Analysis of "BPA-free" Tritan ™ Copolyester Under High Stress Conditions

Paul Dornath; Mentor: Dr. Skip Rochefort; School of Chemical, Biological, and Environmental Engineering (CBEE)
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Background

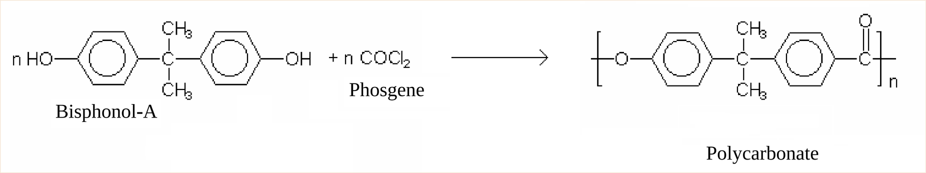
- In the late 1990's, **polycarbonate (PC) plastic**, used by brands such as Nalgene ™ to create plastic bottles, was found to leach some if its monomer, **bisphenol-A (BPA)** under extremely high stress conditions (harsh detergents, autoclaving, exposure to acid).
- Hundreds of studies have been conducted since this time and have shown that under ***normal use conditions*** (anywhere from freezing to a hot day), **BPA does not leach** from the **polycarbonate** in detectable amounts.
- **BPA** can disrupt the endocrine cycle in a significant amount if ingested. The estimated tolerable daily intake ranges from 0.05 mg/kg body weight/day (EPA) to 0.01 mg/kg/day (European Scientific Committee on Food).
- With the conservative estimate, a 70 kg person would have to drink 1 liter of water with a concentration of 700 ppb per day to receive a minimal harmful dose.
- In virtually every study with a detection limit greater that 0.1 ppb, no BPA was detected at room temperature (**Maragou C. et al 2005, Ehlert K et al 2008)**
- In other such studies with lower detection limits, **BPA** was found to migrate at room temperature between 0.11 ppb (with food simulant) to 0.08 ppb. In all cases that tested for consistency, **BPA** leaching diminished after repeated trials, eventually falling below detectable limits (**Kubwabo C. et al 2009, Le H. et al 2007)**

Our Previous Study

- During summer 2008 we analyzed the leaching from **polycarbonate** using similar methods in the literature
- **Polycarbonate** bottles were autoclaved at 121 degrees C at 2 bar of pressure (most extreme literature case)
- Using solid phase extraction and GC/MS, **BPA** was detected
- Standards were used to calibrate GC/MS
- Although standards were used, machine malfunction left only a small amount of data
- Quantitatively, it can only certain that less than 10 ppb of **BPA** leached from the **polycarbonate** bottles under these extreme conditions
- This confirms other studies that show **BPA** does not leach from **polycarbonate** plastic in doses that will cause harm, even under the most extreme conditions

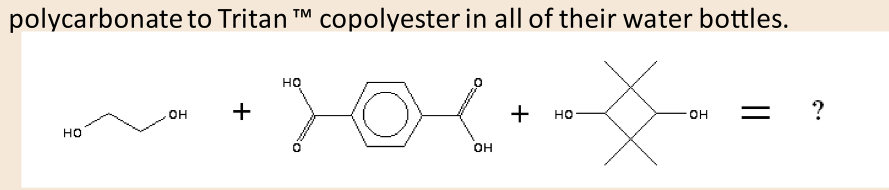
Chemistry of What is Happening

- Bisphenol-A is one of two momomers that make polycarbonate
- It is likely that any BPA that leaches is unreacted monomer from the polymerization and fabrication process.
- This would explain why BPA leaches in such small amounts and why the rate diminishes over time.
- The stress of harsh detergents and acids could cause the ester backbone of the polymer to break down, also releasing more polymer.
- When polymers approach their glass transition point (Tg), molecular mobility is increased, which might facilitate the transport of small molecules through the polymer matrix.
- Tg of polycarbonate = 150 C
- Tg of Tritan ™ Copolyester = 110 C ("BPA-free" material used in new bottles)



Eastman Tritan ™ Copolymer

- Due to consumer demand for a "***BPA-free "*** plastic for a reusable water bottle, Eastman released Tritan ™ copolyester in 2008.
- The company does not wish to disclose any information about this product except the conditions needed to process it.
- Although there is no patent available that has the Tritan ™ copolyester name, it is likely that the following three esters are used to make the polymer: ethylene glycol, terephthalic acid and 2,2,4,4-tetramethyl- 1,3- cyclobutanediol.
- This compound is very similar to polyethylene terephthalate (PETE or # 1 plastic), but with a cyclobutane added to the ester for strength.
- No exact chemical formula is available.
- Nalgene ™ and others (such as CamelBack ™) have now switched from using polycarbonate to Tritan ™ copolyester in all of their water bottles.



Hypothesis

- Since **Polycarbonate (PC)** leaches unreacted monomers under extreme conditions, we predict that **Tritan ™ copolyester** will also leach its monomers when put under similar stress.
- Since the glass transition temperature of Tritan ™ copolyester is much lower than polycarbonate, it will probably leach more unreacted monomers than polycarbonate under stressful conditions such as high heat.
- Since there are so few studies (if any) on Tritan ™ copolyester the experimental results from a study of potential leaching (and the extent of leaching) from Tritan ™ copolyester would be of scientific interest and publishable.

Goals for Summer 2009

- Determine what temperatures *Tritan ™ copolyester* can handle without degradation
- Thermal analysis (DSC) of stress in *Tritan ™ copolyester* water bottles from manufacturing and from heating at experimental leaching conditions.
- Design analytical techniques for more efficient HLPC analysis of water samples obtained from leaching studies
- Run a series of new *polycarbonate* and *Tritan ™ copolyester* bottles through the same extreme conditions and analyze the extent of leaching of their basic monomers using HPLC

Sample Treatment

- Bottles were autoclaved at two temperatures: 121 C (2.02 bar) and 102 C (1.09 bar) for 2 hours.
- This serves to recreate test conditions of polycarbonate tests and to see how the plastic holds up under these conditions
- The plastic should leach but not degrade or deform

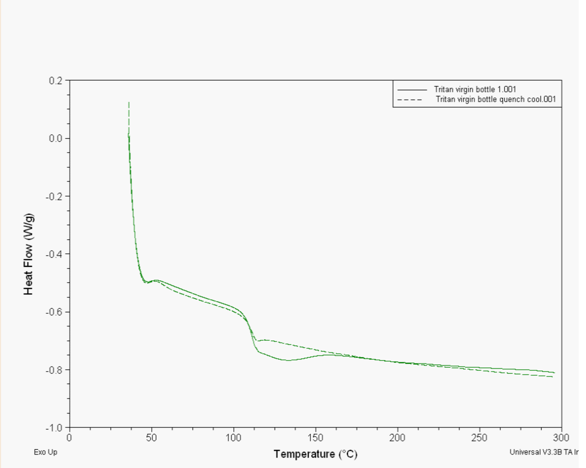
Oven Heating Experiments

- Bottles were placed in an oven with ramping temperature to see if the bottles will break down quickly once their glass transition temperatures have been reached.
- The temperature was ramped from 25 to 125.8 C under 15 in Hg vacuum.
- Kept above glass transition point for half an hour
- Conditions will be harsher in autoclave due to high pressure and humidity

Oven Temp = 125 C

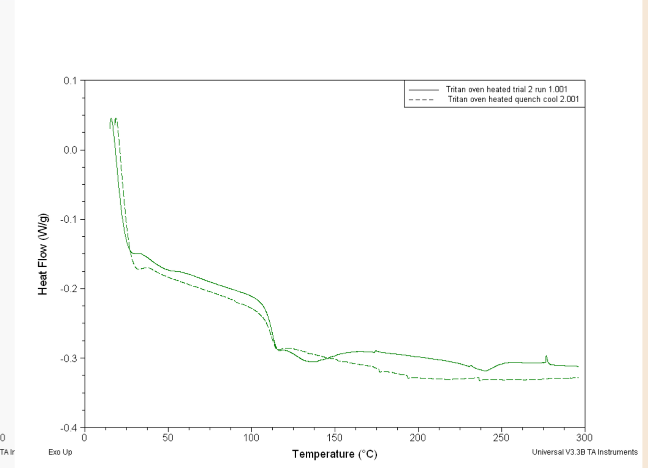
Differential Scanning Calorimetry

- A differential scanning calorimeter (DSC) can be used to measure the glass transition, melting point, crystallization and stresses inside the plastic
  - Smooth slopes show glass transition (Tg)
  - Dips show melting points (Tm)
  - Jagged and rough sections (near Tg) indicate stress in polymer structure
  - Quench cooling allows the plastic to cool without stress
  - A second run is performed on each sample after quench cooling to get a better picture of real physical properties



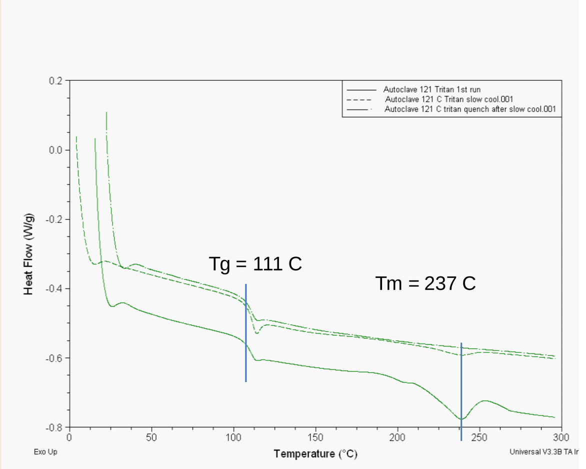
Heat Flow vs. Temperature graphs for Virgin Tritan ™ Copolyester Bottles

- New bottles show high stress from manufacturing
- No melting point observed on either quench cool or initial run



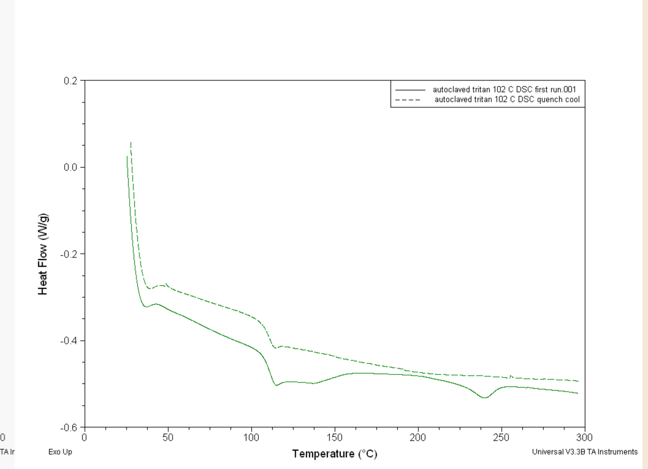
Heat Flow vs. Temperature Graphs for Oven Heated Tritan ™ Copolyester Bottles from 25°C to 120°C

- Additional stress appears after heating and the plastic has a slight melting point.
- Stress has not had time to disappear from structure.
- No melting point observed after quench cool



Heat Flow vs. Temperature Graphs for Tritan ™ Copolyester Bottles Autoclaved at 121°C

- High humidity and heat has allowed plastic to relax and no stress is observed.
- A melting dip appears after the first run and slightly after 2nd run
- No melting point observed during quench cool



Heat Flow vs. Temperature Graphs for Tritan ™ Copolyester Bottles Autoclaved at 102°C

- Some stress is relieved but not as dramatic as 121 C test.
- A melting dip appears after the first run but not after quench cooling

Temperature Studies

- 1) New Tritan ™ copolyester bottle. 2) After 1 hour ramping from 25 to 125 C. 3) 2 hours in autoclave at 102 C. 4) 2 hours in autoclave at 121 C.

Results (so far)

- HPLC analysis still needs to be run, but will be by the end of the summer.
- Results show that Tritan ™ copolyester will likely breakdown if exposed to boiling water due to lower Tg of 110C.
  - Tests are now being run at dishwasher temperatures (55-65 C). If the bottles do no breakdown under these temperatures, these tests will be used for HPLC analysis
- Two hour exposure to high heat causes some crystallization
  - This has not yet been explained but analysis is being conducted
- Bottles have high stress during production
  - The bottles shrink when heated, which is a signature of stress
  - Stress can be seen in DSC as rough sections of the heat flow vs. temperature graph

Future work

- Determine best conditions to treat Tritan ™ copolyester bottles so that plastic will not soften (best use temperatures).
- Run HPLC test on water from both polycarbonate and Tritan ™ copolyester bottles under the same conditions
- Develop standard curve for HPLC method. Analyze HPLC data from water bottles to obtain an extent of leaching
- Determine chemical structure using a surface analysis method (still being considered)

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