive extrusion run was carried out, as per the schematic shown in Figure 5.34, in the Killion extruder, at a total residence time of around 7-10 minutes. Since the feeding protocol in the extruder differs from that in the batch mixer, the total reaction length includes time not only for reaction but also melting and mixing.

Table 5.4 contains extrusion data and product characteristics of the extrudates. Increases in extrudate swell and melt strength are indicative of enhanced melt elasticity; lower melt flow index (MFI) and increased die pressure indicate increased viscosity as a result of the overall effect of the chain extension/branching reactions. These online and offline observations can be related to increase in MW and broadening of MWD.

Property	W/O Triepoxide	With Triepoxide
Die Pressure (MPa)	0.96	15.2
Die Temperature (°C)	270.6	279.6
Extrudate Swell	0.82	3.07
Melt Flow Index	>200	1.06
(g/10min.)		
Melt Strength (10 ⁻³ N)	Not measurable	332

 Table 5.4 Extrusion data and Rheological Properties of Unmodified Vs. Modified RPET

For the TGIC modified RPET T_m peak was 4°C higher than the unmodified RPET as a result of increased chain length, and percent crystallinity was 8% lower than the unmodified RPET as a result of increased branching.

A sequential reactive extrusion/foaming run was carried out with isobutane as a physical blowing agent for foaming of the TGIC modified system in a combined one-step operation to produce low-density foams; very similar process conditions as for the simple reactive modification shown in Figure 5.35 were used. It should be noted that, by contrast to foam extrusion by gas injection of non-reacting polymeric materials, analysis of the one-step process presents several challenges, one of them being that the dissolution and, perhaps, expansion of the blowing agent occurs in a continuously reacting matrix of increasing viscosity and elasticity, and changing structural characteristics.



Figure 5.35 Schematic of Sequential Reactive Extrusion Foaming of RPET+0.75X TGIC with Isobutane

Foamed extrudates produced under the same operating conditions are compared in order to assess the effect of melt modification on foaming. For the unmodified RPET produced at a die temperature of 267.5°C, die pressure of 1200 kPa, and gas injection pressure of 2000 kPa: expansion was 120% and few cells were formed. In the case of TGIC modified RPET produced at a die temperature of 269°C, die pressure of 3800 kPa, with a gas injection pressure of 2200 kPa: expansion was 480%, density of the foam was 0.12 g/cc with a uniform cell structure. Figure 5.36 shows the cross section of the extrudate foam from the melt modified PET using TGIC. Large (\sim 500µm) and relatively uniform cells are evident, although foam appearance could be improved through the use of additional nucleating agents.



Figure 5.36 Foam cross section of TGIC modified PET.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Among five different low MW difunctional and trifunctional epoxy compounds, triglycidyl isocyanurate (TGIC) was shown to be an efficient reactive melt modifier for commercially available PET. The application of chemical kinetics methodology indicates that the TGIC reaction with the higher MW PET is fast enough to be carried out in a continuous extruder reactor. Process stability of PET and, hence, the instantaneous changes in end group content play an important role in determining required stoichiometries of modifiers for chain extension/branching reactions. The required amounts of epoxide for this reaction can be calculated based on initial carboxyl content or time dependent carboxyl content as a result of simultaneously occurring PET thermal degradation. At equivalent stoichiometries and functionalities, tertiary nitrogen containing structures of epoxy modifiers show significantly higher reactivity with PET.

The PET melt modification by TGIC in a batch mixer is sensitive to changes in stoichiometry, temperature, rate of shear and the characteristics of the polyester resin used. The lower MW PET shows overall less activity towards TGIC, possibly due to differences in the evolution of additional end group content. Overall, depending on type and concentration of modifier and the choice of process conditions, products with different degrees of chain extension, branching and/or crosslinking may be obtained.

From a rheological standpoint, PET when melt processed in the absence of epoxide modifier, oxygen and moisture, undergoes scission/crosslinking reactions which result into a net decrease in the overall molecular weight and narrowing of molecular

119

weight distribution. By contrast, reactive modification with TGIC results in an increase in relaxation time and broadening of relaxation time distribution and their corresponding effects on molecular weight and molecular weight distribution, as suggested by changes in melt viscosity and elasticity, and shear sensitivity of complex viscosity. Even small amounts (~800ppm) of the triglycidyl isocyanurate can modify a linear PET polymer to a power law fluid through long chain branching and produce a polymeric melt containing sparsely distributed weak gel-like structures. It is suggested that the sol-gel transition of the reactive system is dictated by the concentration of the epoxide added, under the experimental conditions. By contrast to the 0.5X modified PET, addition of 1.5X (~2000ppm) stoichiometric amount of TGIC results in a structure characteristic of power scaling law model. Based on the results of rheological characterization, it is concluded that certain modified resins have rheological characteristics suitable for certain process operations such as extrusion foaming, blow molding, and thermoforming where linear PET resins have inadequate rheological properties.

An attempt was also made to develop an insight on the evolution of molecular architecture resulting from the melt modification of PET with TGIC through real time FTIR monitoring under controlled conditions. It was not possible to follow the PET/TGIC reaction solely based on monitoring the opening of the oxirane ring. However, it was found that spectroscopic analysis not only provides insights into the PET degradation but also suggests that the structure of TGIC is stable at 270°C for at least first five minutes.

Through chemorheology, melt modification of PET was found to be a function of temperature and frequency at constant TGIC concentration. Chain extension/ branching

of PET by the selected triepoxide results in the formation of critical gel like structures followed by solid like viscoelastic behavior. Gel time varies as a function of reaction temperature as well as the rate of shear or frequency in this case. The value of fractal dimension calculated from literature available models, considering the screening of excluded volume interactions, suggests increasing crosslinking density and real time formation of "tight" network structure.

Based on the kinetic and rheological data developed through the batch mixer experiments and through monitoring the reaction by chemorheology in a dynamic mechanical analyzer, the PET/TGIC reaction was carried out in a single screw extruder. Monitoring of process conditions and product analysis indicate the formation of higher MW and broader MWD structures with their accompanying effects on melt viscoelastic properties. Such structures were easily foamed to low densities in a sequential reaction/ foaming one step operation in the extruder.

Future work should concentrate on the following areas:

- 1. Detailed structural characterization of the reaction products by NMR and GPC.
- In depth characterization of the reaction using FT-IR, by subtracting real time spectra obtained from the spectra at t=0.
- 3. Use of in house synthesized PET polymers with known types and concentrations of catalysts; this to eliminate the uncertainties resulting from possible synergistic or antagonistic effects of catalyst remnants, additional catalysts, and epoxides on rates of reaction.

- 4. Investigation of suitable thermally stable catalysts for the DGEBA and TGG reaction with polyesters at melt temperature conditions.
- 5. Production of PET modified with different amounts of TGIC on a larger scale and with a different protocol of addition to be used for further separate extrusion foaming experiments under different conditions and with different blowing agents.
- 6. For sequential reaction/foaming, there is a need to determine how the solubility of the blowing agent varies with extent of branching/cross linking reactions that may lead to large melt viscosity increases.

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