

Viscoelastic Characteristics of Chain Extended/Branched and Linear Polyethylene Terephthalate Resins

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ABSTRACT: Two chemically modified chain extended/branched polyethylene terephthalate (PET) resins and one unmodified resin, considered to be linear, were characterized in terms of their melt flow, die swell, and viscoelastic properties. The three resins had reportedly similar nominal intrinsic viscosities but exhibited different viscoelastic behavior. The modified resins had lower melt flow index, higher die swell, higher complex viscosity and higher storage modulus than the unmodified one. The Cole–Cole plots of the resins were independent of temperature, and the data for modified resins formed a group that lay below the data group for the unmodified PET. The distribution of relaxation times was determined. The modified resins had higher relaxation strength, G_i , especially at high relaxation times, λ_i . The mean relaxation times of the chain extended/branched resins were approximately an order of magnitude higher than that of the unmodified resin, implying pronounced elastic character. The modified resins had better foaming characteristics in extrusion foam processing than the unmodified one owing to their elastic nature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1371–1377, 2000

Key words: PET; chain extension/branching; foam; elasticity; relaxation time

INTRODUCTION

Most available polyethylene terephthalate (PET) resins of relatively low molecular weight (MW) and narrow molecular weight distribution (MWD) have rheological properties at processing temperatures that are not conducive to applications such as foaming or extrusion blow molding. Effects related to melt viscoelasticity of thermoplastics can, in general, be controlled through additives, or through changes in MW and MWD during re-

actor/postreactor processing by chain extension, grafting, branching, controlled cross-linking, or controlled degradation.¹ Modified PET resins with increased MW, viscosity, and melt strength/elasticity can be produced through chain extension/branching reactions, primarily between the carboxyl/hydroxyl polyester end groups and di- or polyfunctional reagents containing anhydride, epoxy, oxazoline, isocyanate, carbodiimide, hydroxyl, tertiary phosphite, phthalimide, and other groups.² 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 nonlinear counterparts. Changes

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in melt elasticity have been related to changes in the values of viscoelastic functions such as normal stress differences, storage modulus, and parameters of practical importance such as extrudate swell^{3–5}; also, for certain polymers, changes in melt elasticity have been related to extensional viscosity⁶ and melt strength, the latter being related qualitatively to extensional rheology.⁴

Rheological modification of PET may be carried out: 1) during polycondensation, 2) by solid stating in the presence of premixed modifier or, 3) by postreactor modification via reactive extrusion. Common polyester modifiers listed in the open and patent literature include polyanhydrides, such as pyromellitic dianhydride (PMDA), (see for example, Refs. 7–11) and polyepoxides, such as diglycidyl esters or copolymers containing glycidyl functionality (see for example, Refs. 11–17). A suggested reaction mechanism¹⁸ with PMDA involves as a first step linear extension through reaction of terminal polyester hydroxyl end groups with the anhydride functionalities and the formation of two carboxyl groups per incorporated PMDA moiety. Subsequent reactions may involve all functionalities of the PMDA molecule through esterification and transreactions to yield branched or even cross-linked structures. Chain-extension reactions with the glycidyl functionality include esterification of carboxyl end groups and etherification of hydroxyl end groups; secondary hydroxyls formed from these reactions may further react with carboxyl or epoxy groups leading to branching or cross-linking.^{16,17}

There are only few cases where complete rheological data of foamable vs nonfoamable resins are reported. Parameters of importance are usually presented as single point, single temperature, and single shear rate values that are more appropriate for quality control purposes. It is among the objectives of the present work to completely characterize for dynamic mechanical properties two PET resins that are chemically modified with different multifunctional reactants and compare with an unmodified resin with similar nominal intrinsic viscosity. Our earlier work with two of these resins showed significant differences in their foaming behavior during extrusion processing in the presence of physical blowing agents. This work is part of a broader research effort to identify potential applications of postconsumer recyclable PET as the foamed core in laminates for building and construction applications.

EXPERIMENTAL

PET Resins

The following resins were evaluated:

1. Unmodified PET designated as PET-U: Thermoformable APET grade (Traytuf 9506, Shell Chemical Co., Akron, OH); the resin is considered to be linear, with nominal intrinsic viscosity (IV) of 0.95 as reported by the manufacturer.
2. Anhydride modified PET designated as PET-MA: Experimental grade, (Sinco Engineering, Pozzilli, Italy), based on post-consumer bottle material and chemically modified by solid stating in the presence of PMDA.⁸ Nominal IV was reported to be 0.95 after modification¹⁹; details on the insoluble content of the resin and its effect on IV were not available.
3. Epoxy modified PET designated as PET-ME: This resin was produced by reacting postconsumer bottle PET (nominal IV 0.71, Wellman), with 1% by weight of a diepoxide kindly supplied by Karayannidis and Bikiaris.^{16,17} IV of the modified resin was measured in phenol/tetrachloroethane 60/40 w/w solvent at a polymer concentration of 1% and was calculated to be 0.93 by using the Solomon-Ciuta equation in a single point measurement.²⁰ The diepoxide with terminal epoxy end groups used in compounding was *N,N'*-bis[3(carbo-2',3'epoxypropoxy)phenyl] pyromellitimide (MW 569 and MP 270°C), and was synthesized by the reaction of a diimido-diacid [*N,N'*-Bis(3-carboxyphenyl) pyromellitimide] with epichlorhydrin using benzyltrimethylammonium chloride as catalyst (details may be found in Ref. 17). PET-ME was prepared in our laboratories as follows: preweighed dried PET pellets were first added in the Brabender intensive batch mixer (model PL2000) followed after 6 min by 1 wt % diepoxide (25% excess versus the theoretical amount for complete reaction with carboxyl groups).^{16,17,20} Mixing/reaction continued for an additional 10 min under nitrogen atmosphere at 60 rpm and bowl temperature of 280°C.

Characterization

Dynamic mechanical properties of all three resins were determined in a Rheometrics Mechanical

Table I Effect of PET Resin Rheology on Foam Quality^a

Resin	Nominal IV	MFI (260°C/2.16 kg)	Die Swell (270 s ⁻¹ /260°C)	Foam Quality
PET-MA	0.95	4.38	2.86	Good, uniform; high die swell; density 0.12 g/cc fine cell structure, average size 150 μm
PET-U	0.95	10.4	1.39	Poor foam/little expansion/large bubbles
PET-ME	0.93	—	—	—

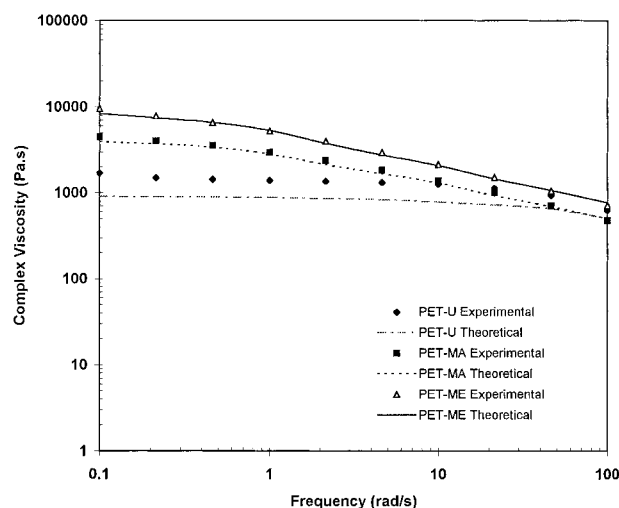
^a Extrusion foaming by CO₂ injection in 3-mm rod die.^{21,22}

spectrometer (RMS 800) in a parallel disk mode. All samples were predried to less than 100 ppm moisture and molded into 25.4 mm (diam) by 1.5 mm (thick) disks. All measurements were conducted at 280°C (and for some resins at 290°C) under nitrogen. Dynamic moduli and complex viscosity were measured as a function of frequency.

Melt flow index and die swell data, (as indicators of melt viscosity and elasticity, respectively), of the unmodified and one of the chemically modified resins were determined earlier^{21,22} and are summarized in Table I along with their extrusion foaming characteristics in rod dies. A single extrusion line equipped with a rod die was used with CO₂ as the blowing agent.^{21,22} Foaming of PET-ME was not attempted, because the die-oxide was only available in small quantities; for the same reasons, melt flow index (MFI) and die swell for the PET-ME resin were not measured.

RESULTS AND DISCUSSION

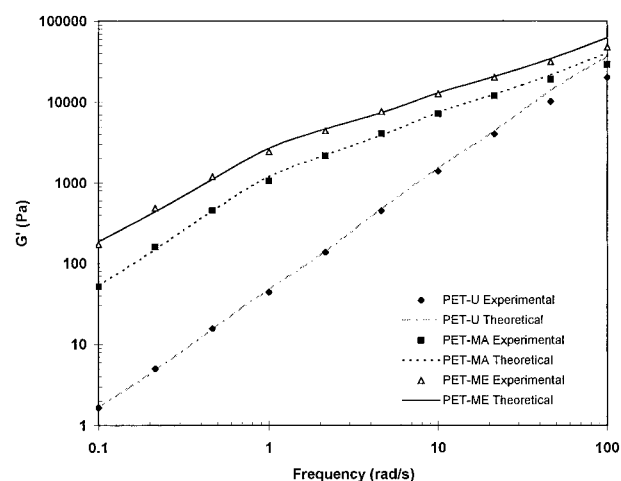
Figures 1–3 contain experimental complex viscosity, storage modulus, and loss modulus vs fre-

**Figure 1** Complex viscosity versus frequency.

quency data for the three resins (PET-U, PET-MA, and PET-ME) along with the theoretical predictions outlined later.

All three resins exhibit Newtonian behavior at low frequencies. However, the Newtonian plateau extends to high frequencies for the unmodified resin PET-U. The plateau deviates from Newtonian behavior at smaller frequencies for the modified PET-MA and PET-ME resins consistent with molecular interpretations. Higher negative slopes of complex viscosity vs frequency curves of the modified resins are indicative of chain branching and higher MWD. Ranking of the resins in terms of complex viscosity, (η^*) at low frequencies is in agreement with their ranking in terms of melt flow index (see Table I).

With regard to storage modulus (Fig. 2), the unmodified resin PET-U has the lowest G' , followed by the modified resin PET-MA, whereas PET-ME has the highest storage modulus. This implies that the elasticity of the resins can be ranked as PET-U < PET-MA < PET-ME. Note the difficulty in foaming to low densities (Table I) the unmodified PET-U resin with the low elastic modulus and low die swell.

**Figure 2** Storage modulus versus frequency.

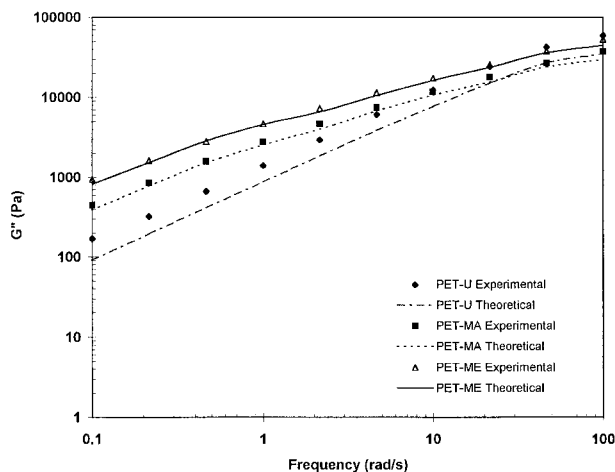


Figure 3 Loss modulus versus frequency.

Figure 3 shows the dependence of loss modulus on frequency. At low frequencies, in the terminal zone, G'' is proportional to frequency for all three resins. The order of the loss modulus is $\text{PET-U} < \text{PET-MA} < \text{PET-ME}$ in the terminal zone. However, because the slopes of the modified resins PET-MA and PET-ME are smaller starting at approximately 1 (rad/s) due to non-Newtonian effects, there exists a crossover at high frequencies.

Oscillatory shear data were also obtained at 290°C for PET-U and PET-MA, but are not shown here. The data at 290°C are qualitatively similar to the data at 280°C, implying that the data can be shifted horizontally, as practiced in the literature for other polymer melts.

In Figure 4, the data are shown in terms of Cole–Cole²³ plots, i.e., loss modulus vs storage modulus. The data obtained for two resins at 290°C are also included. Essentially, two groups of data are observed that are independent of temperature. The higher group consists of data for the unmodified PET-U resin, whereas the lower group is comprised of the data for the modified resins. The independence of the Cole–Cole plot on temperature provides further proof that the G' and G'' data at different temperatures can be shifted along the frequency axis to produce a master curve.

In general, Figure 4 shows that the modified resins are more elastic than the unmodified ones, because for a given value of G'' they have higher G' values. Cole–Cole plots have been discussed for various polymer melts in Nakajima and Harrell.²⁴ It was concluded that branched and high MWD polymers have Cole–Cole plots that lie lower in comparison to polymers that are linear and have low MWD. Higher molecular weight also results in shifting of the mentioned curves to lower values. However, it was shown that the effect of higher molecular weight is not as strong as the effects of branching and MWD. Similar observations are made in this study, because the modified PETs have higher degree of branching, higher MW, and higher MWD than the unmodified resin.

Figure 4 contains a line indicating the values for which $G' = G''$. Although our data, especially those for the modified resins, approach to the line

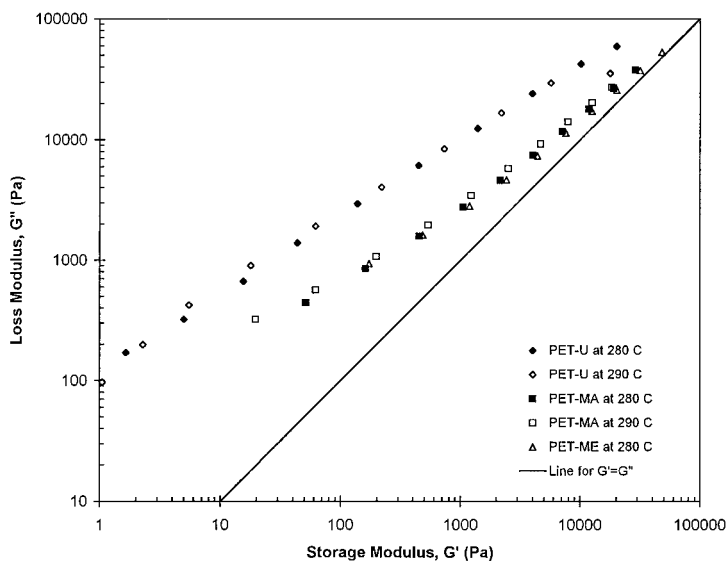


Figure 4 Cole–Cole plot for the PET resins.

at higher G' , i.e., at high G'' or frequency, there is no crossover in the range of the frequencies studied. The occurrence of a crossover has been used as a measure of polydispersity and breadth of MWD for polyolefins.²⁵

Relaxation Times Distribution

In an attempt to characterize the resins further, the distribution of relaxation times is calculated and various molecular parameters are evaluated. The Boltzmann superposition principle describing linear viscoelastic behavior can be given as²⁶:

$$\tau(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt' \quad (1)$$

where τ is the shear stress, $G(t)$ is the linear relaxation modulus and $\dot{\gamma}$ is the shear rate.

The most popular approach to describe the behavior of polymer solutions and melts in linear viscoelastic experiments is the generalized Maxwell Model.²⁷ The function used in this model is:

$$G(t-t') = \sum_{i=1}^N G_i \exp[-(t-t')/\lambda_i] \quad (2)$$

where G_i is the relaxation strength and λ_i the relaxation time. They are determined as N pairs from discrete experimental data.

From oscillatory shear experiments the model parameters (G_i , λ_i) can be determined by using the following equations²⁸:

$$G'(w_j) = \sum_{i=1}^N G_i \frac{(w_j \lambda_i)^2}{1 + (w_j \lambda_i)^2} \quad (3)$$

$$G''(w_j) = \sum_{i=1}^N G_i \frac{w_j \lambda_i}{1 + (w_j \lambda_i)^2} \quad (4)$$

Here, w_j refers to the experimental frequency.

In this study, the linear least squares method²⁹ was used in order to obtain the relaxation time and the relaxation strength. N sets of model parameters, (G_i , λ_i) were determined by using the experimental sets of data [$G'(w_j)$, $G''(w_j)$] with eqs. (3) and (4) given above.

Logarithmically distributed N values of λ_i were chosen within the range of experimental

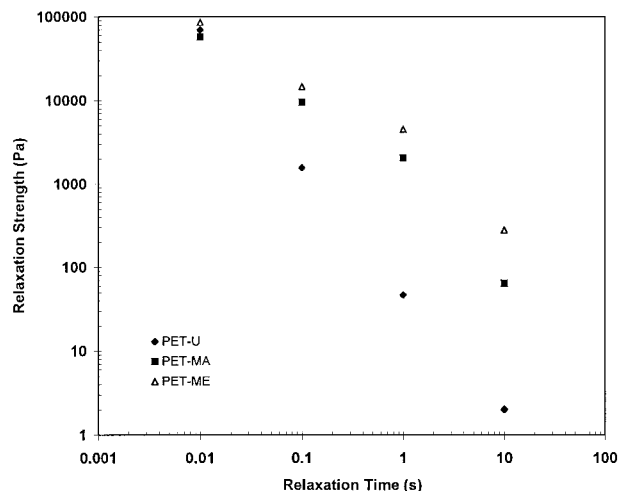


Figure 5 Discret distribution of relaxation times.

frequencies. The values of λ_i were taken as $1/w_j$ within the experimental frequency range. The least squares principle was applied in order to determine the values of G_i .²⁹ The following sum in eq. (5) was calculated:

$$\sum_{j=1}^M \left[\left(\sum_{i=1}^N \frac{1}{G'(w_j)} G_i \frac{(w_j \lambda_i)^2}{1 + (w_j \lambda_i)^2} - 1 \right)^2 + \left(\sum_{i=1}^N \frac{1}{G''(w_j)} G_i \frac{w_j \lambda_i}{1 + (w_j \lambda_i)^2} - 1 \right)^2 \right] = S \quad (5)$$

The sum of the squares of the errors, S , can be minimized by differentiating S with respect to each G_i . The equations obtained from the differentiation can be solved numerically³⁰ by using singular value decomposition (SVD) that is commercially available as a software package program.

Relaxation times and strengths determined from oscillatory shear data are shown in Figure 5 for the resins studied. The relaxation strength decreases with increasing relaxation time for all the resins. Except for the relaxation time of 0.01 s, the order of G_i at a given relaxation time is as follows: PET-U < PET-MA < PET-ME. The modified resins have higher relaxation moduli than the unmodified one especially at high relaxation times owing to the pronounced elastic behavior. In fact, the log G_i versus log λ_i plots for the modified resins have shoulders. The distributions of relaxation times are similar in shape at

290°C for resins PET-MA and PET-U (data not shown); however the curves at 290°C are placed lower than the data at 280°C implying lower G' , G'' , and complex viscosity values at higher temperatures.

The values of G' , G'' , and complex viscosity were calculated from eqs. (3), (4), and (6), respectively.

$$\eta^* = ((G'/\omega)^2 + (G''/\omega)^2)^{0.5} \quad (6)$$

The theoretical values are plotted in Figures 1–3. Agreement between theory and experiment is particularly good for G' , G'' , and η^* for the modified resins and for G' for the unmodified resin. In order to compare the viscoelastic properties of the three resins the following parameters were calculated as follows:

Zero shear viscosity, η_0 , from

$$\eta_0 = \sum \lambda_i G_i \quad (7)$$

Plateau modulus, G_N^0 , from

$$G_N^0 = \sum G_i \quad (8)$$

Mean relaxation time, $\langle \lambda \rangle$, from

$$\langle \lambda \rangle = (\sum \lambda_i^2 G_i) / (\sum \lambda_i G_i) \quad (9)$$

Entanglement density, ϑ_e , from

$$\vartheta_e = \rho_a / M_e \quad (10)$$

in which ρ_a is the amorphous density taken as 1.308 g/cc.

The molecular weight between the entanglements, M_e , is given by:

$$M_e = \rho RT / G_N^0 \quad (11)$$

where ρ is the melt density taken as 1.211 g/cc, R is the ideal gas constant and T is the absolute temperature.

Table II shows the calculated values of the zero shear viscosity, plateau modulus, mean relaxation time and entanglement density. The order of zero shear viscosity is PET-U < PET-MA < PET-ME that for the first two resins is also in accordance with the measured MFI values.

Entanglement density and plateau modulus, i.e., parameters related to high frequencies, are

Table II Calculated Viscoelastic Characteristics of the PET Resins

	PET-U	PET-MA	PET-ME
η_0 (Pa.s) $\times 10^{-3}$	0.92	4.25	9.64
G_N^0 (Pa) $\times 10^{-5}$	0.72	0.70	1.06
$\langle \lambda \rangle$ (s)	0.29	2.03	3.40
ϑ_e (gmol/cc) $\times 10^5$	1.72	1.67	2.52

approximately the same for PET-U and PET-MA. PET-ME has a higher plateau modulus and entanglement density than the other two resins. The mean relaxation times have the order PET-U < PET-MA < PET-ME. The modified resins have mean relaxation times that are approximately an order of magnitude higher than the respective value for the unmodified one, i.e., the modified resins are significantly more elastic than the unmodified one. This is related to the demonstrated improved foamability of PET-MA and the anticipated favorable foaming characteristics of PET-ME.

CONCLUSIONS

Chain extended/branched PETs are characterized by their low MFI, high die swell, high viscosity, high shear sensitivity, and pronounced non-Newtonian behavior, and high storage modulus. The Cole–Cole plots of the modified resins are lower than that of the unmodified resin. The Cole–Cole plots are also independent of the temperature. The modified resins have higher mean relaxation times and relaxation strengths than the unmodified one. The relaxation strength of the modified resins is higher at high relaxation times in comparison to the unmodified resin. Overall, the modified resins are more “elastic” making them more conducive to low density foaming.

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