



# **High Performance Bisphenol A (BPA)-Free Epoxy Resins**

Toxics Use Reduction Institute  
Academic Research Program

# HIGH PERFORMANCE BISPHENOL A (BPA) FREE EPOXY RESINS

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The Toxics Use Reduction Institute  
Academic Research Program

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## Academic Research Program

The Academic Research program is a project of the Toxics Use Reduction Institute (TURI). The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies and, in some cases, evaluate and/or adopt processes and technologies resulting from research. Past projects supported by this program have focused on finding alternatives to the use of toxic chemicals in various plastics applications. These projects, which are described in more detail on TURI's website ([www.turi.org](http://www.turi.org) and click on Industry, Research, Academic Research Program), include:

- 2009 – “Sustainable Routes to Non-Halogenated Flame Retardants Based on Phenolic Monomers” – Profs. Ramaswamy Nagarajan and Jayant Kumar, UMass Lowell Center for Advanced Materials and Department of Plastics Engineering.
- 2009 – “Green chemistry synthesis of nanostructured poly(2,5-dimethoxyaniline)” – Prof. Sanjeev Manohar, UMass Lowell Department of Chemical Engineering.
- 2008 – “Greener” Routes to Halogen Free Flame Retardants – Prof. Jayant Kumar and Asst. Prof. Ramaswamy Nagarajan, UMass Lowell Center for Advanced Materials.
- 2006 – Improved Lead-Free Wire and Cable Insulation Performance Using Nanocomposites – Asst. Prof. Daniel Schmidt and Noble Francis, UMass Lowell Department of Plastics Engineering.
- 2005 – Flame Retardancy Enhancement for EPDM Wire and Cable Coatings Using Nanoclays – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering.
- 2004 – Alternative Stabilizers and Surface Characterization (SEM/EDXS Analysis) of EPDM for Wire and Cable Applications – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering, and Changmo Sung, UMass Lowell Department of Chemical Engineering.
- 2003 – Analysis of Lead-Containing Wire Coating Materials – Prof. Joey Mead, UMass Lowell Department of Plastics Engineering, and Changmo Sung, UMass Lowell Department of Chemical Engineering.
- 2003 – Innovative Materials for Wire and Cable Coating – Prof. Stephen McCarthy, UMass Lowell Department of Plastics Engineering and the Institute for Plastics Innovations.
- 2002 – Innovative Materials for Wire and Cable Coating – Prof. Stephen McCarthy, UMass Lowell, Department of Plastics Engineering and the Institute for Plastics Innovations.

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## Table of Contents

Academic Research Program.....	iii
ABSTRACT .....	1
INTRODUCTION .....	2
2. EXPERIMENTAL .....	5
2.1    Synthesis .....	5
2.2    Removal of TBAB.....	5
2.2.1    Crosslinking .....	6
2.3    Characterization .....	6
RESULTS AND DISCUSSION .....	7
SUMMARY AND CONCLUSIONS.....	11
Appendix A: DSC and TGA Results Summaries.....	13

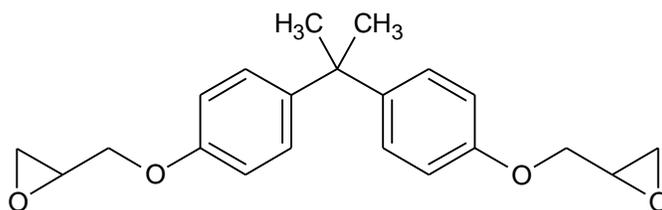
## ABSTRACT

The purpose of this research was to synthesize a Bisphenol A (BPA) free epoxy resin in order to replace existing BPA containing epoxy resins such as liquid Bisphenol A diglycidyl ether (BADGE) and related high molecular weight BPA-based solid epoxies. This represents an important step in the development of BPA free epoxy liners for food and beverage cans and would eliminate the health concerns associated with BPA-based epoxy can liners currently used in food packaging. The epoxy resin in question, 2,2,4,4-tetramethyl-1,3-cyclobutanediol diglycidyl ether (CBDO-DGE), was synthesized via the reaction of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) with epichlorohydrin using tetrabutylammonium hydrogen sulfate (TBAB) as the phase transfer catalyst under basic conditions. Nuclear magnetic resonance (NMR) spectroscopy of the reaction product produced results consistent with successful CBDO-DGE synthesis, a conclusion confirmed by its successful crosslinking using triethylenetetramine (TETA). The curing reactions and thermal properties of the epoxy resin were analyzed in comparison with a conventional BADGE/TETA system. As its purity was improved, the synthesized CBDO-DGE product yielded thermal properties approaching those of the BADGE material.

**Note:** *As of this writing, the work described herein is covered worldwide by a pending patent application. For more information on the IP associated with this work, please contact Jill Murthi, Associate Director, University of Massachusetts Lowell Commercial Ventures and Intellectual Property (CVIP, <http://www.uml.edu/cvip>), 600 Suffolk Street, 2<sup>nd</sup> Floor, Lowell, MA 01854, [Jill\\_Murthi@uml.edu](mailto:Jill_Murthi@uml.edu)*

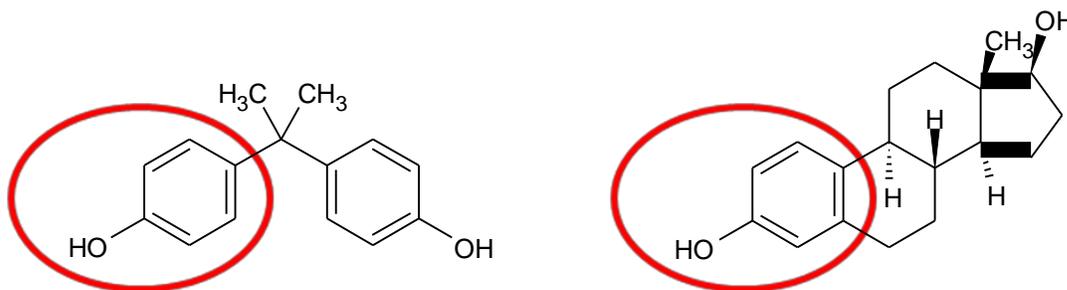
## INTRODUCTION

Today, Bisphenol A (BPA) is found as a major component of common rigid epoxies such as Bisphenol A Diglycidyl Ether (BADGE, shown below).



**Bisphenol A Diglycidyl Ether (BADGE)**

BADGE is part of a family of BPA-based epoxies used as liners for food and beverage containers worldwide. Recently, BPA has been implicated as the source of various adverse health effects due to its structural similarities to the human hormone estrogen (shown below).



**Bisphenol A (BPA)**

**Estrogen (17β-estradiol)**

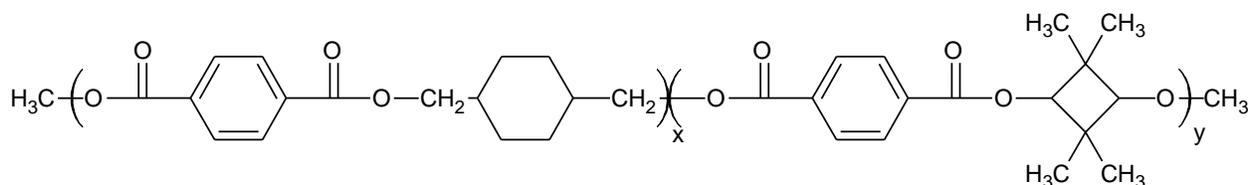
The structural similarities of BPA and estrogen give BPA the ability to act as an endocrine disruptor, with links reported to health problems such as diabetes, heart disease, and cancer<sup>1</sup>. While the magnitude of these risks is still being debated, their existence makes development of alternative, BPA-free, high performance epoxies highly desirable. As such, the purpose of this research was to synthesize a BPA-free epoxy resin able to replace existing BPA containing epoxy resins. This would allow for the

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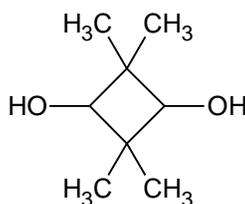
<sup>1</sup> Refer to <http://www.dailytech.com/article.aspx?newsid=19390> (viewed 8/2010).

lining of food and beverage cans with a BPA free epoxy resin, eliminating potential concerns associated with BPA leaching.

The approach taken in this work is best explained via an analogy with the world of thermoplastics. A novel thermoplastic copolyester with the tradename of Tritan (shown below) has recently been commercialized by Eastman Chemical Company.



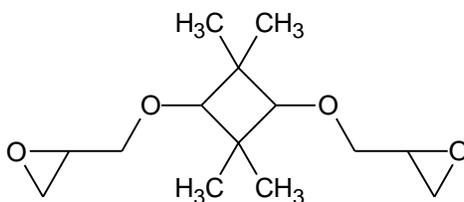
Tritan is BPA-free but has properties very similar to BPA polycarbonate, leading to widespread use as a replacement for polycarbonate in thermoplastic applications. While most of the components of this polymer have been used in thermoplastic polyesters for some time, the key to the success of this material from the standpoint of materials properties has been the use of the newly developed 2,2,4,4-tetramethyl-1,3-cyclobutanediol monomer (CBDO, shown below).



#### **2,2,4,4-Tetramethyl-1,3-cyclobutanediol (CBDO)**

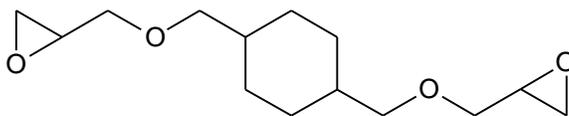
The steric hindrance, and therefore rigidity, of the CBDO molecule is due to the four methyl groups attached to the cyclobutanediol ring. Likewise, the lack of aromaticity and the significant difference in size and shape of the CBDO molecule greatly reduces the possibility of acting as an estrogen mimic – a conclusion borne out by recent third party testing (sponsored by Eastman) of CBDO for estrogenic

activity<sup>2</sup>. The epoxy resin synthesized from this monomer was 2,2,4,4-tetramethyl-1,3-cyclobutanediol diglycidyl ether (CBDO-DGE, shown below).



#### **2,2,4,4-Tetramethyl-1,3-cyclobutanediol diglycidyl ether (CBDO-DGE)**

This epoxy resin, based on the CBDO molecule rather than the BPA molecule, is expected to provide the desired thermal and mechanical properties without the health risks associated with a BPA-based material. In addition to the aforementioned comparisons with BADGE, CBDO-DGE is also compared with a less rigid structural isomer, the commercially available 1,4-cyclohexanedimethanol diglycidyl ether (CHDM-DGE, shown below).

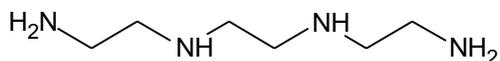


#### **Cyclohexanedimethanol diglycidyl ether (CHDM-DGE), a structural isomer of CBDO-DGE**

In order to assess materials properties, all three epoxy resins of interest here – BADGE, CHDM-DGE and CBDO-DGE– must be crosslinked. Triethylenetetramine (TETA, shown below) is a widely used crosslinker used in epoxy formulations that was chosen to allow the rapid production of a series of analogous cured epoxy networks so as to evaluate the relative strengths and weaknesses of each material.

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<sup>2</sup> Refer to [http://www.eastman.com/Literature\\_Center/T/TRS252.pdf](http://www.eastman.com/Literature_Center/T/TRS252.pdf) for more information (viewed 10/2010).



**Triethylenetetramine (TETA)**

Once the various epoxy resins were crosslinked, the thermal properties of the resultant networks were determined via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The epoxies were then evaluated in comparison with one another.

## **2. EXPERIMENTAL**

### **2.1 *Synthesis***

The epoxy resin, 2,2,4,4-tetramethyl-1,3-cyclobutanediol diglycidyl ether (CBDO-DGE) was synthesized from a mixture of 5.6304 g (0.039 mol) of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO, solid) with 30.5 mL (0.39 mol) of epichlorohydrin (ECH, liquid), and 15.6118 g (0.39 mol) of sodium hydroxide (NaOH, solid), using 1.3354 g (0.0039 mol) of tetrabutylammonium hydrogen sulfate (TBAB, solid) as a phase transfer catalyst. All of the aforementioned reagents were combined in a 250 mL glass bottle, after which 157.6  $\mu$ L (0.0087 mol) of deionized water was added and the mixture vigorously stirred with a Teflon<sup>®</sup>-coated magnetic stir bar while the glass reaction flask was immersed in a silicone oil bath at 40°C. During the reaction, the solution changed from colorless to yellow to orange. After maintaining the reaction for approximately two hours, the resulting orange product was then diluted with a small amount of dichloromethane to allow for complete transfer to a vacuum filtration setup, where the liquid was separated from the remaining solid sodium hydroxide. The filtered product was then transferred to a 125 mL polypropylene jar, which was left open under a fume hood to allow for the evaporation of the dichloromethane and the excess epichlorohydrin. Finally, the resin was placed under vacuum at room temperature for seven days in order to further ensure complete removal of any volatiles (dichloromethane as well as residual water and epichlorohydrin). This yielded a crude product consisting primarily of a mixture of CBDO-DGE and TBAB.

### **2.2 *Removal of TBAB***

The phase transfer catalyst TBAB was found to be highly soluble in water, and was therefore removed from the product through the addition of 75 mL of distilled water to the product, followed by

vigorous stirring for 20 minutes, after which the aqueous layer was decanted, replaced with 75 mL of fresh distilled water, and the process repeated three more times. Once the wash process was completed, the resin was placed under vacuum at room temperature for 4 days in order to remove any residual water from the purified product. The final yield was 7.3701 g (0.029 mol, ~74%) of CBDO-DGE as confirmed via  $^1\text{H-NMR}$  spectroscopy. That said, the product remained orange in color, indicating the presence of at least trace levels of impurities (pure CBDO-DGE should be colorless).

### **2.2.1 Crosslinking**

TETA was used to crosslink the BADGE, CHDM-DGE and CBDO-DGE in order to form solid networks suitable for further characterization. Based on the epoxy equivalent weight calculated for CBDO-DGE (128.17 g/epoxy equivalent), 1 g of TETA crosslinker is sufficient to crosslink 5.34 g of CBDO-DGE at the desired 1:1 stoichiometry of amine hydrogens to epoxy groups. Therefore, 2.0256 g CBO-DGE and 0.4192 g of TETA were placed in a SpeedMixer (FlackTek, Inc., model DAC 150 FVZ) in order to rapidly and evenly mix the TETA and CBDO-DGE. The same process was followed for the crosslinking of BADGE and CHDM-DGE based on their epoxy equivalent weights (170.11 and 128.17 g/epoxy equivalent, respectively). The total masses of these samples were also approximately 2 g. Following mixing, all samples were cured in an oven at 60°C, 100°C, or 140°C for 12, 4, or 1 hours respectively.

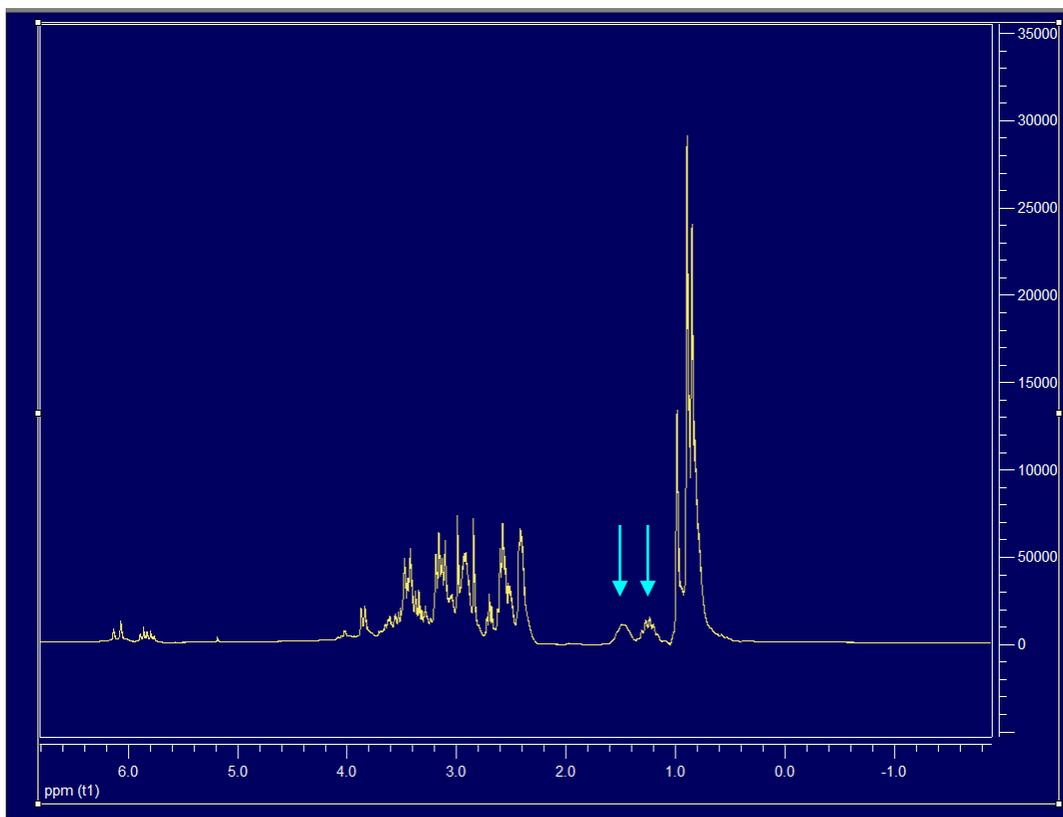
### **2.3 Characterization**

A Bruker Avance Spectrospin 200 MHz nuclear magnetic resonance (NMR) spectrometer was used to determine the structure and composition of the synthesized product. The CBDO-DGE product (1.0 mL) was diluted with deuterated chloroform ( $\text{CDCl}_3$ ) in an NMR tube (5 mm x 7" Pyrex tubes rated for 500 MHz NMRs). Water used in each of the washing steps was rotary-evaporated as well, and approximately 0.5-1 mL of the resultant material was diluted with deuterated water ( $\text{D}_2\text{O}$ ) and analyzed in each case. Proton ( $^1\text{H}$ ) and carbon-13 ( $^{13}\text{C}$ ) NMR spectra were obtained using the Xwin software package.

Following ASTM D7426-08, the glass transition temperature ( $T_g$ ) of the TETA crosslinked samples was obtained using a TA Instruments Q200 differential scanning calorimeter. Likewise, thermogravimetric analysis (TGA) was performed using a TA Instruments Q50 thermogravimetric analyzer.

## RESULTS AND DISCUSSION

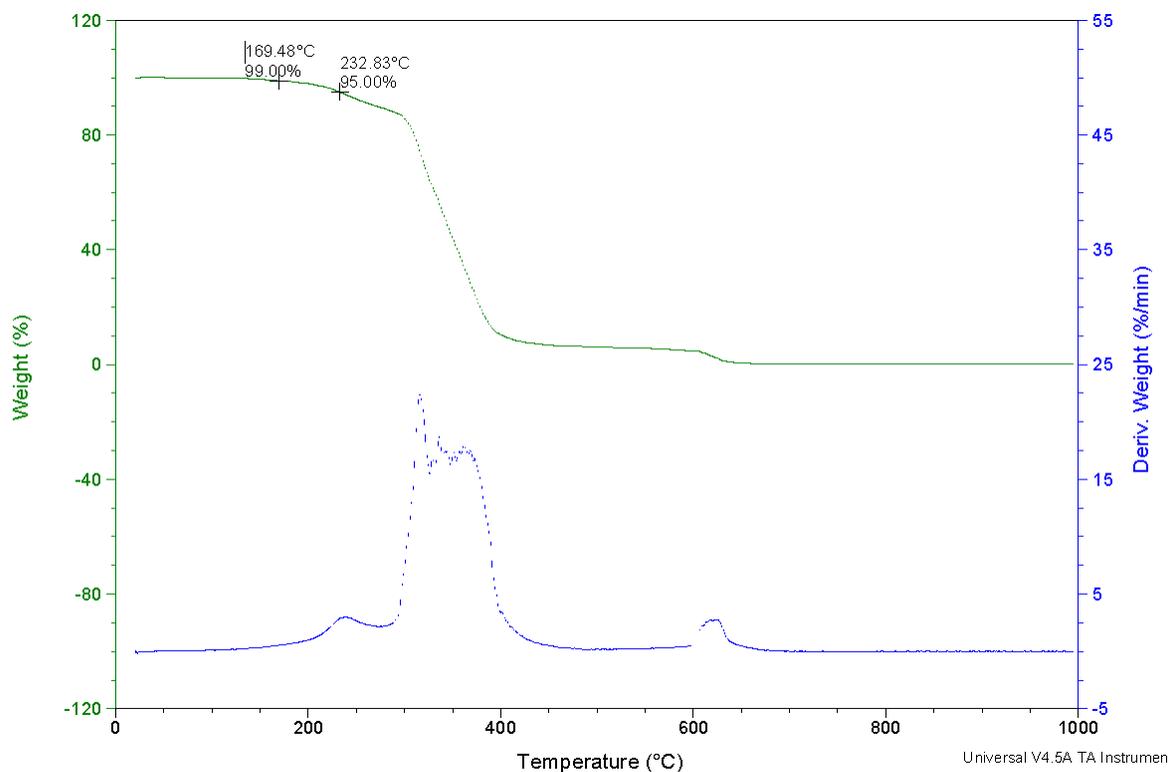
Following synthesis,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of the product were found to be consistent with CBDO-DGE. The  $^1\text{H-NMR}$  spectrum for the initially synthesized CBDO-DGE is shown below in Figure 1. As shown by the presences of the two peaks at approximately 1.1-1.3 ppm, some residual phase transfer catalyst (TBAB) remains in the product.



**Figure 1:**  $^1\text{H-NMR}$  spectrum of the products of the initial CBDO-DGE synthesis; arrows indicate peaks assigned to the TBAB phase transfer catalyst.

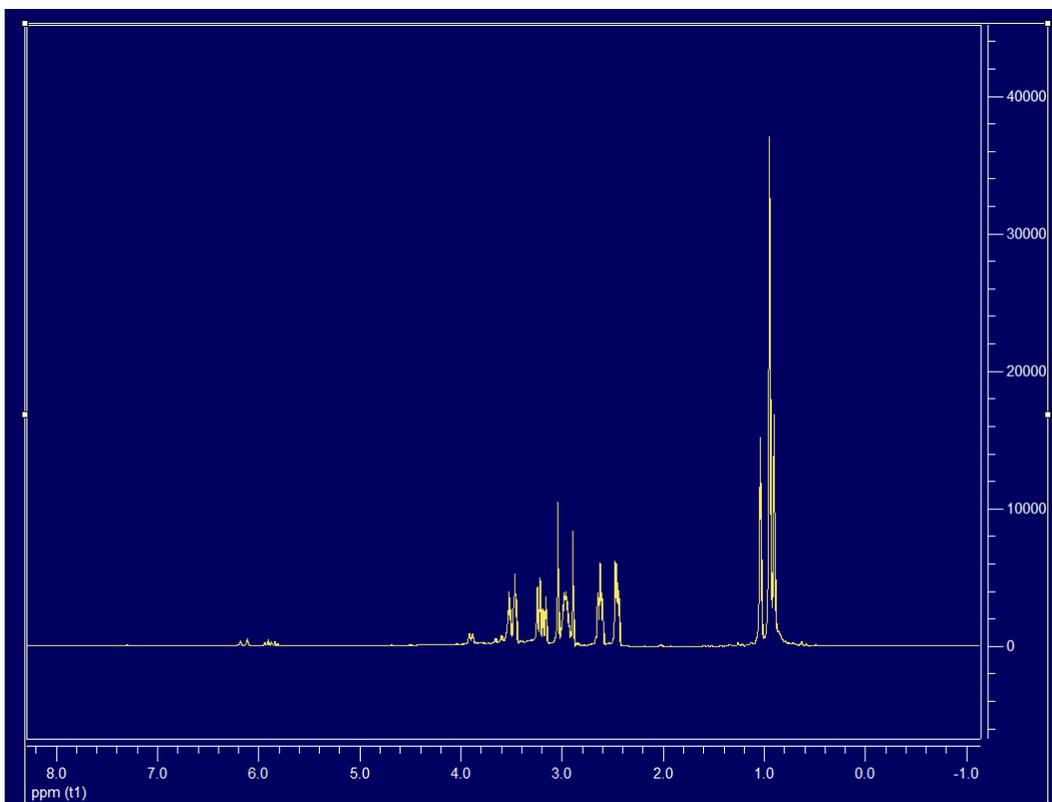
To assess the volatile content, thermal stability and glass transition temperature ( $T_g$ ) of the crosslinked product of the first CBDO-DGE synthesis, TGA and DSC were performed following network formation with TETA at  $60^\circ\text{C}$  for approximately 12 hours. TGA gave a  $T_{\text{onset}}$  value (temperature at 5% mass loss) of  $232^\circ\text{C}$  and a  $T_{\text{max}}$  (temperature at maximum degradation rate) of  $320^\circ\text{C}$ , with no evidence of residual dichloromethane, water or epichlorohydrin observed. From DSC analysis (standard heat/cool/heat type), however, the  $T_g$  values obtained were much lower than expected ( $16^\circ\text{C}$  during 1<sup>st</sup>

cooling cycle, 20°C during 2<sup>nd</sup> heating cycle). These results, coupled with the <sup>1</sup>H-NMR data, implied that residual TBAB was negatively impacting the properties of the crosslinked CBDO-DGE.



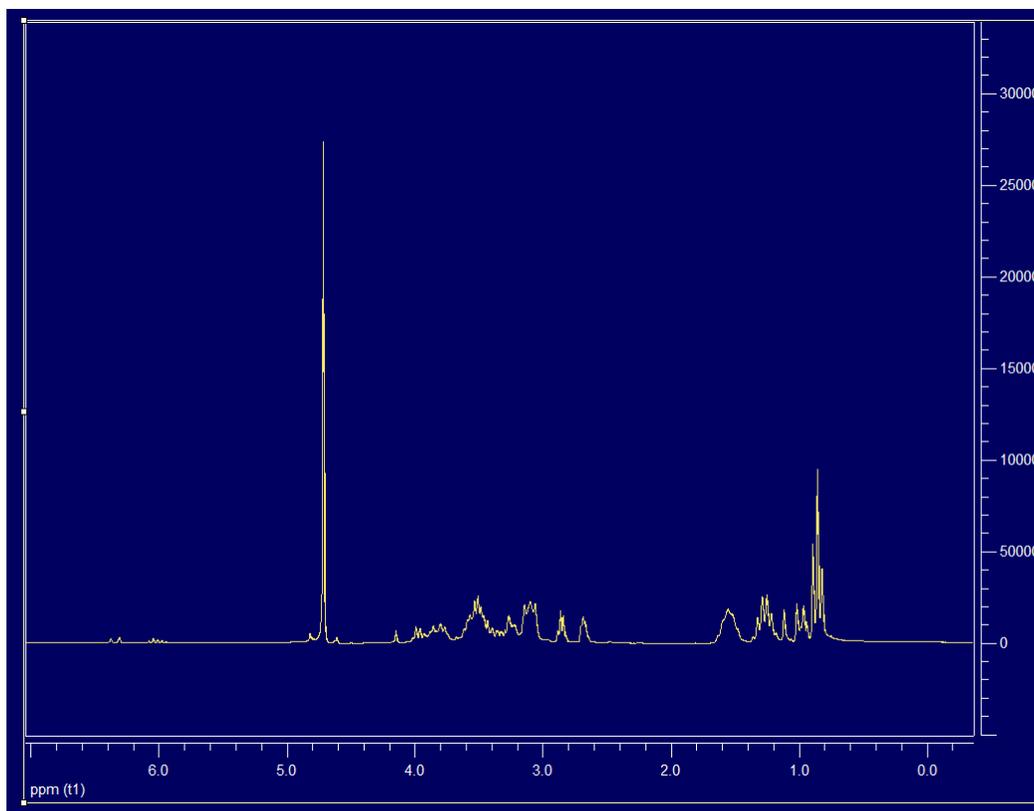
**Figure 2: TGA data from crude CBDO-DGE (1<sup>st</sup> synthesis) following crosslinking with TETA.**

In order to better evaluate the true properties of the CBDO-DGE it was necessary to remove the TBAB impurities from the product. Once a second synthesis was performed, the product was washed with water (in which TBAB was confirmed to be soluble) and <sup>1</sup>H-NMR was used to assess the purity of the product at each washing step. Figure 3 shows the <sup>1</sup>H-NMR spectrum of the product of the second synthesis after four water washes, with the absence of the peaks corresponding to TBAB indicating its successful removal; note that the orange color of the product remained in spite of the washing.



**Figure 3: <sup>1</sup>H-NMR of the 4× water washed product of the second CBDO-DGE synthesis**

Further confirming the efficacy of this purification procedure, Figure 4 shows the <sup>1</sup>H-NMR spectrum of the water used in the initial washing step, with two peaks corresponding to TBAB clearly visible in the range of 1.1-1.3 ppm in addition to peaks corresponding to some amount of the CBDO-DGE product.



**Figure 4:  $^1\text{H-NMR}$  of water used in the first washing step of the product of the second CBDO-DGE synthesis.**

Crosslinking of BADGE, CHDM-DGE and water washed CBDO-DGE with TETA was attempted under three different conditions ( $60^\circ\text{C}$  / 12 hours,  $100^\circ\text{C}$  / 4 hours,  $140^\circ\text{C}$  / 1 hour) in order to ensure that optimally cured materials were produced in all cases. The CBDO-DGE and BADGE were successfully crosslinked at  $60^\circ\text{C}$  and  $100^\circ\text{C}$  while the CHDM-DGE was successfully crosslinked only at  $60^\circ\text{C}$ , with obvious thermal degradation occurring at higher crosslinking temperatures. In general, higher  $T_g$ ,  $T_{\text{onset}}$  and  $T_{\text{max}}$  values were observed in samples crosslinked at the highest cure temperature at which degradation did not occur. From the DSC and TGA data listed in Appendix A, it was determined that the CBDO-DGE material crosslinked at  $100^\circ\text{C}$  yielded a  $T_g$  value was sufficiently above room temperature to warrant further study. In contrast, the CHDM-DGE network gave a significantly lower  $T_g$  value in spite of the fact that CHDM-DGE is a structural isomer of CBDO-DGE. This result confirms the importance of the rigidity imparted by the CBDO.

**Table 1: TETA Crosslinking Experiment Summary**

Sample	60 °C (12 hrs)	100 °C (4 hrs)	140 °C (1 hr)
CBDO-DGE	Successful	Successful, preferred	Degraded
CHDM	Successful, preferred	Degraded	N/A
BADGE	Successful	Successful, preferred	Degraded

The purified CBDO-DGE network cured at 100°C had a  $T_g$  of 49-53°C (~30 °C higher than the network based on the crude CBDO-DGE from the first synthesis), while the BADGE network cured at 100 °C had a  $T_g$  of 117-121°C. As CBDO is known to provide much higher glass transition temperatures in the context of Eastman’s copolyesters, this result, coupled with the color retention observed in the washed CBDO-DGE product from the second synthesis, indicated that some impurities likely remain in the CBDO-DGE and are depressing the  $T_g$  and / or affecting crosslinking as a result. This effect was previously observed following crosslinking of the product of the initial synthesis, wherein the presence of the residual TBAB compromised the properties of the crosslinked material, reducing  $T_{onset}$  and  $T_{max}$  by ~80 °C and ~60 °C, respectively, and reducing  $T_g$  by ~30°C. The networked based on the purified CBDO-DGE, on the other hand, shows thermal stability on par with BADGE, with  $T_{onset}$  and  $T_{max}$  values of 313°C and 382°C respectively, vs. 340°C and 364°C for the equivalent BADGE network. This level of thermal stability in a material with known impurities is already a positive result, though as with the glass transition temperature, further improvements should be achievable if product purity can be further improved.

## SUMMARY AND CONCLUSIONS

In conclusion, CBDO-DGE was successfully synthesized from the CBDO molecule. Residual phase transfer catalyst, TBAB, was found in the original product. A water-based washing process was developed and demonstrated to successfully removed TBAB from the product, as confirmed by  $^1\text{H-NMR}$  spectroscopy. Once the CBDO-DGE was crosslinked with TETA, DSC and TGA data from the crosslinked

networks demonstrated that the removal of the TBAB gave rise to substantial improvements in the thermal stability and glass transition temperature, with thermal properties approaching those of the BADGE-based material and surpassing those of the CHDM-based material. Based on the orange color of the water washed CBDO-DGE, however—pure CBDO-DGE should be colorless—there is clearly room for further improvement of the properties of the CBDO-DGE based materials. Future work will focus on scaling up the synthesis of the CBDO-DGE in order to evaluate mechanical properties and adhesion characteristics. Also being studied is the possibility to achieve higher purity using a dilute acetic acid wash in order to remove both TBAB and any residual sodium hydroxide in the product. The ultimate goal is the synthesis of a high molecular weight CBDO-based solid epoxy specifically applicable to the needs of the can coating industry.

## Appendix A: DSC and TGA Results Summaries

### DSC Results Summary

Sample (curing temperature)	Glass Transition Temperature ( $T_g$ , °C, from 1 <sup>st</sup> cooling cycle)	Glass Transition Temperature ( $T_g$ , °C, from 2 <sup>nd</sup> heating cycle)
CBDO-DGE (60 °C, crude product)	16	20
CBDO-DGE (60 °C, washed product)	28	35
CHDM (60 °C)	27	34
BADGE (60°C)	101	107
CBDO-DGE (100°C, washed product)	49	53
BADGE (100°C)	117	121

### TGA Results Summary

Sample (curing temperature)	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)
CBDO-DGE (60°C, crude product)	232	320
CBDO-DGE (60°C, washed product)	247	338
CHDM (60°C)	290	315
BADGE (60°C)	340	364
CBDO-DGE (100 °C, washed product)	313	382
BADGE (100°C)	344	362