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# Heat-Induced Hardening and the Effect of Aromatic Ring in Epoxy Resins

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**Abstract:** Two epoxy resins were prepared by reacting Bisphenol-A and hydroquinone respectively with epichlorohydrin in the presence of sodium hydroxide as catalyst. The epoxy resins were characterized by Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (<sup>1</sup>H-NMR), and Differential Scanning Calorimetry (DSC). The epoxy resins were mixed with hardener and heated up to 140 °C for crosslinking. Interestingly, the resins were also found to harden without the addition of hardener but not crosslinked, as proven by Soxhlet extraction. Pendulum hardness of the films showed that the film became harder with the increase of time and temperature of heating.

**Keywords:** Epoxy resin, Bisphenol A, Hydroquinone, Heat-induced Hardening, Aromatic Rings

## 1. Introduction

Polymers are obtained by polymerization, that is, the process of joining the small repeating units (monomers) together to form big molecules [1]. Polymers can be generally classified into two major groups, which are thermoplastic and thermoset.

Thermoplastics are moldable after heat application and will solidify after cooling [2]. Their physical properties are due to the high molecular weight and the polymer chains associate through intermolecular forces. Thermoplastics may be recovered by heat or the usage of appropriate solvents. On the other hand, thermosets start with low molecular weight polymers (liquid) and solidify by cross-linking of the polymer chains. The cross-linking will form a network of polymeric chains and this process is irreversible. Thermoplastics obtain their physical properties by having high molecular weight, while thermosets do so by the formation of a network. Both of them have their own weaknesses. The thermoplastics are usually solid and heat is required to melt them so they can be molded into the required shape. The melt viscosity is even higher for higher molecular weight thermoplastics, such as Ultra High Molecular Weight Polyethylene (UHMWPE) [3]. Thermosets do not

suffer this problem as they are generally in liquid form which makes them easy to be applied. However, once cured, they can never be returned back to their original liquid state. Recycling of thermosets is always problematic due to this reason [4].

Epoxy is a colloquial name for the epoxide functional group and also a name for adhesive that join substrates together or cover surfaces. Epoxy resins have been used widely in many applications because of their good properties in many aspects, such as superior mechanical performance, outstanding adhesion, good dimensional stability, and good corrosion resistance [5, 6].

With this work, it has been demonstrated that the epoxy resin may also be hardened without the use of hardener. This is a thermoplastic epoxy resin but behaves like a thermoset resin, except for the crosslinking. Until now, the description of hardening of epoxy resin by heat alone is yet to be found elsewhere. Usually hardening of epoxy is done by chemical cross-linking using low molecular weight toxic polyamines and other cross-linkers. This simple yet novel idea will save time, cost, and workers from exposure to the toxic cross linkers. It may not be suitable for heat-sensitive materials but will be useful for some applications, for example construction, home decoration, art, 3D-printing, packaging, and others as well where suitable.

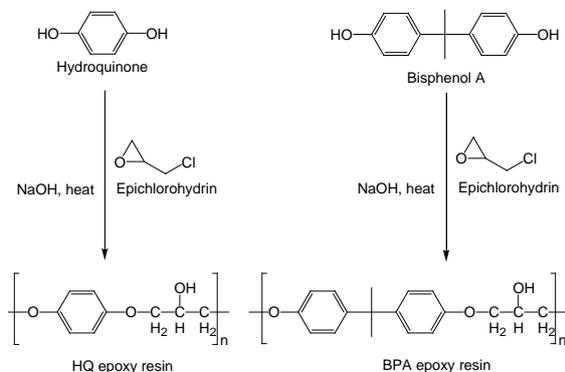
To prove the point, monoaromatic (hydroquinone) and diaromatic (Bisphenol A) compounds have been used and the resultant epoxies are tested on their ability to harden with just heat. Both BPA and HQ serve as monomers for the synthesis of epoxy resin. In order to synthesize an epoxy resin, the structure of the monomer must contain two –OH functional groups attached directly to aromatic ring in order to enable reaction with epichlorohydrin. In the structure of BPA, there are two benzene rings, and two –OH groups, whereas hydroquinone contains one benzene ring with two –OH groups.

## 2. Experimental 2.1 Materials

Bisphenol A (BPA) (Aldrich), hydroquinone (HQ) (System), epichlorohydrin (Fluka), sodium hydroxide (NaOH), dimethyl formamide (DMF) (R&M), potassium hydrogen phthalate (KHP), benzene (Fisher), 37 % hydrochloric acid (HCl) (QReC), and potassium hydroxide (KOH) (Merck) were used as received unless stated otherwise.

## 2.2 Synthesis of BPA and HQ epoxy resin

BPA (52.44 g, 0.23 moles), epichlorohydrin (124.88 g, 1.35 moles), and distilled water (2 mL) were stirred and heated until reflux. The solution was cooled until the temperature dropped to 80 °C. NaOH pellets (5 g) were added slowly to the solution. The reflux process was then continued for further 45 minutes. After the excess epichlorohydrin was removed by vacuum distillation, the solution was cooled and benzene (30 mL) was added. White crystals were precipitated and filtered. The filtrate was further heated at a temperature less than 120 °C. Finally, the epoxy resin was put inside the oven at 140 °C for 10 minutes to obtain BPA epoxy resin. For HQ epoxy resin, the procedure was similar to the synthesis of BPA epoxy resin with the exception that BPA was replaced with HQ (25.33 g, 0.23 moles). The reactions are illustrated in **Figure 1**.



**Figure 1.** Synthesis of HQ and BPA epoxy resins

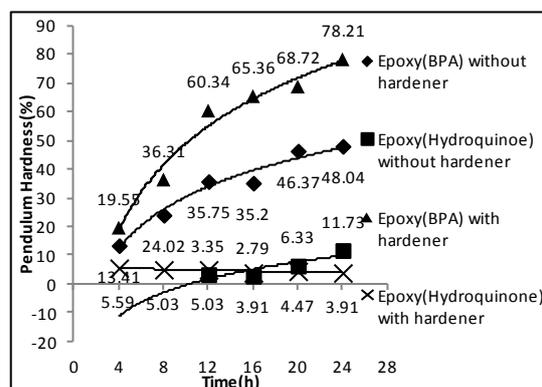
## 2.3 Determination of Epoxide Equivalent

KOH (1.18 g) and KHP (4.10g) were dissolved separately with distilled water (100 mL). A few drops of phenolphthalein indicator was added into KOH (10 mL) and titrated with KHP. 37 % HCl (25 mL) was dissolved in DMF (100 mL). 10 mL of this mixture was titrated with standardized KOH. Epoxy resin (1 g) was dissolved in DMF hydrochloride solution (50 mL). The mixture was refluxed for about 20 minutes. The mixture was cooled and 10 mL of the mixture was titrated with KOH solution.

## 3 Results and Discussions

### 3.1 Pendulum Hardness Test

BPA epoxy resin was coated on glass using bar coater without adding any hardener and heated at temperature 140 °C for 4, 8, 12, 16, 20, and 24 hours (h). Then, the BPA epoxy resin was mixed with hardener (diethylene tetramine) and heated as above. The same steps were repeated on hydroquinone epoxy resin. Films formed on the glass were then tested for pendulum hardness. The film formed from HQ epoxy resin without hardener only started to harden after 12 h, thus the results were taken started from 12 h onwards. The results showed that film formed from BPA epoxy resin with hardener had the highest pendulum hardness. The pendulum hardness of BPA epoxy resin with or without hardener and HQ epoxy resin increased as the heating time increased. Interestingly, those films without hardener also harden as the temperature increased. This was unusual since the resin should melt/soften with the increase of temperature. Soxhlet extraction proved that these films without hardener were not crosslinked, since no residue left after 24 h of extraction in acetone. For HQ epoxy resin with hardener, the result fluctuated. Both BPA epoxy resin with and without hardener had higher pendulum hardness than HQ epoxy resin. This was due to the greater amount of benzene rings in the BPA (2 aromatic rings) versus HQ (1 aromatic ring). The results were shown in **Figure 2**.



**Figure 2.** Pendulum hardness of film formed from epoxy (BPA) and epoxy (HQ) without and with hardener

### 3.2 Average Molecular Weight and Viscosity

Epoxide equivalent and viscosity of the epoxies were determined. The average molecular weight and viscosity of BPA epoxy resin was higher than HQ epoxy resin. The results showed that average molecular weight was related the viscosity of the epoxy resin. The epoxy resin with higher molecular weight will have higher viscosity. The molecular weight and viscosity influenced the time needed for

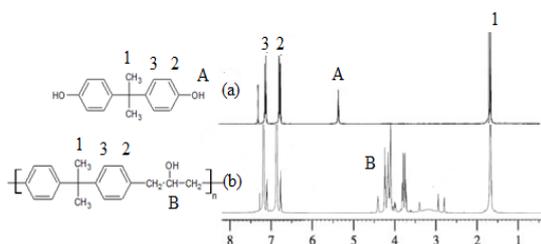
the epoxies to harden, as the HQ epoxy resin with low viscosity took longer time to harden.

**Table 1.** Average Molecular Weight and Viscosity of Epoxy Resins

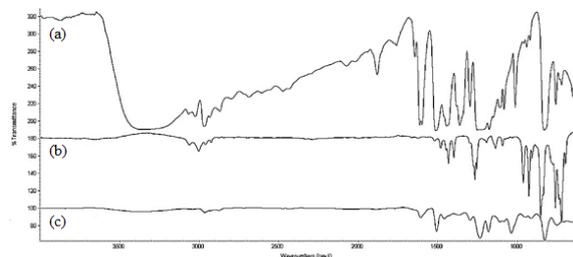
Epoxy	Average Molecular Weight (g/mol)	Viscosity (mPa.s) at 25 °C			
		Reading 1	Reading 2	Reading 3	Average
BPA	2454.0	35521	36350	37074	36315
HQ	648.2	167.8	166.3	160.5	164.9

### 3.3 FTIR and NMR analysis

BPA and its epoxy resin were characterized and compared. The <sup>1</sup>H-NMR spectra of BPA and its epoxy resin were presented in **Figure 3**. The peak at 1.6 ppm corresponded to methyl hydrogen and the peaks at 6.5-7.2 ppm corresponded to aromatic hydrogen's. The disappearance of the peak at 5.2 ppm which was relative to hydroxyl groups and the presence of the peaks at 3.7-4.3 ppm corresponded to propyl backbone for the BPA epoxy revealed successful condensation reaction. FTIR spectra in **Figure 4** had different patterns in fingerprint region, confirming the spectrum of the product (BPA epoxy) was different from its precursors (BPA and epichlorohydrin).



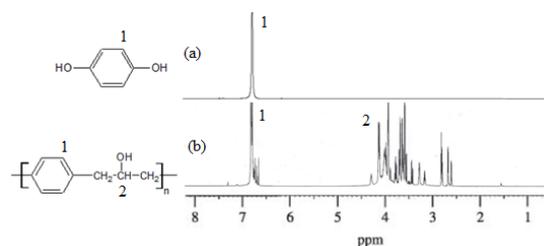
**Figure 3.** <sup>1</sup>H-NMR in CDCl<sub>3</sub> of (a) BPA and (b) its epoxy.



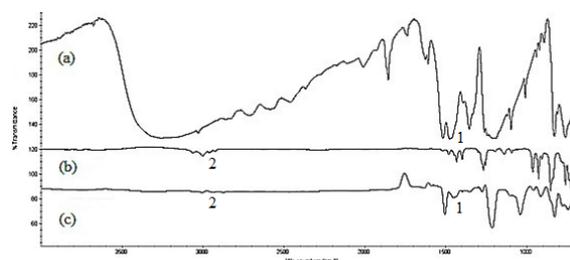
**Figure 4.** FTIR spectra of (a) BPA, (b) epichlorohydrin, and (c) BPA epoxy resin.

For HQ epoxy resin, based on <sup>1</sup>H-NMR analysis, the reaction was observed to be success (**Figure 5**). FTIR spectrum of the epoxy contain the band assigned to methyl group and aromatic group (2940-2960 cm<sup>-1</sup> and about 1500 cm<sup>-1</sup>), proven that the epoxy were successfully synthesized (**Figure 6**). The NMR and FTIR spectra before and after heat-induced hardening were also similar even down to

the fingerprints region (FTIR), suggesting no chemical changes happened during heating.



**Figure 5.** <sup>1</sup>H-NMR spectra in CDCl<sub>3</sub> of (a) hydroquinone, and (b) its epoxy. The peaks at 3.4-4.1 ppm were from the propyl backbone which appeared after the synthesis.



**Figure 6.** FTIR spectra of (a) hydroquinone, (b) epichlorohydrin, and (c) its epoxy. The band at 2940-2960 cm<sup>-1</sup> was assigned to the methyl group in the epichlorohydrin, while the band at about 1500 cm<sup>-1</sup> was assigned to the aromatic group.

### 3.4 Differential Scanning Calorimetry

The DSC result of BPA epoxy resin with and without hardener had a peak at 346.65 °C and 312.98 °C respectively (**Figure 7a and 7b**), while the result of HQ epoxy resin with and without hardener had a peak at 337.46 °C and 304.55 °C respectively (**Figure 8a and 8b**). This proved that both resins had higher thermal stability after addition of hardener. BPA epoxy resin had higher thermal stability than HQ epoxy resin either with or without hardener. BPA contains two benzene rings which conferred higher thermal stability as compared to HQ epoxy resin. The self-induced hardening was possibly due to the physical rearrangement of aromatic part in the epoxy backbone.

### 4. Conclusion

Epoxy resins added with hardener had higher pendulum hardness and thermal stability. BPA epoxy resin had better surface hardness and thermal stability than HQ epoxy resin. This can be attributed to the BPA epoxy resin which contained more benzene rings in its backbone than HQ epoxy resin. Surprisingly, they were also capable to harden with heat alone sans the hardener. The heat-induced hardening was not because of chemical changes but most likely due to physical rearrangement of aromatic moieties inside the epoxy backbone.

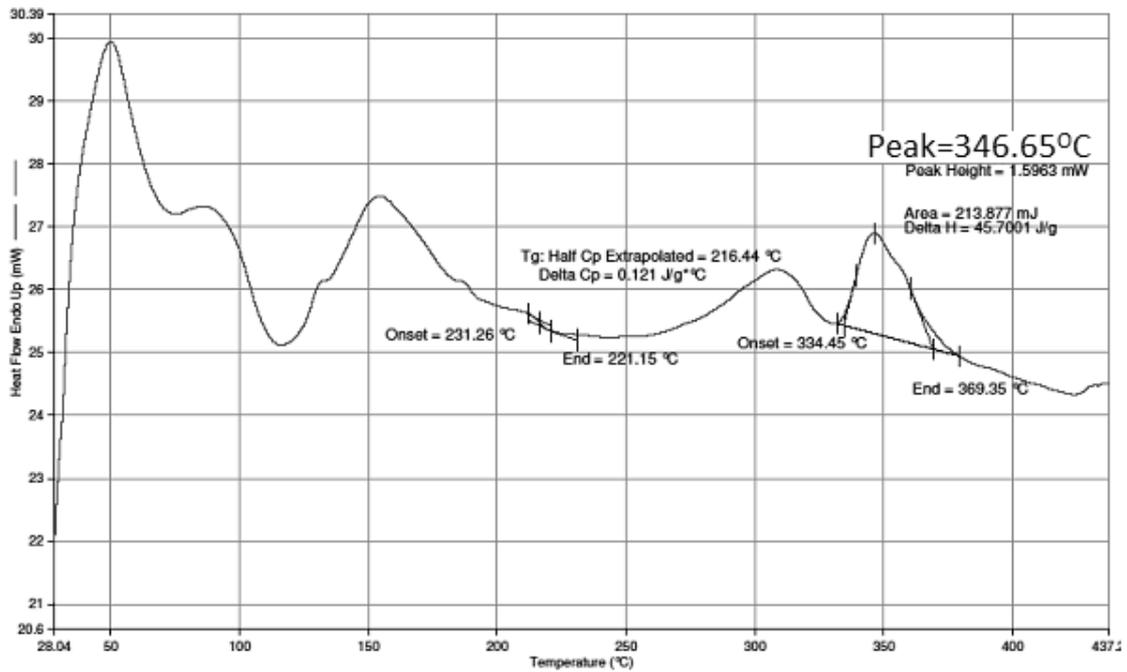


Figure 7 (a) DSC of BPA epoxy resin with hardener

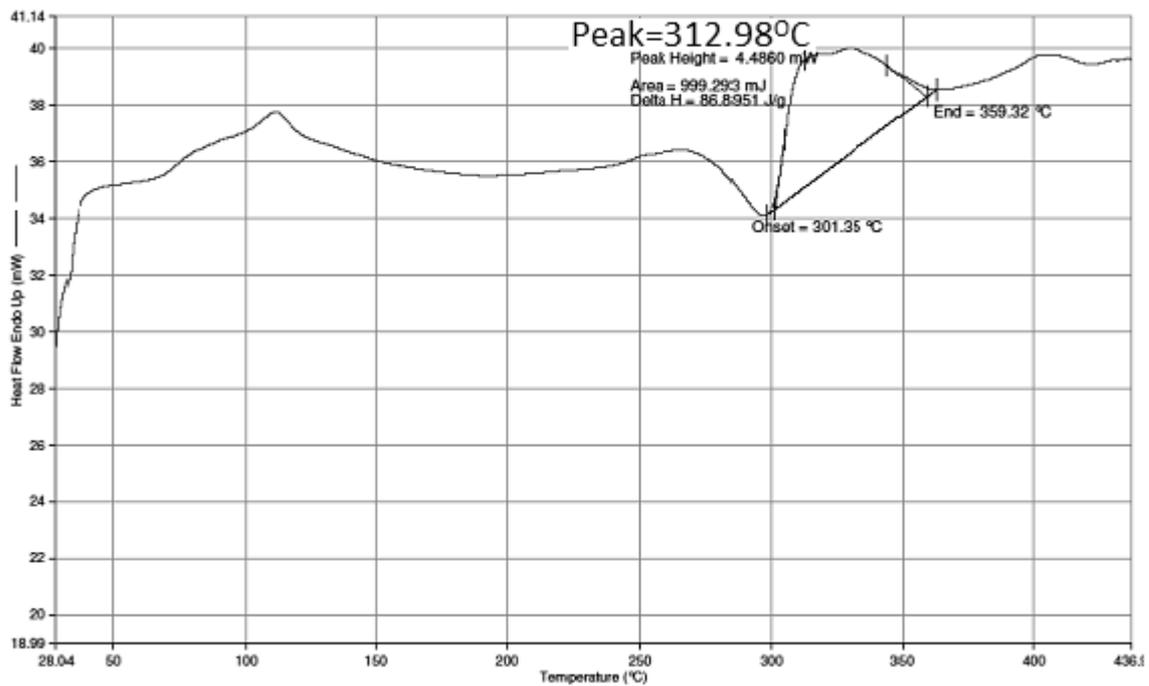


Figure 7 (b) DSC of BPA epoxy resin without hardener

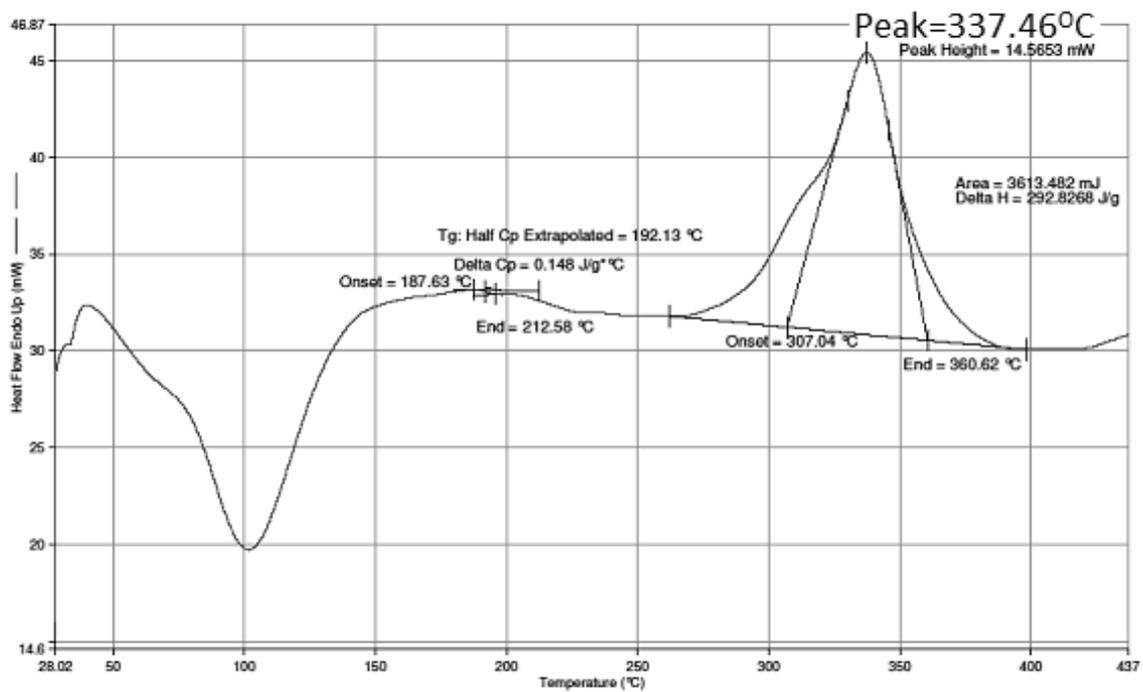


Figure 8 (a) DSC of HQ epoxy resin with hardener

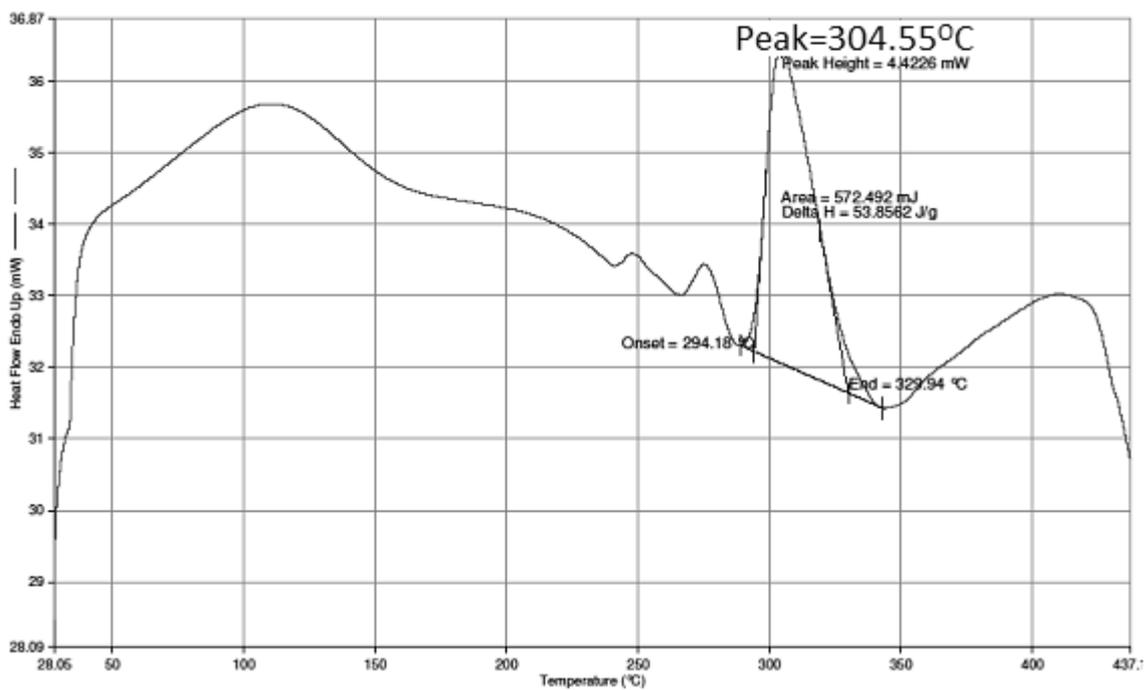


Figure 8 (b) DSC of HQ epoxy resin without hardener

## 5. Acknowledgements

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