# CHAPTER II

# THEORY

## 2.1 Metal Containers

In the field of metal containers, various kinds of metal containers have been developed. They are used to contain a wide variety of products such as beverages, foods, aerosol products, paints, medicines, and many other products. The metal containers have many advantages because of their rigidity and high thermal resistance. They can withstand outside or inside pressure and high temperature. Nowadays, materials as tinplate and aluminum have become universally adopted for the manufacture of containers and can ends for foods and beverages as detailed below.

### 2.1.1 Tinplate

Tinplate is the oldest material, and the most important material for metal containers. Tinplate is low-carbon steel coated with tin by hot dipping or electrodeposition. The use of tin coating generally to protect the base steels from rust, corrosion and produces a bright appearance. There are many applications of tinplate due largely to several qualities of this material such as mechanical strength and resistance to working condition, low toxicity, and the ability to withstand the extremes of temperature (*47, 48*).

### 2.1.2 Aluminum

Aluminum was used for packaging of fish, milk, meat, and vegetables. Its widespread adoption in packaging came when techniques for rolling and decorating thin aluminum foils were perfected. Now aluminum is widely used for beers and carbonated beverages. The advantages of aluminum as a food packaging material are as follows:

1. No taste and odor: Aluminum can be used for the most sensitive product such as beer.
2. No sulfide staining: Aluminum does not produce sulfide staining caused by sulfur containing food products.
3. Workability: Aluminum requires less strength for draw or draw and ironing operations.

On the other hand, the poor resistance to acid or chloride-containing products is the main disadvantage of aluminum. In general, aluminum has excellent resistance to a wide range of corrosive compounds, but when the pH of the food is low, they react with aluminum. Additionally, chloride in the foods has a strong corrosive action, so in the case of foods with acid and high chloride contents, the aluminum surface must be coated to prevent contact.

## 2.2 Metal Can Manufacturing

Can manufacturing processes can be divided into 3-piece and 2-piece cans and can ends. The 2-piece can manufacturing can be further grouped into draw and wall ironing (DWI or DI) or drawn and redrawn (DRD) (*47, 48, 49, 50*).

### 2.2.1 Three-Piece Cans

Open-top or three-piece cans consist of the can body and two end pieces. They are made from tinplate. Before the bodies are formed, coatings are usually applied to the steel surfaces. After the coatings are applied, the sheets are transported to the fabrication process. The first stage is cutting the tinplate that cured with protective coating and then bent into cylinders. Next, the overlapped edges are welded or cemented, then sprayed with coating called a “side seam stripe” to protect exposed metal along the seam. For ends forming, they are stamped out of the metal sheets. The cylinders are flanged in preparation for the attachment of ends, and are narrowed down to reduce the size of the ends, which reduces the amount of material used to make the ends. Finally, one end, top or bottom is seamed on the body.

### 2.2.2 Two-Piece Cans

Two-piece cans are made by forming a cup shaped container with one piece of aluminum or steel and then attached an end to it. Two-piece cans (a seamless body and an end) are manufactured either as draw and wall ironing (DWI or DI) or drawn and redrawn (DRD). After the process, various coatings are applied and cured. These processes are described below.

1. DWI cans (Draw and Wall Ironing Cans)

The DWI process produces thinner wall than the DRD process and is used to produce aluminum cans for carbonated beverages where the gas pressure are added to support the cans. DRD cans are thicker and able to withstand the vacuum in the container.

In the DWI process, the circular piece is first drawn into a shallow cup. Then, it is forced to reduce thickness of the wall and increase the can height about three times to the required content, but the base dimension remains unchanged, as illustrated in Figure 2.1. The internal lacquer is applied by spraying. The thickness of the coating depends on the aggressiveness of the contents such as cans that contain very aggressive products may require a thicker initial coating or use a second coating. The number of spray coats also depends on the type of material: aluminum or steel.



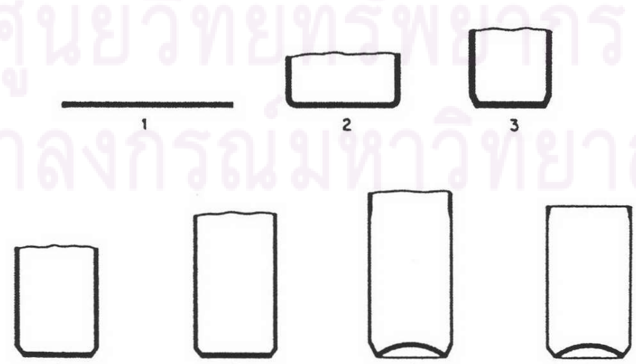



**Figure 2.1.** Operation sequence in manufacturing Draw and Wall Ironing cans (DWI).

2. DRD Cans (Draw and Redraw Cans)

DRD produced from a single pressing operation. The initial stages are similar to the DWI process, but instead of ironing to reduce the wall thickness, metal is moved from the base of container to the wall by decreasing the diameter. Hence, the wall and base thickness as well as the surface area are identical to the original blank, as opposed to the DWI cans of which the wall thickness is much lower than the base thickness. A typical DRD process is shown in Figure 2.2.

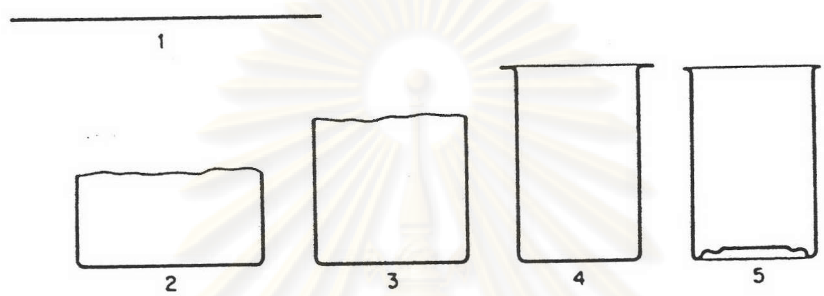



**Figure 2.2.** Operation sequence in manufacturing Draw and Redraw cans (DRD).

The DRD cans are made from pre-enameled sheets requiring no coating repair after the can is formed. This may be an advantage since it is cheaper to apply lacquer onto sheet than to formed cans. The two-piece steel and aluminum DRD cans are used as container for food products, including pet foods, tuna, salmon, and snack. Additionally, they are also used for non-food products such as car wax and shoe polish.



Modification of the DWI and DRD process is called draw thin redraw (DTR). First, a large-diameter blank is cut and a cup is formed. Then the can diameter is reduced and height is increased during the first drawing operation, while maintaining the thickness of the can. Finally, the diameter is further reduced and height is increased to can size during the second redraw operation. The side wall of the finished can is about 15% thinner than the original metal and thinner than the bottom. The wall thinning is performed by stretch forming during drawing, to protect the organic coating. The DTR process is shown in Figure 2.3

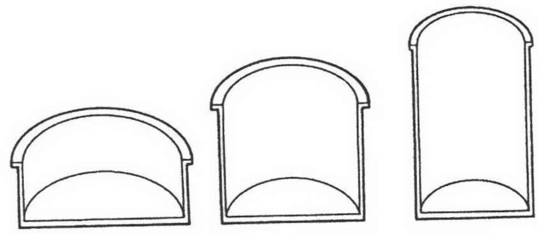



**Figure 2.3.** The Draw Thin Redraw (DTR) process.

### 2.2.3 Easy-Open Ends

The ends are stamped out from tinplate sheet that have generally been coated on both sides: interior coating and printing on exterior. After stamping, the ends are scored in an oval can and a tab is attached to form an "easy open" end. Because of these steps are performed after the end piece has been coated, the coating may be damaged. Repair coatings are applied after these steps to restore the coatings. There are two main types of the easy-open end:

a) With pouring aperture: pear shaped, used for dispensing liquids (beverages, oils, etc.)
b) With near full aperture: used for solid products

## 2.3 Protective Coatings

Interior coatings are applied to protect the can from corrosion by the contents and to protect the contents from being contaminated by dissolved metal from the can (*51*). In addition, pigmented interior coatings may be applied to improve the visual appearance of the inside wall. The primary purpose of the interior coating is to form a barrier between the can and its contents. Moreover, they are used for the prevention of organoleptic changes which might occur as a result of the dissolution of the metals from the container into food. Furthermore, it prevents the discoloration of food and to avoid the discoloration of the internal surface of cans, especially with foods that are rich in sulfur such as fish, meat, and certain vegetables. In general, coatings must be resistant to chemicals, flexibility, and adhesion to the metal surface. Moreover, coatings are applied before to fabrication processes, such as coatings for ends and 2-

piece draw and redraw cans must be able to withstand the heat during pasteurization processes. Metal deformation with the disruption of the surface can happen in the DWI operation, such container must be recoated the internal surface after fabrication. If lacquers are damaged during container manufacture, they will not give complete protection to the can. Therefore, post-fabrication repair of lacquering is very important.

Metal cans are used in a wide variety of products. The formulation of the internal coating depends on the can manufacturing process (method used in shaping the metal), the nature of the food contents because of the chemical properties of the contents are different and most important, the expected shelf life of canned foods (*50*). Internal coatings are categorized as food and non-food coatings due to the differences in properties and the regulations for edible products. Because of the unique requirements of different products contained in cans, varieties of internal coatings are available. The coatings generally used for food contact surface are acrylics, epoxy-phenolics, oleoresins, phenolics, and vinyls (*47, 51, 52*).

**Oleoresins:** These are the first lacquers ever used in food canning. They are widely used for fruit cans. The advantages of oleoresin coatings have been low cost and high resistance to fruit acids. However, they lack resistant to sulfide-containing foods such as green beans, butter beans, meats, etc. Thus, the sulfur absorbing chemicals such as zinc oxide are incorporated in to the formulation.

**Phenolics:** They are usually synthesized by the reaction of phenol with formaldehyde as shown in Figure 2.4. The reaction under alkaline condition with excess formaldehyde results in ortho- and para-substitution into the aromatic ring of the phenolic. The ratio of reactants may vary, producing resols (also called one-stage phenolics), and novolacs (also called two-stage phenolics). These materials are found widely used because of their good chemical resistance and resistance to sulfide staining. However, their weakness requires very careful control at high temperatures 190-195 °C. Moreover, they have low resistance to cracking under bending (low flexibility). Hence, their use is limited to three-piece bodies and ends. More often, they are used in combination with epoxy-phenolic coatings.

**Acrylics:** The most common usage of acrylics is the manufacture of pigmented and decorative coatings where high temperature resistance is required. As for phenolics, they are often used in combination as epoxy-acrylics.

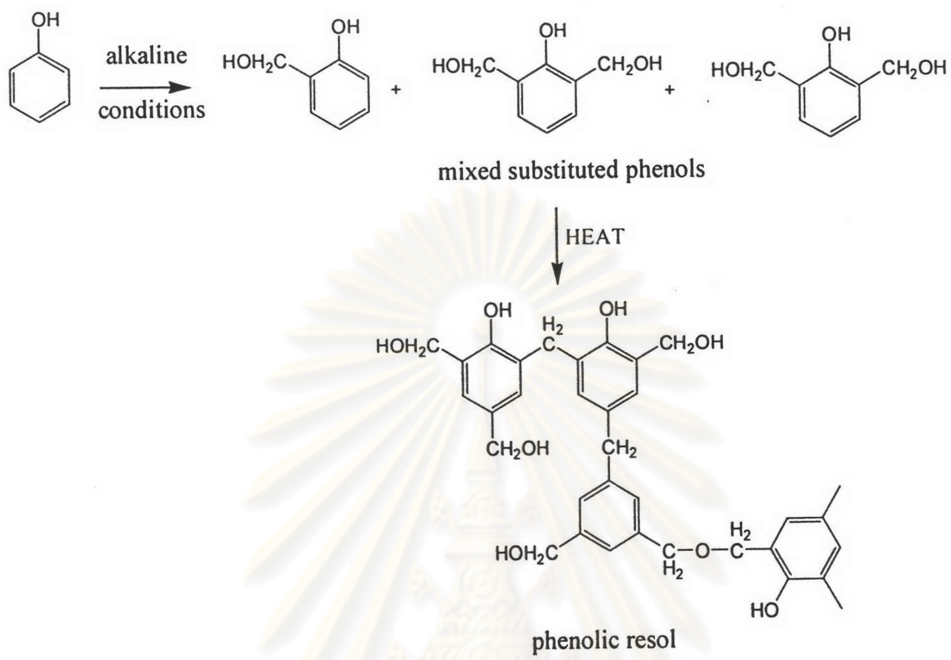
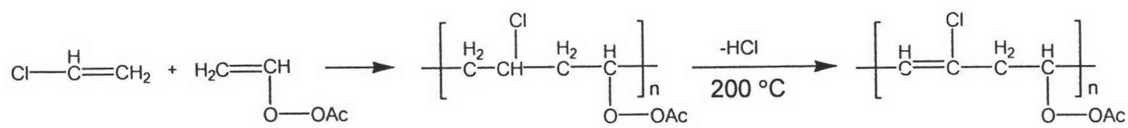



**Figure 2.4.** The reaction of phenol with formaldehyde to create phenolic lacquers.

**Epoxies and epoxy-phenolics:** Epoxy resins such as BADGE, bisphenol-A-diglycidyl ether, are produced from the condensation reaction between epichlorohydrin and bisphenol A. They are resistant to acids, and have good heat resistance and flexibility. In addition, they are also coated with zinc oxide or metallic aluminium powder to prevent sulfide staining from meat, fish and certain vegetables. Moreover, they usually used in combination with epoxy-acrylics, epoxy-amides, or most importantly, as epoxy-phenolics. The combination as epoxy-phenolics provides an excellent lacquer that has good adhesion properties of epoxy resin and with high chemical and heat resistance properties of phenolic resin.

**Vinyls (Organosol, PVC):** The monomers are vinyl chloride and vinyl acetate as shown in Figure 2.5. The adhesion of coatings may be improved by co-polymerizing with small percentages of maleic anhydride. Vinyl resins may also be blended with other resin groups such as epoxies, phenolics and alkyds. These coatings show good adhesion and flexibility. Their flexibility allows them to be used for can ends as well as drawn cans. Moreover, they are resistant to acid but their main disadvantage is their high sensitivity to high temperature used in heat sterilization. The vinyl products are completely absent of taste and are suitable for beer and soft drink.




Vinyl chloride  Vinyl acetate  Poly(vinyl chloride-co-vinyl acetate) Organosol Resins  Thermal degradation Product

**Figure 2.5.** The reaction of vinyl chloride with vinyl acetate to synthesize vinyl lacquers.

As explained above, the production of two-piece cans and easy-open ends requires coatings of high flexibility, since the lacquers are applied before shaping the cans or lids. This is an important reason for the selection of organosol coatings regardless of their poor heat resistance property. Hence, in order to establish the suitability of a coating for particular food products, it is necessary to know their corrosion characteristics, properties of such coatings, and the processing of food cans.

The analysis of can coatings and the migration from coatings into foods attracts great attention after BADGE has been found in unexpected amount in canned food. Therefore, great attention has been paid to the study of BADGE and the occurrence of BADGE in can lacquers and canned foods (*17*).



## 2.4 BADGE

2,2-Bis(4-hydroxyphenyl)propane bis(2,3-epoxypropyl) ether or Bisphenol-A-diglycidyl ether (BADGE), $C_{21}H_{24}O_4$, (CAS No. 1675-543) is commonly used as a bifunctional monomer or cross-linker in epoxy-base coatings and very widely used in food cans a coating of the internal surfaces. The epoxy polymers are obtained by the reaction of bisphenol A and epichlorohydrin as shown in Figure 2.6.

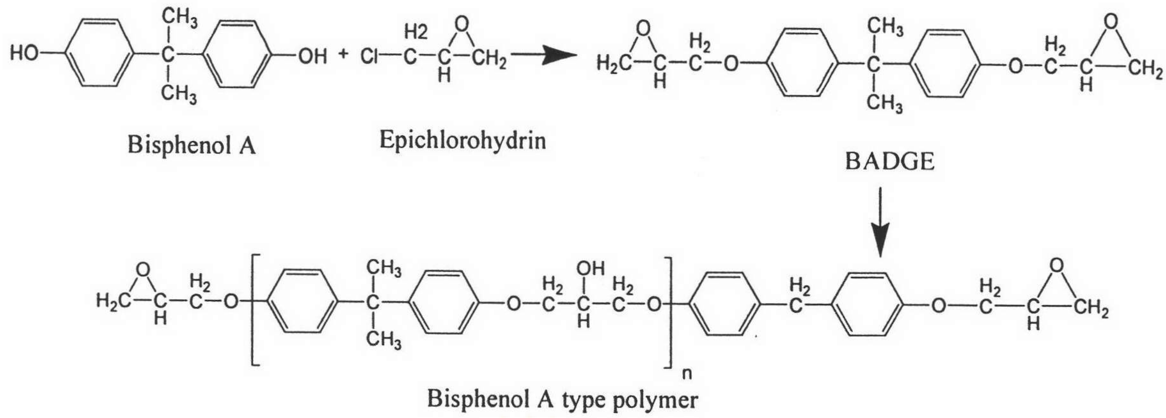



**Figure 2.6.** Synthesis of Bisphenol A type resin.

The varying degree of condensation (n) depends on the reaction condition and the mole ratio of the reactants. Small amounts of further reaction products such as di-BADGE, tri-BADGE (linear or branch) and cyclo-di-BADGE occur as by-products in the technical synthesis.

## 2.5 Reaction products of BADGE

Many studies have showed that BADGE is not the only compound released from can coating, but there are many reaction products of BADGE as well.

### 2.5.1 Hydrolysis Products

It was observed in all food simulants that rapid hydrolysis of BADGE is likely to occur. As expected, BADGE is sensitive to hydrolysis in contact with aqueous foodstuffs (*14*), so special attention was given to study the stability of BADGE under migration test condition such as 10 day at 40 °C. The formation of mono- and di-hydrolysis products (BADGE.$H_2O$ and BADGE.$2H_2O$, respectively) occurred by opening one and two epoxide rings. These investigations found that BADGE was completely hydrolyzed in all three aqueous food simulants after 10 days at 40 °C. A kinetic study revealed the approximate half-lives of BADGE in aqueous food simulants under the 10 days at 40 °C as shown in Table 2.1.

**Table 2.1.** Hydrolysis of BADGE in aqueous food simulants at 40 °C. (*53*)

| Food Simulant | Half-life time (days) |
|---|---|
| Distilled water | 1.1 |
| 3% (w/v) Acetic acid | 0.15 |
| 15% (v/v) Ethanol | 1.4 |

### 2.5.2 Chlorohydroxy Products

When BADGE is used as the scavenger for hydrochloric acid that formed by the degradation of polyvinyl chloride (PVC) base lacquers, the epoxy groups of BADGE react with hydrochloric acid and help stabilize the polymer as shown in Figure 2.7. The chlorohydroxy compounds (BADGE.HCl and BADGE.2HCl) are the potential carcinogens found due to the analogy to chloropropanediols.

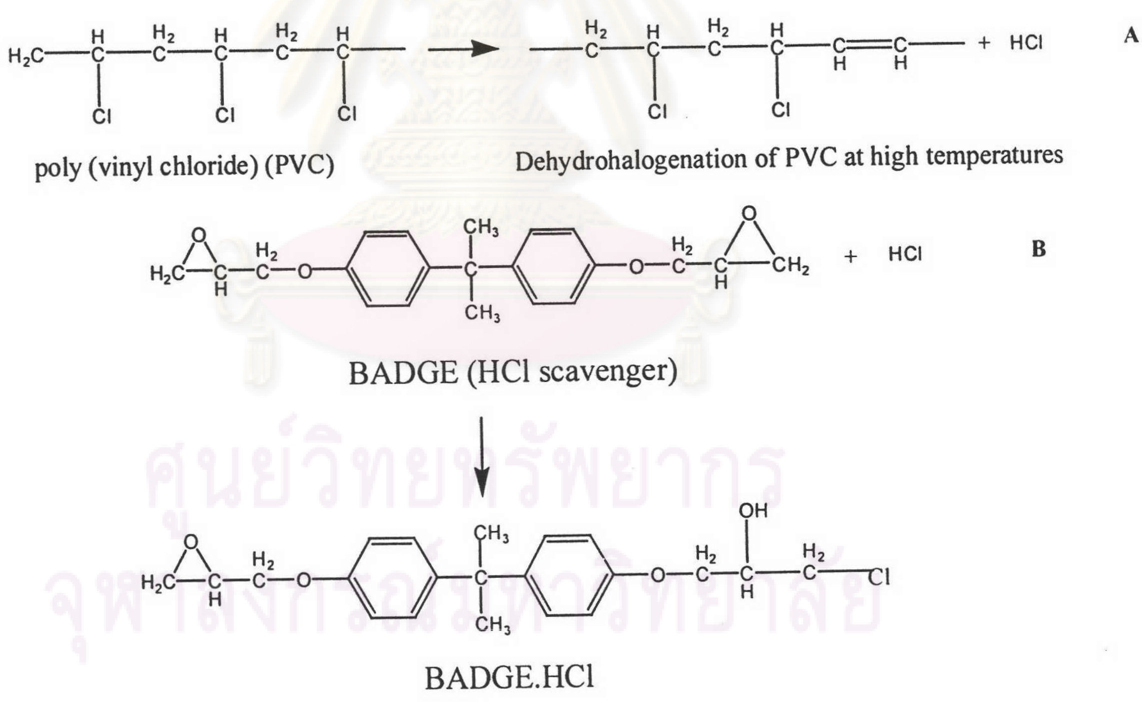



**Figure 2.7.** Degradation of PVC at curing temperature (A) and BADGE reacts with HCl results in BADGE.HCl (B).

In addition, BADGE.HCl can be further hydrolyzed in aqueous-based foods. The result derivative is BADGE.HCl.$H_2O$. Overall reaction products of BADGE are illustrated in Figure 2.8.

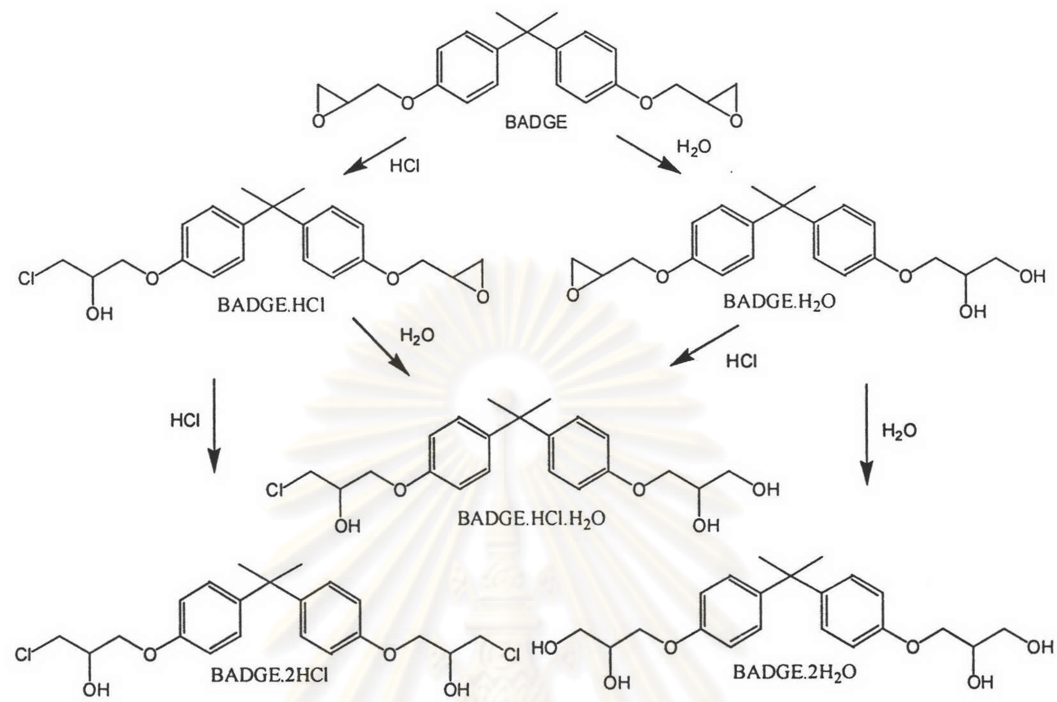



**Figure 2.8.** Bisphenol-A-diglycidyl ether (BADGE) and its reaction products.

### 2.5.3 Oligomers (*54*)

The legislation assumes that the migration from can coatings consists of oligomers too. The dimers and trimers form of BADGE and bisphenol A occurred during the production of the resin. For example, BADGE and bisphenol A can react with dimer result in both long chain and cyclic structures as shown in Figure 2.9.



### 2.5.4 Products of Side Reactions

Components migrate from epoxy coatings may react with solvents (alcohols such as butanol, butoxyethanol, and methoxypropanol) or formaldehyde forming dioxolanes. The structures of the side reaction products are illustrated in Figure 2.9.

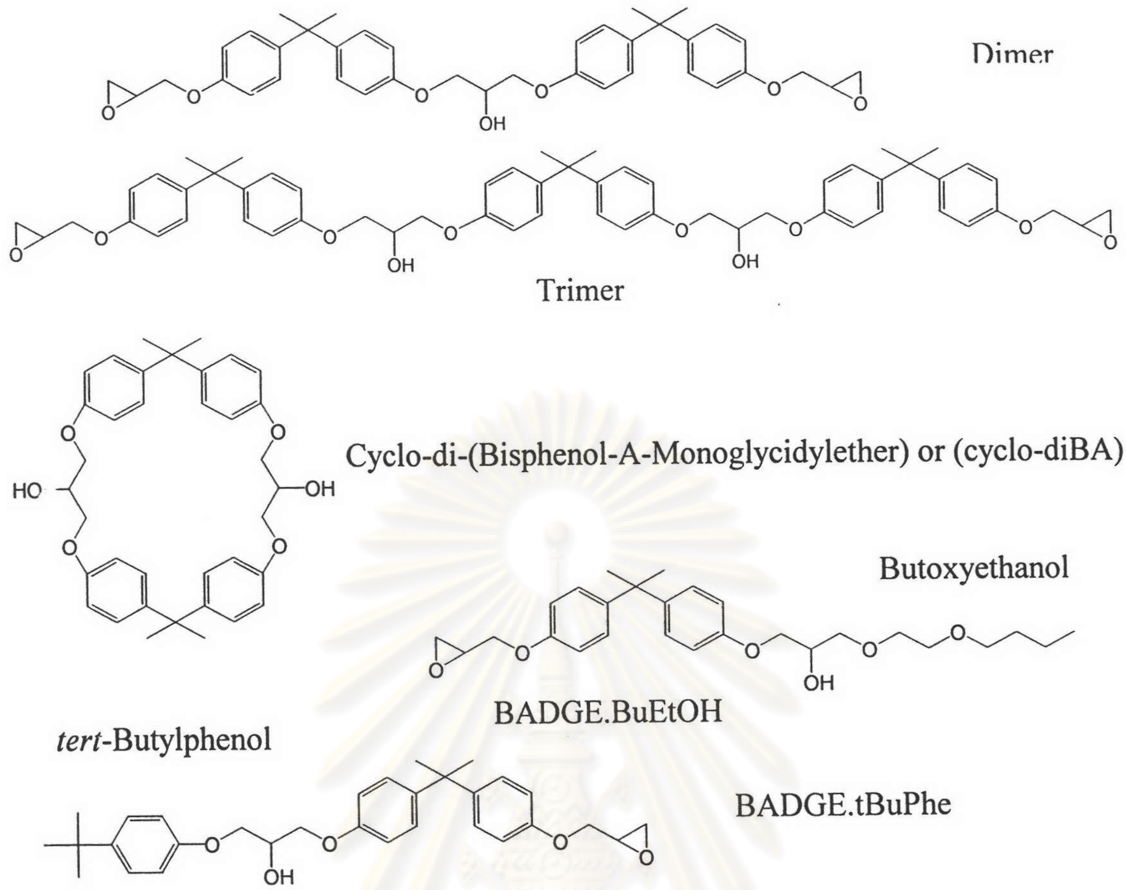



**Figure 2.9.** Some chemical structures of Bisphenol A type substances related to can coatings.

## 2.6 BFDGE

Bis[4-(glycidyloxy)phenyl] methane or Bisphenol-F-diglycidyl ether (BFDGE) was used to substitute BADGE in organosols since there was a post of legal limits in Europe. BFDGE replaced BADGE as an additive for scavenging hydrochloric acid released from PVC during heat curing. BFDGE obtained by the reaction of bisphenol F and epichlorohydrin. Bisphenol F is produced by the reaction of phenol and formaldehyde, which attacks the phenol at the ortho- and para- sites. With this effect, three isomers of the bisphenol F are formed: *o,o*-, *o,p*-, and *p,p*-. Subsequently, BFDGE occurs in three isomers as shown in Figure 2.10. Since the ortho-position is less reactive than para-, the *o,o*- isomer is the least abundant component.

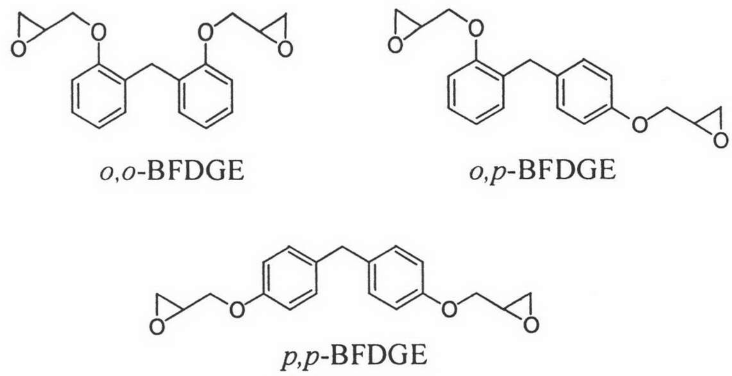
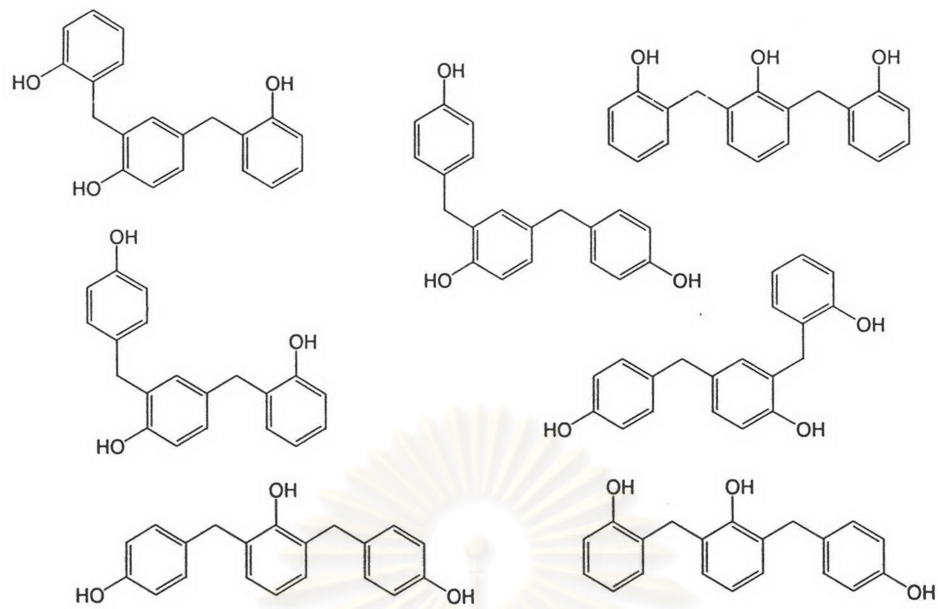



**Figure 2.10.** Chemical structures of BFDGE isomers.

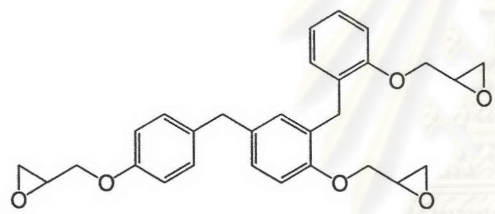
In the same way, reaction of bisphenol A and epichlorohydrin produces BADGE polymer as well as by products such as oligomers (dimer, trimer, etc.). But because the steric effect on the phenolic ring of bisphenol A, epichlorohydrin can only attack at *p,p*-position results in only one isomer.

Because technical products of BFDGE are usually the mixtures of the 2-ring isomers and compounds of three and more phenolics rings, they are called Novolacs, which includes bisphenol F as the basic compound. Novolacs are complex mixtures of components with varying numbers of aromatic rings and positional isomers. For example, the structures of three-ring Novolac consists of 7 isomers, as shown in Figure 2.11.

Epoxy novolacs (Novolac Glycidyl Ether, NOGE) are formed by reaction of novolac and epichlorohydrin in the same way as the synthesis of BADGE. One out of 7 isomers of 3-ring NOGE is shown in Figure 2.11. Additionally, epoxy compounds reacting with phenols yield oligomers, as resulted in BADGE. So there are large numbers of isomers. Thus, the complexity of the migration caused by NOGE is further increased.



7 isomers of Novolacs



One out of 7 isomers
of 3-ring NOGE

**Figure 2.11.** Structures of 7 isomers Novolacs compounds with 3-ring and one out of 7 isomers of 3-ring NOGE.

The reaction products of BFDGE can further react with water and chloride similar to BADGE and result in BFDGE.$H_2O$, BFDGE.2$H_2O$, BFDGE.HCl, BFDGE.HCl.$H_2O$, and BFDGE.2HCl as shown in Figure 1.1.