

Parameters Affecting the Chain Extension and Branching of PET in the Melt State by Polyepoxides

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ABSTRACT: This article describes the chemical modification of polyethylene terephthalate (PET) with a variety of compounds containing reactive glycidyl group(s). Four different modifiers, namely, diglycidyl ether of bisphenol-A (DGEBA), *N,N'*-bis[3(carbo-2',3'-epoxypropoxy) phenyl]pyromellitimide (BGPM), triglycidyl glycerol (TGG), and triglycidyl isocyanurate (TGIC) were compared for their reactivity toward PET in the melt phase. It was found that the presence of tertiary nitrogen in the structure of the epoxide modifiers plays the role of in-built catalyst for their reaction with the end groups of PET. TGIC as a modifier was selected for the detailed investigation of the simultaneously occurring degradation and chain extension/branching reactions in a batch-melt mixer. The reactions were followed by torque changes, analyzing the products for residual carboxyl

content, and by determining insoluble content. It is shown that the rate of the reactive modification of PET melt by TGIC depends upon stoichiometry, temperature, rate of shear, and the chemical composition and the molecular weight (MW) of the PET resin. In general, the results indicate an increase in melt viscosity and insoluble content, whereas an overall decrease in carboxyl content occurs, as defined by the choice of mixing conditions and stoichiometry. Analysis of the batch kinetic data can be useful to define the process requirements for carrying out the reactive modification in continuous extrusion equipment. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 643–652, 2003

Key words: PET; chain extension; branching; degradation; polyepoxides; reactive melt modification; batch reactor

INTRODUCTION

Polyethylene terephthalate (PET) is a commercially significant polymer used in the manufacture of fibers, beverage bottles, photographic films, and so on.¹ Most of the available PET resins of relatively low molecular weight (MW) and narrow molecular weight distribution (MWD), including recyclable resins, have rheological properties at processing temperatures that are not compatible with processes, including foaming or extrusion blow molding.^{2,3} Extrusion foaming of PET to low densities (<0.2 g/mL) is of current interest because of its potential usage in packaging, construction, and transportation applications, providing advantages such as high-temperature dimensional stability, good mechanical properties, and recyclability.^{4,5} During the cell growth phase of a foaming operation, the polymeric melt undergoes intense elongational deformations which are not sustained by the typically narrow MWD of most PET resins, characterized by low values of melt viscosity, melt strength, and melt

elasticity.⁵ As a result, uncontrolled cell expansion and unstable growth of bubbles may occur. Increases in zero shear melt viscosity and intrinsic viscosity, improvement in melt strength and die swell along with high shear sensitivity, as well as increase in storage modulus have been related to the observed resistance to bubble coalescence and overall stability of the fine cellular structure during extrusion foaming by gas injection.^{4–6} Improved rheology is associated with increases in MW and MWD as a result of chain extension and branching.^{4–7} Long chain branching has also been suggested to enhance tension-stiffening behavior in elongational flow.⁸

Reactive modification has been defined as an application of traditional reactions of organic chemistry to polymers.⁹ One of the attractive ways of improving melt strength of PET is the use of reactive chain extenders or modifiers such as multifunctional epoxy or anhydride compounds.^{10–11} Epoxies have been identified as one of the most suitable functionalities to interact with the nucleophilic end groups (*viz.*, hydroxyl and carboxyl^{2,11}) present in the polyester. The PET–epoxide system represents a complex set of concurrent reactions (melt degradation and chain extension/branching) with poorly defined reaction kinetics, which provide the initiative for this research. The batch results were analyzed to define conditions for

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subsequent continuous reactive extrusion experiments and one-step extrusion runs involving sequential reactive modification/foaming. Multifunctional epoxides with structures having an electrophilic glycidyl group in the vicinity of a tertiary nitrogen atom have been compared in this article with non-nitrogen-containing structures. The modification reactions were evaluated on the basis of rate of torque increase, reaction temperature, stoichiometric amount of modifier added, chemical composition of PET, carboxyl group content, insoluble content in the reacted product, and rate of mixing in the batch mixer.

EXPERIMENTAL

Materials

High molecular weight PET (HPET)–Rhopet S78 (Rhodia Ster, S.A., Sao Paulo, Brazil) with nominal intrinsic viscosity (I.V.) of 0.78 and measured pellet carboxyl content (CC_p) of 27.4 equiv/ 10^6 g was used. The reported hydroxyl content was 62 equiv/ 10^6 g.¹²

Medium molecular weight PET (MPET) with nominal I.V. 0.58 (Scientific Polymer Products, Ontario, NY) and measured CC_p of 23.5 equiv/ 10^6 g was used.

The following diepoxides containing glycidyl functionality: laboratory synthesized *N,N'*-bis[3(carbo-2',3'-epoxypropoxy) phenyl] pyromellitimide (BGPM), with a melting point of 270°C,¹¹ and diglycidyl ether of bisphenol-A (DGEBA; EPON 828[®]), CAS No. 25068-38-6 (Sigma-Aldrich, St. Louis, MO) were used.

The following triepoxides containing glycidyl functionality: triglycidyl isocyanurate (TGIC), CAS No. 2451-62-9 (Sigma-Aldrich)^{9,13} and triglycidyl glycerol (TGG), CAS No. 25038-04-4 (Polysciences Inc., Warrington, PA) were used.

Structures and important physical properties of the modifiers are given in Figure 1 and Table I, respectively. With the exception of BGPM, all other modifiers were commercially available materials.

Processing

Melt modification of PET resins was carried out in an intensive batch mixer (Brabender Plasticorder PL2000[®]) on predried materials under nitrogen blanket, to minimize the possibility of hydrolytic and thermooxidative degradation. In a typical experiment, ~ 56.3 g of PET pellets, dried overnight to < 0.01 wt % moisture at 120°C (to minimize hydrolytic degradation), was first added in an intensive mixer heated at a preset chamber temperature and ~ 6 min 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

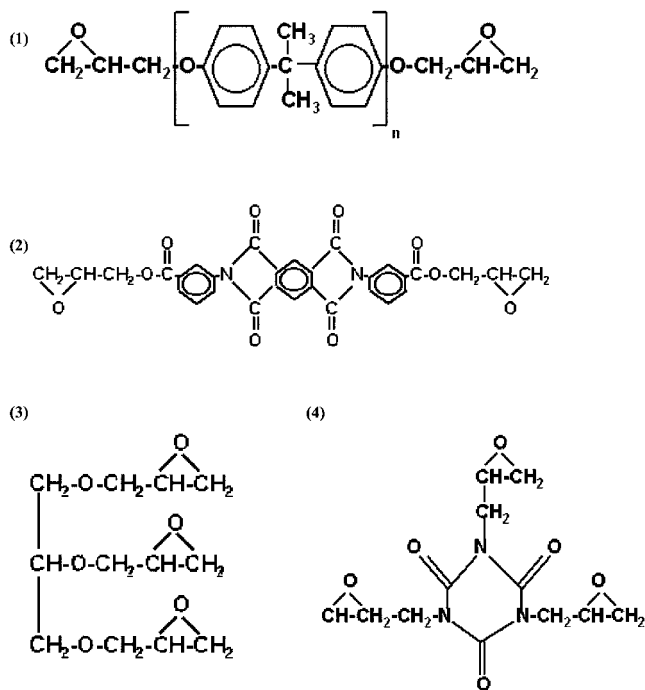


Figure 1 Chemical structures of modifiers: (1) diglycidyl ether of bisphenol-A (DGEBA); (2) *N,N'*-bis-[3(carbo-2',3'-epoxypropoxy) phenyl] pyromellitimide (BGPM); (3) triglycidyl glycerol (TGG); and (4) triglycidyl isocyanurate (TGIC).

9 min. The effects of temperature and stoichiometric addition of TGIC on the overall rate of modification were investigated by setting the chamber temperature at 270, 285, and 300°C and by varying the amount of addition by 0.5X, 1X, and 1.5X (X = times stoichiometric amount) based on the initial carboxyl content (CC_0), while maintaining the rate of mixing at 60 rpm. Due to the exothermic nature of the reactions and as a result of shear heating, melt temperatures during processing increased by ~ 5–7%. The effect of rate of mixing on the overall modification rate was examined by setting the rotor speed at 40, 60, and 80 rpm.

Characterization

Carboxyl content (CC) of the PET resins before and after processing in the batch mixer was determined according to Pohl's method¹⁴ by titrating offline 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 offline by dissolving the samples in hexafluoroisopropanol (HFIP) at room temperature. After 24 h, the solution was filtered by using a 1- μ m filter and the residue was washed with the solvent and then dried under vacuum for 48 h at room temperature. Differences in weight measurements were used to determine the insoluble content. Isothermal thermogravimetric anal-

TABLE I
Characteristics of Modifiers

| Modifier | Molecular weight (MW) | Physical form | Functionality | Reported M.P./ [B.P] (°C) | Isothermal TGA thermal stability ^a |
|-------------------|-----------------------|--------------------|---------------|--------------------------------|---|
| DGEBA (diepoxide) | 348 (Average) | White powder | Di- | 283–286 [397–400] ^b | 90.9 |
| BGPM (diepoxide) | 569 | Yellow powder | Di- | 270 ^c | 99.8 |
| TGG (triepoxide) | 260 | Clear brown liquid | Tri- | Not available | 75.6 |
| TGIC (triepoxide) | 297 | White powder | Tri- | 100 ^c | 88.8 |

^a Wt. % residual following heating to 270°C for 240 s and held for 400 s under nitrogen.

^b Suppliers data.

^c Measured.

ysis (TGA) of the modifiers was carried out by using a Model QA 50 (TA Instruments) analyzer in a nonpressurized system under nitrogen blanket for a total time of ~ 19 min; 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 wt loss % was monitored.

RESULTS AND DISCUSSION

Process stability of PET in a batch mixer

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 2. After an initial melting period, torque decreased noticeably for HPET as a result of degradation reactions. Difference in torque levels in HPET and MPET could be due to the comparatively lower initial molecular weight of MPET, as indicated by their respective intrinsic viscosities, or effects of different comono-

mers or stabilizers. 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 (see below).

Figure 3 shows the thermal degradation reactions that are believed to occur during melt processing of PET.¹⁵ Other degradation mechanisms of PET, namely hydrolytic and thermooxidative, are considered to be negligible under the selected experimental conditions. More details about PET degradation are given by Yoda et al.¹⁵ In the case of thermal degradation, at first, random scission of PET chain takes place, initiated by chain cleavage forming carboxylic end groups and vinyl esters, aldehydes, and carbon dioxide.¹⁵ Yoda further suggested that vinyl esters accumulate to a certain concentration and then react with polyester chains, resulting in extension/branching/crosslinking and acetaldehyde generation. Through end-group degradation, additional carboxylic 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 crosslinking while forming a soft gel-like material.¹⁵ Transesterification reactions may also be important as well as subsequent reactions with the hydroxyl end groups of the polyester.¹⁶ In general, thermal degradation of PET results in an increase in carboxyl content and a decrease in hydroxyl content.^{4,17} Thus, changes in the instantaneous concentration of PET end groups available for reaction with the present modifiers and formation of crosslinked structures is anticipated; these complex degradation phenomena lead to an overall decrease in melt viscosity and reduction in molecular weight.

Most of the work presented in this article was carried out by using HPET. Figure 4 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 lowered torque curves (300°C < 285°C < 270°C). Corresponding temperature curves are also shown in the upper half of the figure. Figure

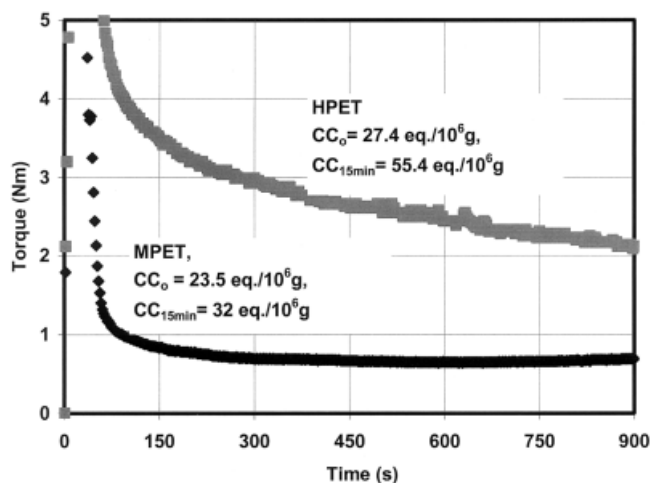
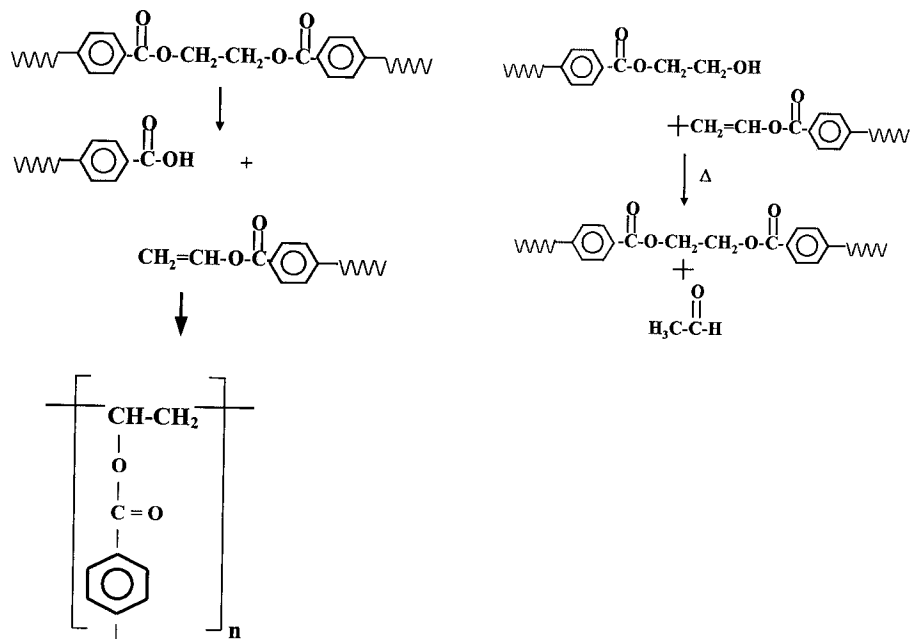


Figure 2 Torque evolution in an intensive batch mixer for HPET (nominal I.V. = 0.78) and MPET (nominal I.V. = 0.58) at chamber temperature = 270°C, 60 rpm. Initial pellet carboxyl content (CC_p or CC₀) and carboxyl content at 900 s (CC_{15 min}) are also shown.

Chain Cleavage Degradation



End Group Degradation

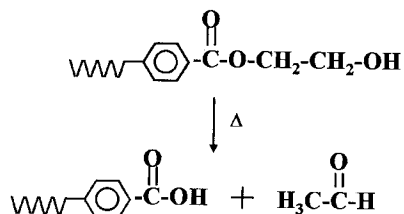


Figure 3 PET thermal degradation reactions.

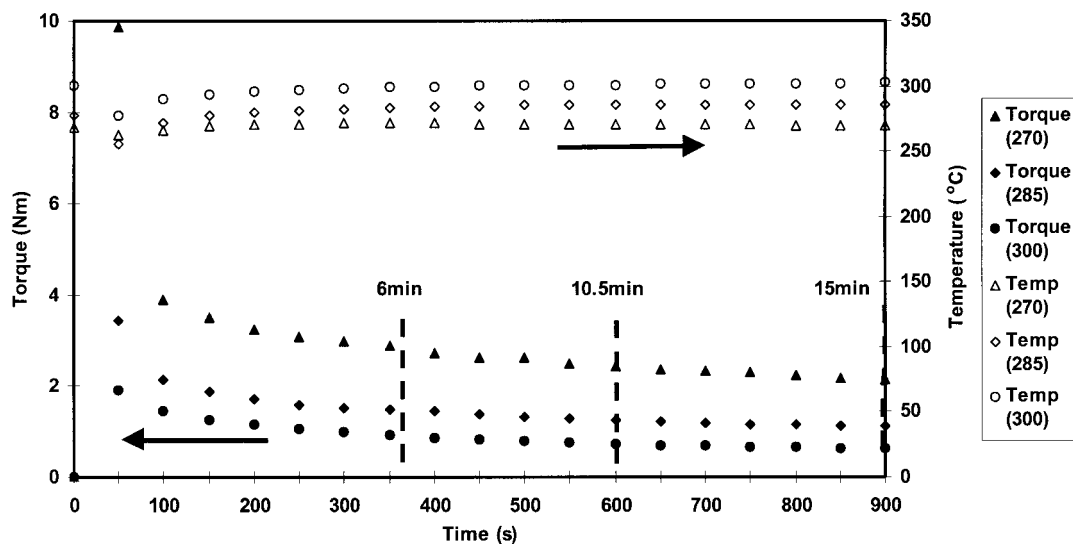


Figure 4 Blank HPET torque/time and temperature/time runs at 270, 285, and 300°C chamber set temperatures.

TABLE II
First-Order Rate Constants for Torque Decrease in the
Batch Mixer at 60 rpm, at Various Chamber
Temperatures During HPET Control Runs

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

4 suggests that about 6 min 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.

The kinetics of the degradation reactions of PET were analyzed by treating the initial torque/time data (between 6 and 10.5 min) from Figure 4, in the form of rate expressions analogous to those derived in chemical kinetics. Six minutes corresponding to an initial torque value represented the time of addition of the reactive modifiers as will be shown below. The first-order rate equation:

$$-d\tau/dt = k\tau \quad (1)$$

where τ is the torque (Nm) proportional to melt viscosity and consequently to molecular weight, t is time (s), and k is the rate constant (Nm s⁻¹) 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 II indicate the expected effect of temperature on rate of MW reduction.

For the rate study, the experiments were stopped at the end of a residence time of 15 min, the time corre-

sponding to severe degradation becoming visible through the yellowish shade of the cooled melt from the mixer.¹⁸ As also reported earlier, degradation was accompanied by an overall real time increase in the carboxyl content.^{4,16,17} Data for three time intervals and three temperatures are shown in Figure 5. As anticipated, an increase in the melt mixing temperature resulted in the formation of a 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 the access of the neutralizing species to the entrapped carboxyl groups and, thus, result in incorrect experimental CC values.

Thermal stability of the modifiers

The experimental reaction/melt temperatures (270–300°C) were equal to or higher than the known melt temperatures of the five modifiers listed in Table I. TGA of the five additives at a typical process temperature (270°C) showed significant differences in their thermal characteristics (Fig. 6). 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 min 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.

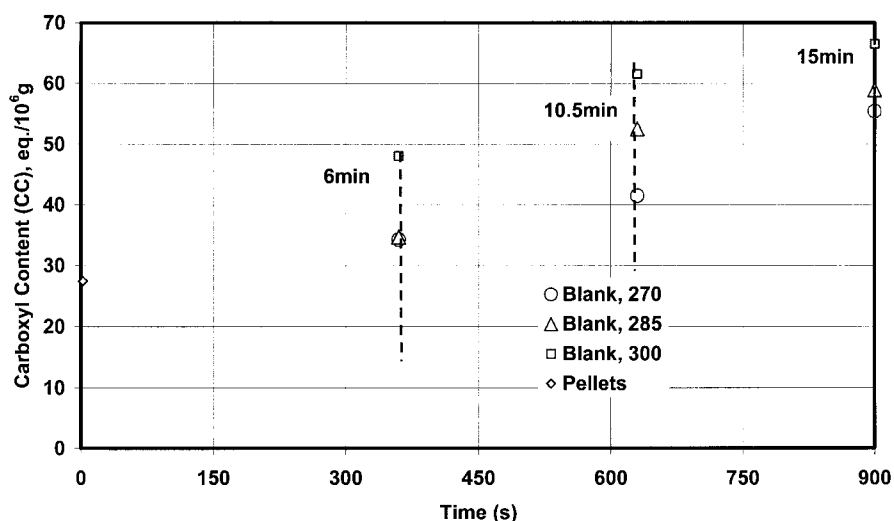


Figure 5 Carboxyl content versus time data at 270°C (○), 285°C (△), and 300°C (□) for melt-processed HPET. Data for unprocessed pellets, $t = 0$ s (◇) are also shown.

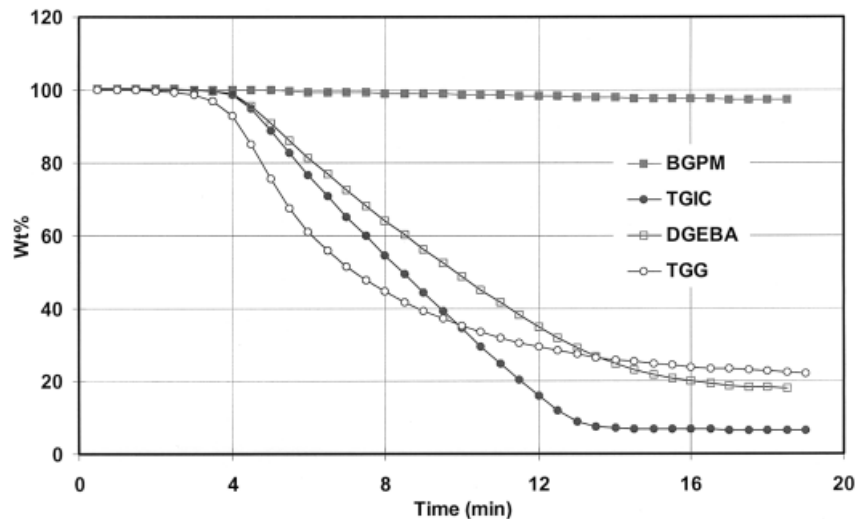


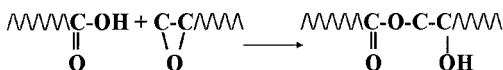
Figure 6 Isothermal TGA data at 270°C of reactive modifiers (total time of the test 19 min = initial heating ramp of 4 min from room temperature to 270°C + heating under nitrogen blanket for 15 min).

Reactions of modifiers

Figure 7 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.⁴ 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 Figure 7. 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.^{4,17} On the basis of this assumption, the theoretical modifier amount for the reaction was calculated from^{4,19}:

$$\text{Wt \%} = (\text{MW} \times \text{CC}) / (f \times 10^4) \quad (2)$$

Esterification



Etherification

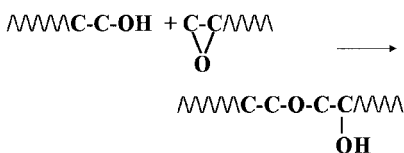


Figure 7 Initial reactions between PET end groups and epoxy-containing modifiers under operating conditions.

where MW is the molecular weight of the modifier, CC is the initial (CC_p or CC_0) or instantaneous (CC_t) carboxyl content of the polyesters in equiv/ 10^6 g, and f is the functionality of the epoxide. Note that the real time formation of CC as a result of degradation would unbalance eq. (2). Thus, theoretically, an amount of modifier in excess of stoichiometry (based on CC_0) 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 crosslinked structures may be formed.

Runs in Figures 8 and 9 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 eq. (2) based on the initial pellet carboxyl group content (CC_0) actually corresponded to 0.8X stoichiometry if the calculations were based on $\text{CC}_{6 \text{ min}}$ 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 tertiary amine functionality as an in-built catalyst in the vicinity of the glycidyl group in the structure of epoxides. Tertiary amines are known catalysts for the epoxy/carboxyl or epoxy/hydroxyl reactions.^{20–22} Note that the trifunctional epoxide (TGIC) results in an increase in the evolution of torque up to 900 s, whereas for the difunctional modifier (BGPM), torque reaches a maximum at about 600 s, decreasing thereafter, possibly due to degradation.⁴ It is of interest that Huang et al.

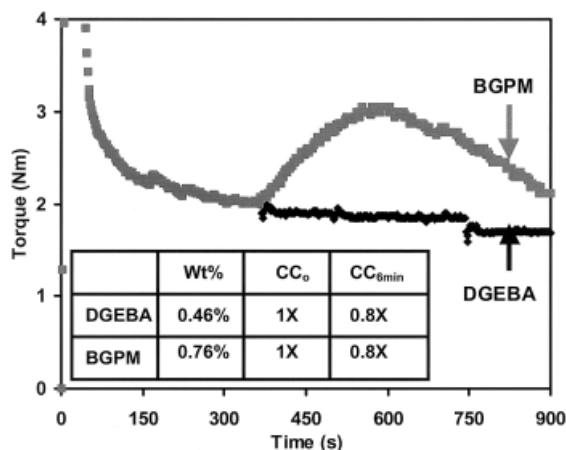


Figure 8 Effect of type of diepoxide on torque versus time curves for HPET at 270°C and 60 rpm. Stoichiometries of DGEBA and BGPM based on initial carboxyl content (CC_p or CC₀) and carboxyl content at the time of modifier addition (CC_{6 min}) are shown.

studied mixtures of DGEBA and PET in the absence of a catalyst by differential scanning calorimetry and suggested the possibility of interchange reactions as shown by an increase in glass transition temperature, at concentrations of DGEBA exceeding 20 wt %.²³

Reactions of TGIC with HPET and MPET

Figure 10 shows HPET/TGIC torque-time data at different stoichiometries, at 60 rpm and at a chamber temperature of 300°C. The experiments were stopped when the chamber temperature was increased by >3% from the set temperature because of frictional effects and the exothermic nature of the reaction. Stoichiometric amounts were based on CC₀ and CC_{6 min}. 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 upward, suggesting increasing reaction rates and increased molecular weight as a result of chain extension/branching reactions. Branched structures with long chains offer increased resistance to flow as a result of entanglements. As anticipated, the percentage increases in torque from the baseline were increasing functions of the stoichiometric amount of the epoxide added and the melt temperature. When the amount of modifier is increased to 1.5 times, the stoichiometric amount based on CC₀, material processibility became extremely difficult. Hence, 1.5X approximately defines an upper bound for retaining a limited degree of thermoplasticity.

In Figure 11, two types of PET, namely, HPET and MPET, are compared for the same stoichiometric concentration of TGIC on the basis of CC₀. 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 (Fig. 2). 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 Figure 3.

Figure 12 shows the variation of CC of HPET processed for 15 min of processing at 270, 285, 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 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 1- μ m-size filter is shown in Figure 13. 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

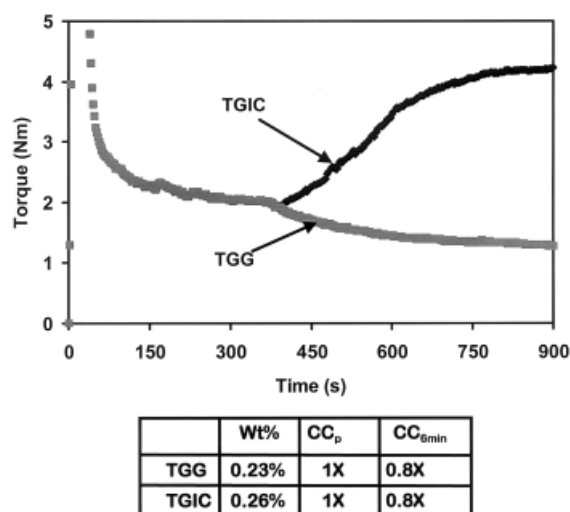


Figure 9 Effect of type of triepoxide on torque versus time curves for HPET at 270°C and 60 rpm. Stoichiometries of TGG and TGIC based on initial carboxyl content (CC_p or CC₀) and carboxyl content at the time of modifier addition (CC_{6 min}) are shown.

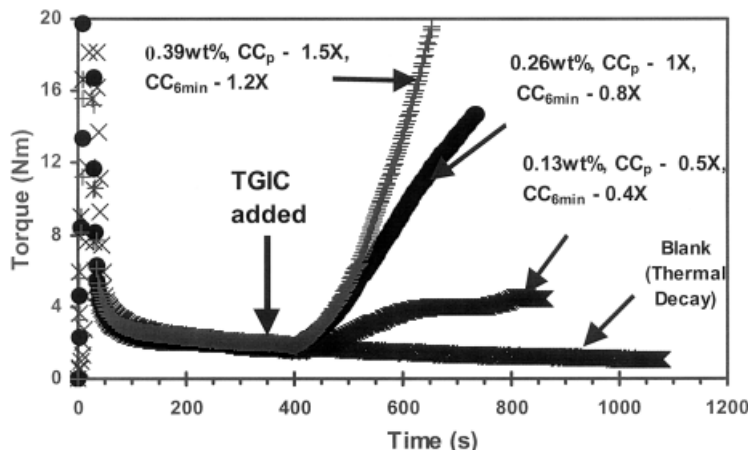


Figure 10 Effect of TGIC concentration on torque/time curves for HPET at 60 rpm, and set chamber temperature = 300°C. Stoichiometries based on initial carboxyl content (CC_p or CC_0) and carboxyl content at the time of modifier addition ($CC_{6\text{min}}$) are shown.

modifier contained a certain amount of insolubles as a result of branching/crosslinking resulting from degradation. 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 13 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 12.

Figure 14 shows the effect of mixing speed on the torque development of HPET after TGIC was added at about 360 s. It is noticed that at 40 rpm, the torque is increasing continuously with time, indicating unfinished modification up to 900 s. In this case, it is apparent that chain extension/branching reactions are the dominating mechanism. In the case of 60 rpm, the

torque reached a plateau at about 900 s, 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 postplateau period. During the postmodifier addition period (after 360 s), the torque/time slope increased with increasing 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.

The 80 rpm curve from Figure 14 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.⁵ on tetraglycidyl diamino diphenyl dimethane (TGDDM) modification of PET where two different peaks were reported. The first peak was claimed to be due to reaction between

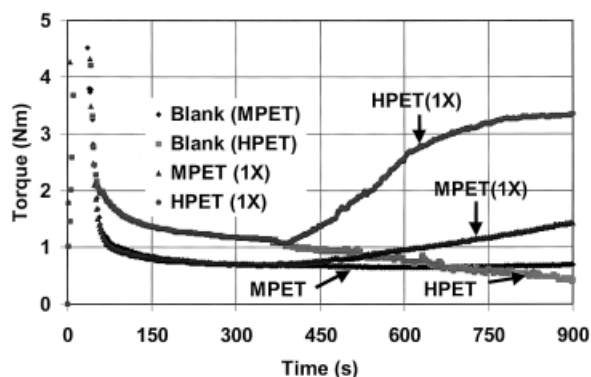


Figure 11 Effect of type of PET on torque/time curves obtained through the addition of 1X stoichiometric TGIC amount based on CC_0 . Set chamber temperature = 270°C, 60 rpm.

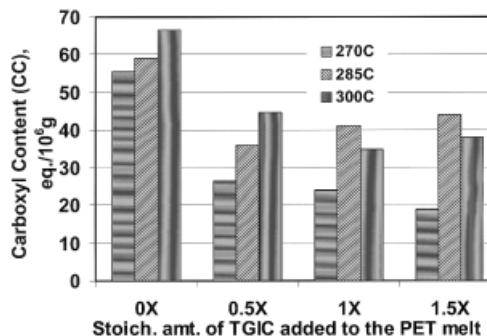


Figure 12 Variation of CC of HPET measured after 15 min processing versus amount of TGIC added at different process temperatures (stoichiometry is based on initial pellet carboxyl content).

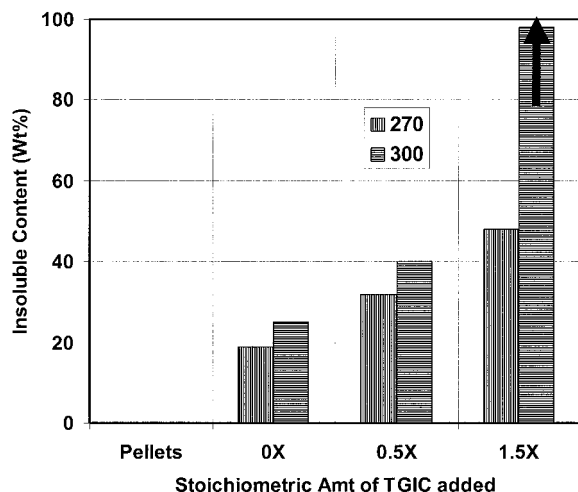


Figure 13 Insoluble content of the HPET at the end of melt mixing for 15 min at 60 rpm and two chamber temperatures (270 and 300°C) with and without TGIC. Data are compared to those of unprocessed pellets.

carboxyl and glycidyl groups and the second higher peak was claimed to be due to reaction between hydroxyl and glycidyl groups. Because of the complexity associated with hydroxyl groups determination,⁴ no attempt was made in this work to verify the extent of reaction between hydroxyl end groups or secondary hydroxyl groups, with epoxy functionalities.

Estimation of rate of HPET modification by TGIC

In the current 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 reac-

tions. 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 360 and 630 s) obtained at different temperatures and stoichiometries were also found to follow the first-order rate equation:

$$d\tau/dt = k\tau \quad (3)$$

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.¹⁶ The authors have used an elaborate gel permeation chromatography (GPC) apparatus modified with multiple detectors with dichloromethane/HFIP/tetra ethyl ammonium chloride as an eluant 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 compatibility of PET solvents with the stationary phase.

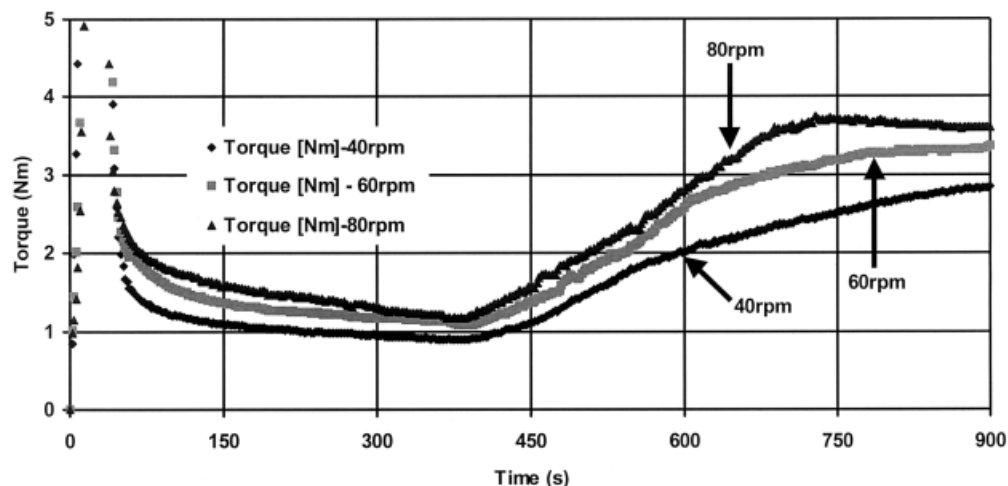


Figure 14 Effect of rpm on torque/time curves of HPET reacted with TGIC at set chamber temperature = 270°C, 0.26 wt % of TGIC, CC_p , 1X, $CC_{6 \text{ min}}$, 0.8X.

TABLE III
First-Order Rate Constants for Torque Increase in the Batch Mixer at Various
Reaction Conditions of HPET with TGIC

| Stoichiometric amount of TGIC added (based on CC _{6 min}) | Reaction temp. = 270°C (Nm s ⁻¹) | Reaction temp. = 285°C (Nm s ⁻¹) | Reaction temp. = 300°C (Nm s ⁻¹) |
|---|--|--|--|
| 0.5× | 0.0018 | 0.0018 | 0.0058 |
| 1× | 0.0022 | 0.0040 | 0.0112 |
| 1.5× | 0.0030 | 0.0066 | 0.0090 |

From Table III it is evident that the calculated rate constants (k) increase with temperature and amounts of TGIC. The estimated reaction half-lives based on these k values range between 60 and 90 s. 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 in an estimated a total residence time of about 7–10 min.

CONCLUSION

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 on the basis of 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, rate of shear, and the chemical composition of the polyester resin. The lower MW PET shows overall less activity toward TGIC, possibly due to differences in the evolution of additional end-group contents. 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.

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