THE RELATIONSHIP BETWEEN STRUCTURE AND THERMAL AND MECHANICAL PROPERTIES OF THERMOPLASTIC POLYESTER MATERIALS

Jeffrey A. Jansen, The Madison Group, Madison, Wisconsin

Abstract

Three different thermoplastic polyester materials were evaluated to investigate the connection between the structure of the materials and their properties. Three materials representing distinct characteristic structures were selected to contrast the results. The resins evaluated included polycarbonate, with carbonate ester functionality; poly(ethylene –co- 1,4-cyclohexanedimethylene terephthalate), a poly(ethylene terephthalate) copolymer; and poly(ethylene naphthalate), with two condensed aromatic rings. The characteristics tested as part of this work included tensile properties to illustrate the short-term mechanical attributes, glass transition temperatures to represent the thermal response of the materials, and creep modulus to demonstrate the time dependency.

Introduction

The goal of this paper is to explore the relationship between the structure of different polyesters and their thermal and mechanical properties. The characteristic performance of individual plastics is the direct result of their unique molecular structure. Inherently, polymeric materials have a distinctive structure, as compared with other materials, which results in their distinguishing short-term and long-term properties. This structure includes a) a relatively high molecular weight resulting from chains formed by a great number of covalently bonded repeating units, b) the entanglement of these individual polymer chains, and c) the presence of weak intermolecular forces, such as hydrogen bonding and Vander Wal forces, between the polymer molecules that allow movement and disentanglement of the individual polymer chains. While plastics can be characterized by their collective attributes, the variation within the properties demonstrated by different plastics arises from diversity in their structure and molecular weight. Additionally, they often contain additives, such as fillers and reinforcements, anti-degradants and stabilizers, flame retardants, and plasticizers to enhance their properties. However, the underlying attributes of a plastic material are determined by the polymer. It is common to focus on the thermal and mechanical properties of plastics to explain their performance. However, the polymer chemistry, particularly the structure, drives the thermal and mechanical response, and is at the core of performance.

Material Background

Thermoplastic polyesters, also known as saturated or linear polyesters, include polymers produced through condensation reactions, which contain the ester functional group, as presented in Figure 1.
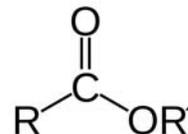

Figure 1. The ester functional group is shown, where R and R' represent connecting covalently bonded functional groups.

In general, an ester is an organic chemical compound derived from an organic acid in which one hydroxyl functional group is replaced by an alkoxy functional group. In most cases, esters are produced form the reaction between a carboxylic acid and an alcohol. This is the case regardless of whether the ester is monomeric or polymeric. Polymerization reactions for polyesters include a difunctional carboxylic acid known as a diacid, and a difunctional alcohol, also known as a diol.

Esters contain a carbonyl center, which results in 120 degree bond angles. The ester linkages in the polyesters are polar. The carbonyl oxygen atom has a partial negative charge, and the carbonyl carbon atom has a partial positive charge. The positive and negative charges from different ester groups are attracted to each other. When the attraction occurs across different polymer chains, this leads to intermolecular bonding and facilitates an orderly structure that promotes crystallinity[1]. Also important to the performance of polyesters, ester functional groups have a moderate level of hydrogen bonding, and participate in hydrogen bonds as hydrogen bond acceptors.[2] This plays a role in the intermolecular forces that keep the individual polymer chains bonded together.

Overall, esters are structurally flexible linkages, because rotation about the carbon-oxygen-carbon bonds has a low barrier.[2] This has important ramifications for the thermal and mechanical properties of polyesters.

Three different thermoplastic polyester resins were evaluated as part of this work, which represent different structural characteristics. The three materials were polycarbonate (PC), a poly(ethylene terephthalate) copolymer (Co-PET), and poly(ethylene naphthalate) (PEN). These three materials represent a diverse range of structural functionality. While having different structures, these three materials represent a single general polymer

class and are all amorphous in nature, in the as-molded state. This allows a comparison of the thermal and mechanical performance, based upon structure.

Polycarbonate

Organic carbonates, including carbonate-based polymers, are a special type of ester, in which the carbonyl group is bonded to two alkoxy groups, as shown in Figure 2.
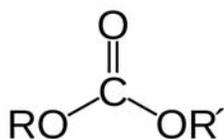

Figure 2. The carbonate functional group is shown, where R and R' represent connecting covalently bonded functional groups.

Polycarbonate (PC), specifically bisphenol A polycarbonate, can be condensation polymerized through one of two primary methods. The first is the reaction between bisphenol A (BPA), an aromatic diol and phosgene, an acid halide. The second type of polymerization involves the combination of bisphenol A and diphenyl carbonate, an aromatic carbonate. Both types of polymerization occur through a multi-step reaction that results in the formation of intermediate alcohol, carboxylic acid, and ester functionalities.
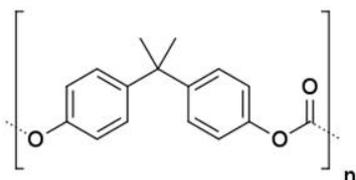

Figure 3. The structure of polycarbonate is shown.

A review of the PC structure, as shown in Figure 3, reveals that the benzene rings in the main chain hinder the mobility of the polymer molecule[3] relative to other polymer chains. However, high rotational mobility of the carbonyl group within the carbonate, is anticipated.

Because of the regular structure, it could be expected that PC may at least partially crystallize. However, the bisphenol A functional group contributes to the inability of polycarbonate to crystallize. Crystallinity is only formed through a high-temperature solution process. The exclusively amorphous nature of PC results in a recognized high level of toughness.

Poly(ethylene terephthalate) Copolymer

Copolymers of poly(ethylene terephthalate) (Co-PET), often simply termed copolyester resins or polyester copolymers, are produced when more than one glycol and/or more than one difunctional carboxylic acid are used during the polymerization of polyesters. Due to the presence of these comonomers, the chains of copolyesters tend to be less regular than those of normal homopolyesters, and thus, have a lower tendency to crystallize. As a result, copolyesters can be amorphous or semicrystalline, depending on the types and concentrations of comonomers used.[4]

Specifically, the copolyester resin evaluated as part of this study was described as poly(ethylene-co-1,4-cyclohexanedimethylene terephthalate), a polyester consisting of terephthalic acid, ethylene glycol and 1,4-cyclohexanedimethanol, with the molar ratio of ethylene glycol to 1,4-cyclohexanedimethanol kept at about 70/30.[5] The structure is shown in Figure 4.
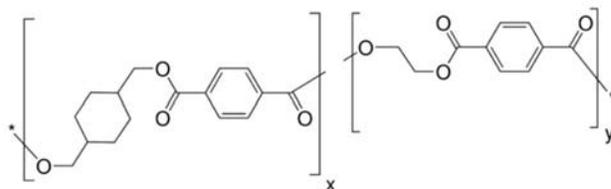

Figure 4. The structure of poly(ethylene-co-1,4-cyclohexanedimethylene terephthalate) is shown.

Other researchers working with this material have reported that the crystallinity displayed by poly(ethylene-co-1,4-cyclohexanedimethylene terephthalate) was lower than in the parent homopolyesters.[6]

Poly(ethylene naphthalate)

Poly(ethylene naphthalate) (PEN) is a polyester polymerized through a condensation reaction including naphthalene-2,6, dicarboxylic acid, a difunctional organic acid and ethylene glycol, a diol.
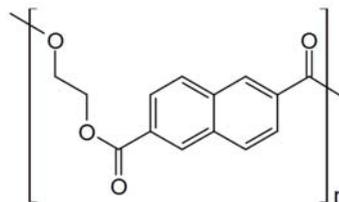

Figure 5. The structure of poly(ethylene naphthalate) is shown.

The structure of PEN, as shown in Figure 5, includes two condensed aromatic rings. This naphthalene structure is planar, and that causes the molecular chain to be relatively rigid[4, 7]. The presence of the naphthalene ring increases the aromatic nature of the material. Also, the structure results in the material being relatively slow to crystallize.[8] Because PEN crystallizes slowly, under the conditions of injection molding, the morphology is exclusively amorphous. Comparatively, PEN crystallizes more slowly than poly(ethylene terephthalate) (PET)

because of the bulkiness and the stiffening action of the naphthalene ring, compared with the benzene ring.[4]

Testing

Tensile Properties

Tensile tests were performed on samples representing the three polyester materials in accordance with ASTM D638 at 25 °C. Injection molded Type I tensile bars were tested using a universal mechanical tester equipped with a contact extensometer, at a crosshead speed of 2 in./min. The average results of five specimens are presented below in Table 1.

Table 1. Tensile Test Results

Parameter	Polycarbonate	Poly(ethylene naphthalate)	Polyester Copolymer
Modulus, MPa	2,477	2,595	1,982
Tensile Strength at Yield, MPa	61.5	78.4	48.7
Elongation at Yield, %	5.98	6.58	4.11
Tensile Stress at Break, MPa	59.8	39.2	24.5
Elongation at Break, %	111	13	60

Temperature Dependency and Glass Transition

The three polyester materials were evaluated for temperature-dependent behavior by dynamic mechanical analysis (DMA). The samples were evaluated from -50 °C at a heating rate of 2 °C/min. to an upper temperature based upon each material's thermal response. The center portion of the ASTM D638 Type I tensile bar was tested under an oscillatory stress at a frequency of 1 Hz in accordance with ASTM D4065. The storage modulus (E'), loss modulus (E"), and tan delta (E"/E') were plotted as a function of temperature. The glass transition temperatures (T_g) were determined as the localized maxima in the loss moduli. The resulting DMA thermograms are shown in Figures 6 through 8.
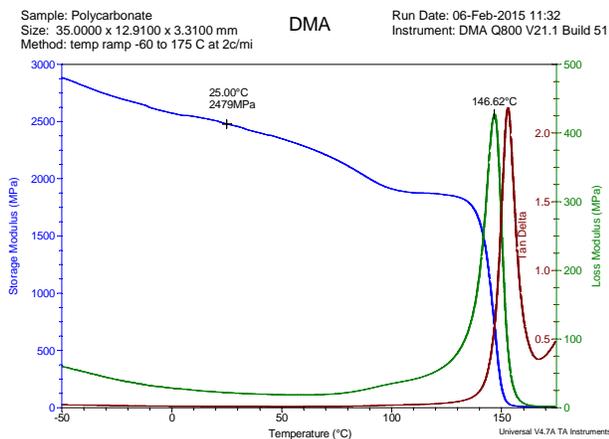
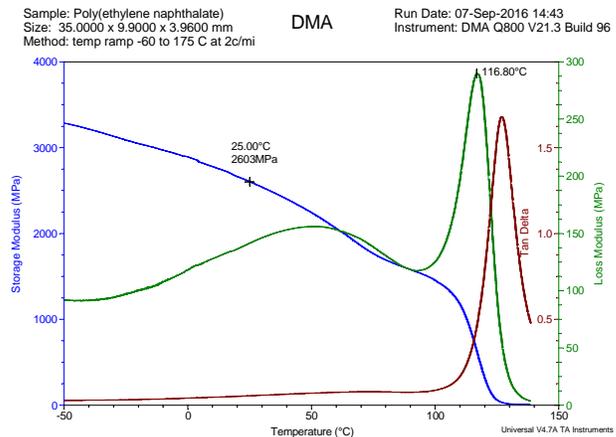Figure 6. The DMA temperature sweep for polycarbonate is presented.

Figure 7. The DMA temperature sweep for the poly(ethylene terephthalate) copolymer is presented.
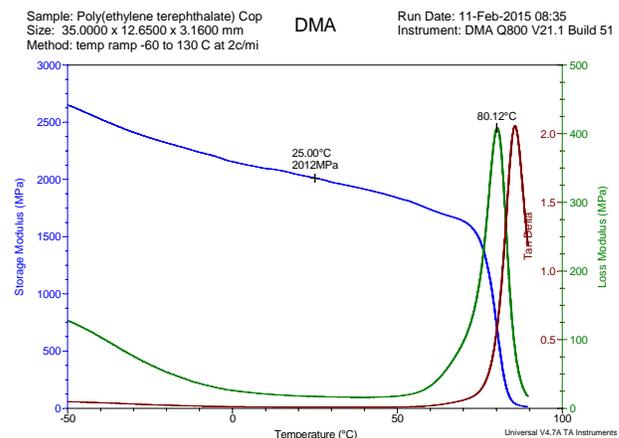
Figure 8. The DMA temperature sweep poly(ethylene naphthalate) is presented.

Time Dependency

The three materials were further evaluated to determine and compare their time dependency. The assessment of creep properties was conducted via dynamic mechanical analysis (DMA) by running multiple determinations for fifteen-minute periods at isothermal conditions ranging from 10 °C in increments of 5 °C to an upper limit based upon the thermal response of each of the materials. The evaluations were conducted using a dual cantilever configuration and a stress of 1.0 MPa for polycarbonate and the poly(ethylene terephthalate) copolymer and 1.2 MPa for poly(ethylene naphthalate).

These data were used to develop master curves for the materials that extend to 200,000 hours at the reference temperatures of 25 °C utilizing time temperature superposition (TTS). The results are illustrated as a semi-log plot of apparent modulus as a function of time in Figures 9 though 11.
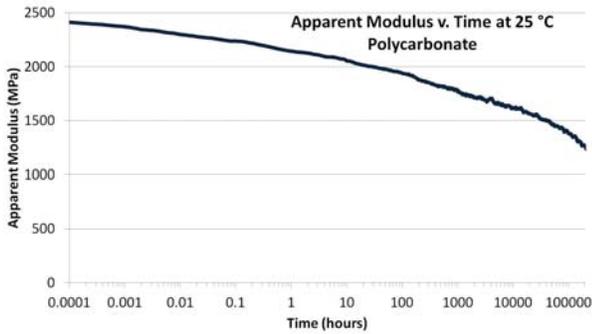
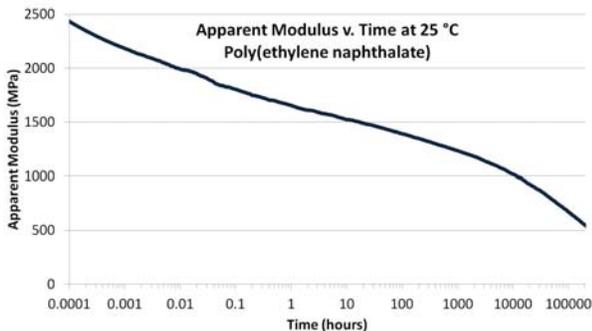*Figure 9. The plot of apparent modulus over time is shown for the polycarbonate.*

Figure 10. The plot of apparent modulus over time is shown for the poly(ethylene naphthalate).
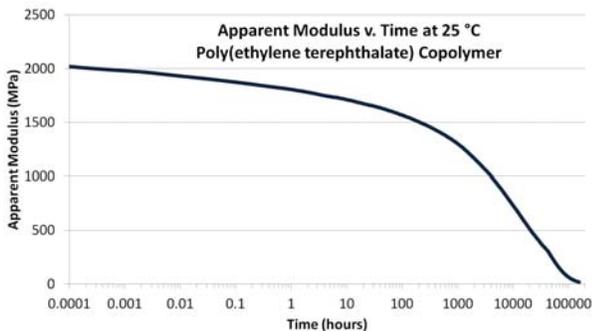

Figure 11. The plot of apparent modulus over time is shown for the poly(ethylene terephthalate) copolymer.

Properties

Tensile Properties

A review of the tensile test results showed a significant difference in the mechanical properties of the three materials. The PEN demonstrated the highest modulus, and the greatest tensile strength. This correlates with the structure of the material. The structure of PEN has several features that produce this stiffness and strength. In particular, PEN includes two condensed aromatic rings on the polymer chain backbone. This produces a planar structure and inherent chain rigidity.[7] This results in elevated strength and modulus compared with other thermoplastic polyesters, especially PET and to a lesser degree associated copolymers.

The modulus of PC, while lower than that of PEN, is still relatively high. The rigidity of the molecule, more so than the intermolecular attraction forces between the benzene rings or the polar groups leads to the excellent mechanical properties.[3] This is demonstrated through a comparison with PET, which has a similar macromolecular structure.

Elongation at break is a good assessment of inherent ductility, and as such toughness, of a plastic resin. Polycarbonate, noted for excellent impact resistance, had the highest elongation at break, substantially above both other materials. Structurally, the ductility is thought to be associated with the high rotational mobility of the carbonyl group.[9, 14] Some additional chain mobility may also be facilitated by the bisphenol A structure.

Compared with PEN and PEN, the Co-PET exhibits lower tensile strength and modulus. This is consistent with the differences in structure, as the copolyester does not possess the rigidity within the polymer backbone created by the naphthalene rings or bisphenol A, present within the other two materials. The copolyester structure, however, does afford a relatively high level of rotational mobility within the carbonyl functional group, and to some degree within the 1,4-cyclohexanedimethyl structure, and this accounts for the relatively high elongation at break.

Temperature Dependency

Through the DMA temperature sweep, PC demonstrated a steady decline in storage modulus with increasing temperature through approximately 145 °C, as shown in Figure 6. Above that temperature, the material exhibited a relatively sharp decrease in modulus, as the material underwent a glass transition.

The PEN underwent a continuous decline in storage modulus with increasing temperature from subambient through room temperature, continuing to approximately 100 °C as shown in Figure 7. Above that temperature, the material underwent a rapid decline in modulus associated with the glass transition of the material. The almost total reduction in the storage modulus associated with a glass transition, is consistent with the test sample material being exclusively amorphous. The results also showed an inflection in the reduction in the storage modulus coupled with a localized maximum in the loss modulus at approximately 60 °C. This is thought to represent a secondary transition within the PEN, corresponding to increased molecular mobility above that temperature.

The results obtained on the Co-PET showed a decline in storage modulus corresponding with increasing

temperature through approximately 70 °C, as shown in Figure 8. Above that temperature, the material presented a sharp decrease in modulus, as the material went through glass transition.

A direct comparison of the storage moduli for the three polyesters, illustrating definite differences in temperature dependency between the materials is illustrated in Figure 12.
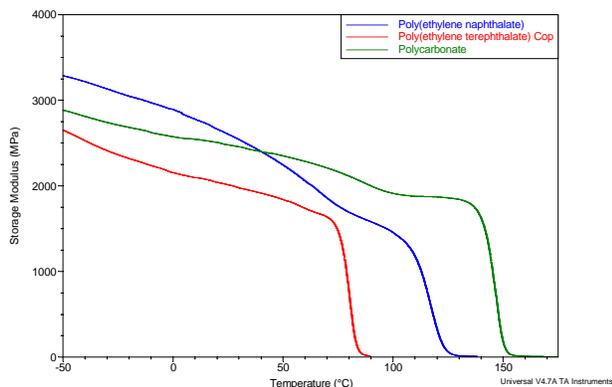

Figure 12. Overlay showing the difference between the three polyesters in the temperature dependency of the storage modulus.

Glass Transition

The glass transition temperatures (T_g) of the three polyesters were determined during the DMA temperature sweep, as the maximum in the loss modulus. The results are presented in Table 2, and illustrated as plots of the loss modulus in Figure 13.

Table 2. Determined Glass Transition Temperatures

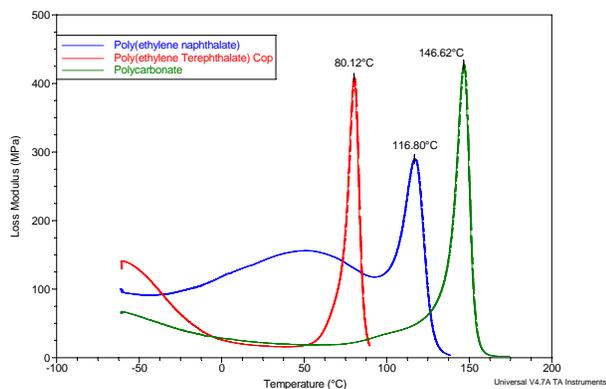| Parameter	Polycarbonate	Poly(ethylene naphthalate)	Polyester Copolymer
Glass Transition	147 °C	117 °C	80 °C

Figure 13. Overlay showing the loss moduli of the three polyester resins.

The value of the glass transition temperature is dependent on the mobility of the polymer chain. Generally, the more immobile the chain, the higher the value of glass transition[10]. In comparing polymeric structure, anything that restricts rotational motion within the chain should raise the glass transition temperature[11]. Thermodynamically, a polymer chain that can move easily, relative to other entangled chains, will change from a glassy state to a rubbery state at a relatively low temperature. If the polymer chains are not as mobile, then a relatively higher temperature will be required to transition the material to the rubbery state.[11]

Another factor that plays a role in the glass transition temperature is the inherent stiffness of the polymer chain. Functional groups that serve to stiffen the chain will reduce the flexibility of the polymer molecule[11], and thus raise the value of the glass transition temperature.

A third factor affecting the glass transition, is the level of intermolecular forces holding the individual polymer chains together. The greater the level of intermolecular forces binding the chains, including hydrogen bonding, dipole attractions, and Vander Wal forces, the higher the glass transition temperature will tend to be for otherwise consistent materials.

Of the three polyesters, PC clearly demonstrates the highest glass transition temperature. Several factors are thought to account for the comparatively high value. The relatively high rigidity of the PC molecule as a whole is a factor in the high glass transition temperature.[3] The bisphenol A functionality, which contains two aromatic rings and an intermediate isopropyl group, significantly contributes to polycarbonate's stiff backbone.[12] There is also some thought that the minimal molecular rotation about the bonds within PC plays a role in the high glass transition temperature.[12]

The planar and rigid structure of PEN produced by the naphthenic ring affords the material a moderately stiff and rigid backbone.[13] This results in an elevated glass transition temperature compared with PET, which has a benzene ring.

Relative to poly(ethylene terephthalate) homopolymer, the poly(ethylene-co-1,4-cyclohexane-dimethylene terephthalate) copolymer has a slightly higher glass transition temperature, 80° C, compared with a literature value of 75° C[13]. This elevation in glass transition is thought to be associated with the loss of mobility of the copolymer associated with the 1,4-cyclohexane-dimethylene functionality.

It would be expected that different relative concentrations of the two diol comonomers, ethylene glycol and 1,4-cyclohexanedimethanol would produce a

range of glass transition temperatures. Likewise, a different diol comonomer, with a different structure, such as 2,2,4,4-tetramethyl-1,3-cyclobutanediol, would also be expected to produce a material with varying thermal properties.

Time Dependency

A review of the creep responses of the materials over time showed very good agreement with the temperature dependent behavior demonstrated during the DMA temperature sweeps. For all three materials, the change in apparent modulus, as illustrated in the creep mater curves, generally followed the reduction in the storage modulus.

Consistent with the temperature dependent properties illustrated in the DMA temperature sweep, the PC presented the most creep resistance, as indicated by the highest level of apparent modulus retention. This is evident through the comparison shown in Figure 14. The creep response of the PC and the Co-PET paralleled each other with an obvious offset in modulus, reflecting the inherent relative stiffness of the two materials. The staggered sharp decline in apparent modulus compared favorably with the drop in storage modulus associated with the glass transitions of the materials.

The creep behavior of the PEN also closely matched the temperature profile. The PEN started with the highest apparent modulus, but presented an initial decline at a rate greater than that of the other two materials. In the temperature sweep, this reduction in storage modulus was identified as a secondary transition that allowed enhanced molecular mobility. After the initial reduction, the apparent modulus decline leveled off, similar to the storage modulus response to temperature. Finally, a more steep decline was identified that equated to the glass transition.

All three polyesters displayed a creep response that was analogous to the temperature dependant behavior. Overall, the observed activity was consistent with the equivalency of time and temperature for thermoplastic materials. The equivalence of time and temperature was apparent not only in the performance of individual materials, but through a comparison of the three materials, and their performance relative to each other, as illustrated in Figure 14.

The creep data were also plotted to allow an assessment of the relative retention of apparent modulus over time. The time scale was extended in order to facilitate the determination of the points in time where the materials experienced an order of magnitude reduction in the initial modulus value. This normalized data, as shown in Figure 15, allowed a better analysis and comparison of the effects that structure had on the creep response. This further demonstrates the equivalence in performance between PC and the Co-PET over the short range. Once the effects of the structural configuration associated with

the lower glass transition take effect, the Co-PET undergoes a much earlier reduction in apparent modulus. This normalized comparison also illustrates the short-term changes within PEN, and a clear dual mechanism in the overall creep response.
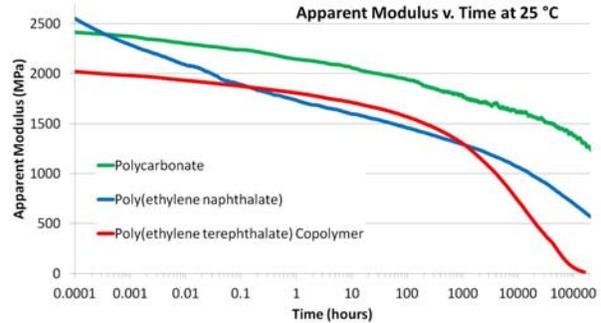

Figure 14. Overlay plot showing the apparent modulus versus time for the three polyester materials.
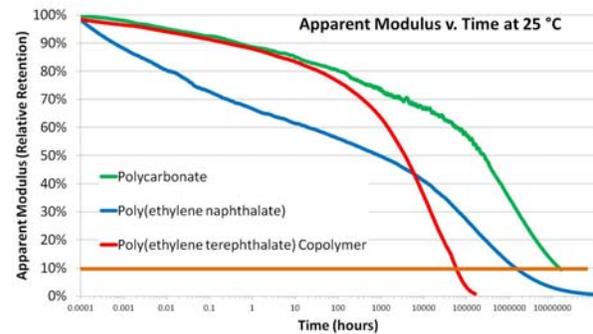

Figure 15. Overlay plot showing the relative retention of apparent modulus versus time for the three polyester materials highlighting the time to 10% retention.
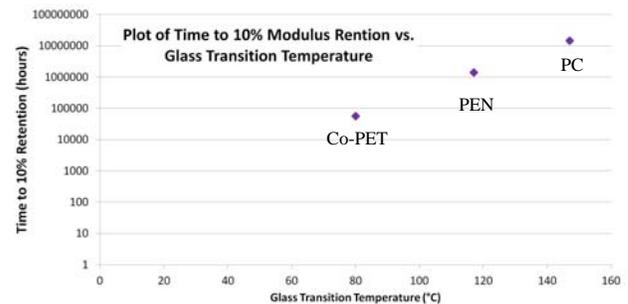

Figure 16. Plot showing the correlation between the projected time to 90% loss of apparent modulus and glass transition temperature.

The identified time for creep to produce a 90% loss in the apparent modulus, as shown in Figure 15, was plotted against the glass transition for the three materials. This level of change, in order of magnitude, was selected as it represented a substantial, but not total loss of apparent

modulus of the material over time associated with creep. A review of the data showed a correlative trend between the glass transition temperature and the time required for 90% apparent modulus loss, as illustrated in Figure 16.

Conclusions

It is the conclusion of this work that a direct correlation was evident between the thermal and mechanical properties of the three polyesters evaluated and their respective structures. In particular, structure influences polymer chain stiffness, molecular mobility, and intermolecular bonding between the chains. This manifests as thermal and mechanical properties. The relationship between structure and performance has been evaluated and demonstrated for many years.[14, 15]

Further, the work appears to support a correlation between the glass transition temperature and long-term creep performance. Higher glass transition temperatures are accompanied by enhanced creep resistance, as measured by the time required to produce the apparent modulus to 10% of its original value. Further work, including polymers with significantly different structures and functional groups would need to be performed to verify this relationship.

References

1. University of Southern Mississippi, Department of Polymer Science, "Polyesters", http://pslc.ws/macrog/pet.htm, (December 12, 2017)
2. Jerry March, "Chapter 3 Bonding Weaker than Covalent" in Advanced Organic Chemistry, Wiley-Interscience Publication (New York, New York, 1992), 75-93.
3. H. Domininghaus, *Plastics for Engineers* (Munich: Carl Hanser Verlag, 1993), 424
4. Marianne Gilbert, editor, *Brydson's Plastic Materials* (Amsterdam: Elsevier, 2017), 537
5. Ryuichi Sugie, Toru Nishimura, Motoki Hiratsuka, U.S. Patent 6,333,113 (2001)
6. Nathalie Gonzales-Vidal, Antxon Martinez de Ilarduya, Sebastián Munozguerra, Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, "Copolyesters Obtained by Ring Opening Polymerization", http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.1011.2361&rep=rep1&type=pdf, (December 12, 2017)
7. Teijin, "Teonex$^®$ Polyethylene naphthalate (PEN resin)", https://www.teijin.com/products/resin/products/teonex/, (December 12, 2017)
8. Myer Kutz, editor, Applied Plastics Engineering Handbook (Norwich, New York: William Andrew, 2016)
9. DESCO Eningeering Plastics Solution Company, "Resin Info – PC", http://www.edesco.co.kr/e_html/data01_5.php, (December 12, 2017)
10. Francesco Puoci, editor, *Advanced Polymers in Medicine*, (Heidelberg: Springer, 2015), 79
11. Lisa Lever, University of South Carolina Upstate, "Polymer Chemistry – Factors Influencing T_g", http://faculty.uscupstate.edu/llever/polymer%20resources/FactorsTg.htm, (December 12, 2017)
12. Carlos Buitrago, University at Buffalo, "Polycarbonate", http://wwwcourses.sens.buffalo.edu/ce435/PC_CB.pdf, (December 12, 2017)
13. J.A. Brydson, *Plastics Materials*, (Amsterdam: Elsevier, 1999), 723
14. R.F. Boyer, "Dependence of Mechanical Properties on Molecular Motion in Polymers", *Polymer Engineering and Science*, Vol. 8, No.3 (July, 1968): 161-185.
15. W.E. Wolstenholme, "Correlation of Physical and Polymer Chain Properties", Polymer Engineering and Science, (April, 1968) 142-150