

5.25 Epoxy Resins and Phenol-Formaldehyde Resins

T Takeichi, Toyohashi University of Technology, Toyohashi, Japan

N Furukawa, Sasebo National College of Technology, Nagasaki, Japan

© 2012 Elsevier B.V. All rights reserved.

5.25.1	Introduction of Epoxy Resins	723
5.25.2	Basic Characteristics of Epoxy Resins	724
5.25.3	Synthesis of Epoxy Resins	724
5.25.3.1	Synthesis of Glycidyl-Type Epoxy Resins	724
5.25.3.2	Synthesis of Glycidyl Ethers of Novolac Resins	725
5.25.4	Curing of Epoxy Resin	725
5.25.4.1	Curing by Primary Amines	726
5.25.4.2	Curing by Anhydrides	726
5.25.4.3	Other Curing Agents	727
5.25.4.4	Catalytic Curing Agents	727
5.25.5	General Properties of Epoxy Resins	728
5.25.5.1	Glass Transition Temperature of Cured Epoxy Resins	728
5.25.5.2	Thermal Degradation of Epoxy Resins	729
5.25.5.3	Toughening of Epoxy Resin	729
5.25.5.4	Liquid Crystalline Epoxy Resins	729
5.25.6	Introduction of Phenolic resins	730
5.25.7	Novolac	732
5.25.7.1	Bisphenol F	732
5.25.7.2	Random Novolac	732
5.25.7.3	High-Molecular-Weight Novolac	733
5.25.7.4	High <i>Ortho</i> Novolac	733
5.25.7.5	Heterogeneous Two-Phase Process	734
5.25.7.6	Curing of Novolac	735
5.25.7.7	Non-Hexa Cure	736
5.25.8	Resol	736
5.25.8.1	Methylol Phenols	736
5.25.8.2	Oligomers	737
5.25.8.3	Curing of Resol	738
5.25.9	Transformation of Phenolics	738
5.25.9.1	Epoxy	739
5.25.9.2	Cyanate Esters	739
5.25.9.3	Benzoxazines	740
5.25.9.3.1	Typical benzoxazines	741
5.25.9.3.2	Molecular design of benzoxazines	742
5.25.9.3.3	High-molecular-weight benzoxazine precursors	743
5.25.10	Natural Products as Phenolics	744
5.25.11	Modification by Alloys and Co-curing	745
5.25.11.1	Modification of Phenolics by Alloying	745
5.25.11.2	Modification of Benzoxazine by Alloying	746
5.25.11.3	Alloying of Benzoxazine with Polyimide	747
5.25.11.4	Alloying of Benzoxazine with Bismaleimide	748
5.25.12	Hybrids and Composites	748
5.25.12.1	Preparation of Hybrids by Layered Clay	748
5.25.12.2	Preparation of Hybrid by Sol-Gel Process	748
5.25.13	Conclusion	749
References		749

5.25.1 Introduction of Epoxy Resins

An epoxy resin is defined as a molecule containing more than one epoxy group capable of being converted to a thermoset form. The term, epoxy, is used to indicate the resins in both the thermoplastic (uncured) and thermoset (cured) state.

Epoxy functional groups are prepared (1) by the reaction of olefins with oxygen-containing compounds such as peroxides or peracids, and (2) by dehydrohalogenation of chlorohydrines (**Figure 1**). But, the most important preparation method for epoxy resins is (3) by the reaction of epichlorohydrin with a suitable di- or polyhydroxy

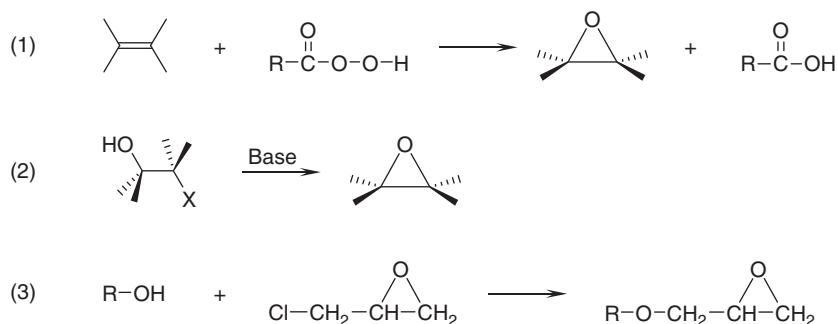


Figure 1 Preparation of epoxy functional group.

compound or other active hydrogen-containing compounds.

In 1927, Schrade reported the first attempt to prepare resins from epichlorohydrin. In 1936, Castan produced a low-melting, amber-colored epichlorohydrin – bisphenol A resin which was then reacted with phthalic anhydride to produce a thermoset. In 1939, Greenlee explored the epichlorohydrin–bisphenol A synthesis route for the production of new resins for coatings. The epichlorohydrin–bisphenol resins were the outgrowth of research by many workers on the substituted ethylene oxide derivatives. The first resins, the reaction products of epichlorohydrin and bisphenol A, were produced commercially in 1947. Due to the many researches devoted to epoxy, rapid commercial utilization of the diglycidyl ether of bisphenol A resins became possible after World War II.

5.25.2 Basic Characteristics of Epoxy Resins

A number of advantageous properties have led to the rapid growth of epoxy resins and their use in a wide range of industries. The liquid resins are low-viscosity liquids, which readily convert to the thermoset upon mixing with the curing agent. Other liquid resins, such as phenolics, polyesters, acrylics, and so on, cure in a similar fashion, but the liquid epoxy resins possess a rather unique combination of properties as follows.¹

1. Low viscosity: The liquid resins and their curing agents form low viscosity and easy-to-process (or modify) system.
2. Easy cure: Epoxy resins cure quickly and easily at the temperature range from room temperature to 150 °C, depending on the selection of the curing agent.
3. Low shrinkage: One of the most advantageous properties of the epoxy resin is the low shrinkage during the cure. Epoxy resins react without evolving volatile by-products.
4. High adhesive strength: Because of the presence of polar hydroxyl and ether groups, the epoxy resins are excellent adhesives. The resins cure with low shrinkage; therefore, the various surface contacts between the liquid epoxy resin and adherents are not disturbed during cure.
5. Good chemical resistance: The chemical resistance of the cured epoxy resin depends considerably on the curing agent used. Outstanding chemical resistance can be obtained. Overall, most epoxy resins possess extremely

high resistance to alkali and good to excellent resistance to acid.

6. High electrical insulation: Epoxy resins are excellent electrical insulator.
7. High mechanical properties: The strength of properly formulated epoxy resins usually surpasses that of other type of resins. This is probably the result of their low shrinkage, which minimizes stresses that otherwise would weaken the mechanical structure.
8. Versatilities: The epoxy resins are one of the most versatile among the plastics. The basic properties may be modified in many ways: by blending of the resin types, by selecting curing agent, and by use of modifiers and fillers.

On the other hand, solid epoxy resins are mainly used for solution coatings. The higher molecular weight materials are reacted with methylol-containing resins. The epoxy resin backbone affords toughness, scratch resistance, and chemical resistance. Solid resins of intermediate molecular weight may be crosslinked by heating, and cured films may be developed which provide excellent properties. The excellent adhesion, ease of cure, mechanical strength, and high chemical resistance are also the important advantages of the solid epoxy resins as the liquid epoxy resins.

5.25.3 Synthesis of Epoxy Resins

5.25.3.1 Synthesis of Glycidyl-Type Epoxy Resins

The first commercial epoxy resins were the reaction products between epichlorohydrin and bisphenol A, the reaction giving the diglycidyl ether of bisphenol A (DGEBA) of higher molecular weight species. The structure of the resin is shown in **Figure 2**.¹

The low-molecular-weight liquid products have an n value about 1 or below. When the n value is above 1, the resins are brittle solids. DGEBA is obtained by reacting epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The reaction occurs in two steps (**Figure 3**): (1) the formation of a chlorohydrin intermediate, and (2) the dehydrohalogenation of the intermediate to the glycidyl ether. Sodium hydroxide catalyzes the reaction to produce the chlorohydrin intermediate, acts as the dehydrohalogenating agent, and neutralizes the formed HCl. In order to obtain the monomeric DGEBA, 2 mol of epichlorohydrin is theoretically required for each mole of

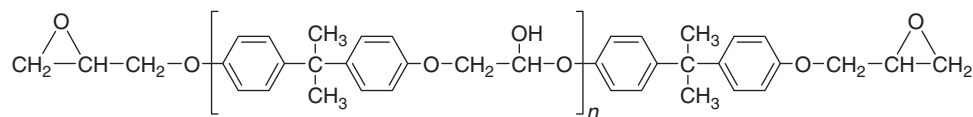


Figure 2 Structure of typical epoxy resin.

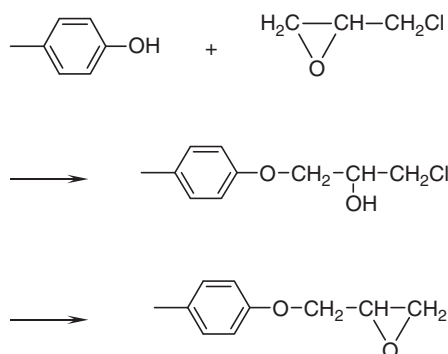


Figure 3 Reaction of epichlorohydrin with phenol.

bisphenol A. However, when this ratio is employed, the yield of monomer is less than 10%, with the remaining material being higher molecular weight products. To obtain high yield of monomeric product, excess epichlorohydrin is employed, and yields of 90% or higher are then possible. The usual DGEBA having an average molecular weight of approximately 380 is the commercial liquid epoxy resin.

It is possible to synthesize higher molecular weight epoxy resins by reacting epichlorohydrin and bisphenol A in the presence of excess sodium hydroxide. It should be noted that such a molecule contains many alcoholic hydroxyls (**Figure 4**) and contains no more than two epoxy groups. Synthesis of higher molecular weight epoxy requires not only the consumption of the epoxy group in the epichlorohydrin, but also, in order to connect successive bisphenol A groups, the consumption of some of the epoxy groups formed by dehydrohalogenation.

Therefore, it should be possible to control the degree of polymerization by regulating the ratio of epichlorohydrin and bisphenol A when employing sodium hydroxide in excess of the amount required to carry out the reaction. Typical data for

various ratios in terms of resultant molecular weight are summarized in **Table 1**.

5.25.3.2 Synthesis of Glycidyl Ethers of Novolac Resins

Novolac resins are also suitable intermediates for the synthesis of polyglycidyl ether resins. The novolac-based epoxy resins (**Figure 5**) are synthesized by the reaction with epichlorohydrin in the same fashion as are the bisphenol A-based resins. The number of glycidyl groups per molecule in the resin is dependent on the number of the phenolic hydroxyls in the starting novolac, the extent to which they are reacted, and extent to which the lowest molecular weight species are polymerized during synthesis. Theoretically, all the phenolic hydroxyls may be reacted. But, in practice, selective epoxidation offers an advantage when the novolac contains more than three phenolic hydroxyls. If complete epoxydation is accomplished, steric factors will prevent the reaction of some of the epoxy groups during cure. The glycidyl ethers of novolacs are also commercially important because of their high functionality.¹

5.25.4 Curing of Epoxy Resin

Epoxy functional groups react readily with various chemicals as shown in **Figure 6**. As a result, the most valuable property of epoxy resins is their ability to transform readily from the liquid (or thermoplastic) state to hard thermoset solids. The conversion normally occurs without the evolution of by-products. The conversion is accomplished by the addition of curing agent (hardener, activator, or catalyst). Some curing agents catalytically promote curing, and others participate directly in the reaction and are chemically bound into the resin. The cured structure may be a homo epoxy polymer or a hetero polymer composed of epoxy resin and curing agent, or a mixture of both types. Depending on the particular agent, curing may be

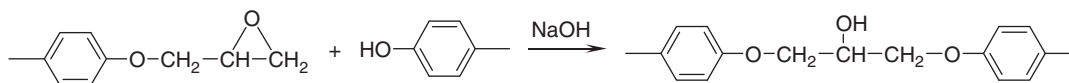


Figure 4 Reaction of epoxy resin.

Table 1 Effect of varying ratios on molecular weight of epoxy resins

Mole ratio epichlorohydrin/ bisphenol A	Mole ratio NaOH/ epichlorohydrin	Softening point (°C)	Molecular weight	Epoxide equivalent	Epoxy groups per molecule
2.0	1.1	43	451	314	1.39
1.4	1.3	84	791	592	1.34
1.33	1.3	90	802	730	1.10
1.25	1.3	100	1133	862	1.32
1.2	1.3	112	1420	1176	1.21

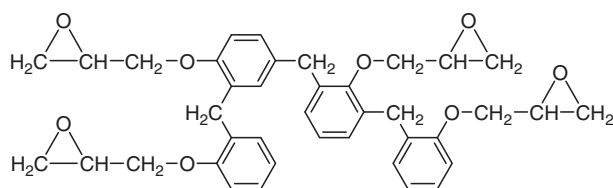


Figure 5 Structure of novolac-based epoxy resin.

accomplished at room temperature with heat produced by exothermic reaction, or require external heat. The reactivity of the epoxy differs, depending on whether the epoxy is located terminal or internal.

The epoxy group may react either anionically or cationically. Both types of reaction are important in epoxy resin technology.^{1,2} In the anionic mechanism, the epoxy ring may be opened in various fashions to produce an anion (**Figure 7(a)**). The anion is an activated species, and capable of further reaction. In the cationic mechanism, the epoxy groups may be opened by acids (**Figure 7(b)**).

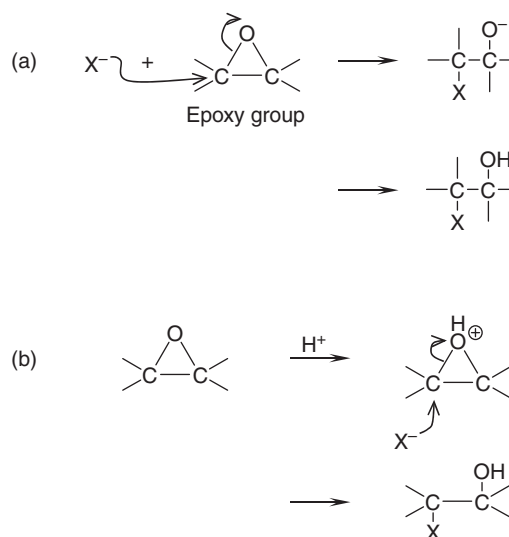


Figure 7 Ring-opening reaction of epoxy resin.

5.25.4.1 Curing by Primary Amines

One of the most important and most frequently used curing agents is amine. The reaction of primary amine with epoxy proceeds as shown in **Figure 8**. The reaction proceeds in two steps. (1) At the first step, the primary amine reacts with epoxy, forming secondary amine and a hydroxyl group. (2) At the second step, the secondary amine reacts with another epoxy, forming tertiary amine and another hydroxyl group. (3) The hydroxyl groups thus formed also react with epoxy, contributing the development of the network.

In the case of aliphatic amines, the k_1/k_2 ratio is approximately 2. After the initial reaction between primary amine and epoxy, the reaction between secondary amine and epoxy proceeds in parallel with the initial chain extension reaction. In the case of aromatic amines, the k_1/k_2 ratio is as large as 7–12. Therefore, in this case, chain extension of epoxy with primary amine preferentially proceeds, and Lewis acid is used as an accelerator.

The primary amines can be used effectively as epoxy curing agents, since the primary amine group is bifunctional with the

epoxy resin. If more than one primary amine is present in a molecule, crosslinked structure results through the reaction with diepoxides. Generally, the tertiary amines formed by the reaction of two epoxy groups with a primary amine are not effective catalysts, though tertiary amines may cause further reaction as Lewis bases.

5.25.4.2 Curing by Anhydrides

Another important and frequently used curing agent for epoxy is cyclic anhydride. Cyclic anhydride does not react directly with epoxy group. In order for the reaction to occur, first of all, ring opening of the anhydride is necessary. The ring may be opened either by active hydrogen as water or hydroxyls.

In the absence of an accelerator, the curing of epoxy by anhydride proceeds as shown in **Figure 9**. At first, anhydride reacts with the hydroxyl group of epoxy, affording ester and carboxylic groups. The carboxylic group then reacts with epoxy, forming hydroxyl group, which reacts further with another anhydride. This curing system is acidic, and ether linkage also forms from the reaction between epoxy and hydroxyl group.

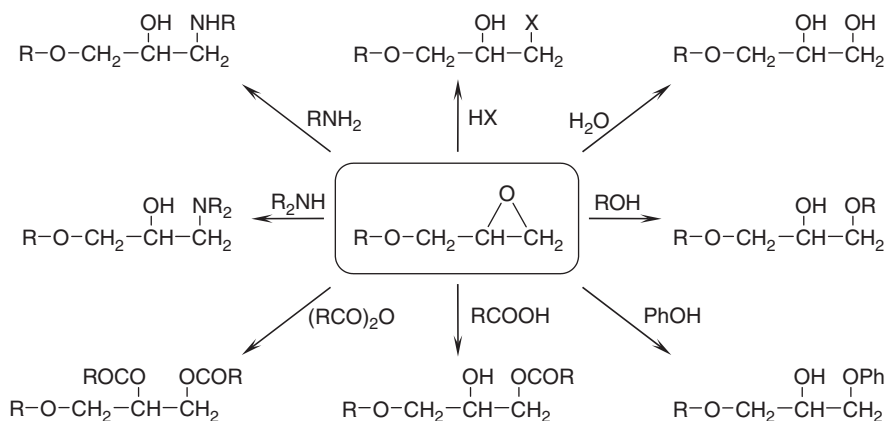


Figure 6 Reaction of epoxy functional group.

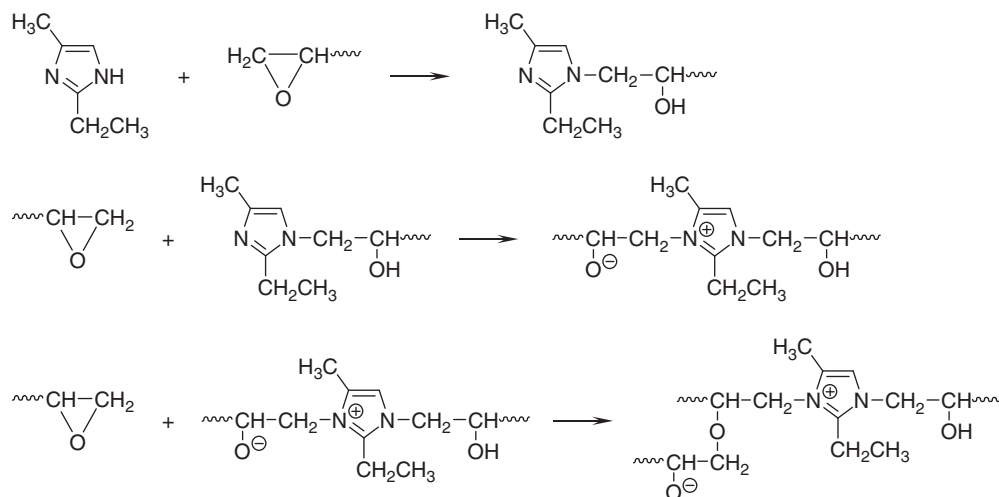


Figure 10 Curing of epoxy by imidazole.

catalyze effectively at relatively low temperature, and afford cure products with good thermal properties. Catalytic mechanism of imidazole is shown in **Figure 10**. At first, secondary amine reacts with epoxy, and then another amine reacts with epoxy to form ionic complex, followed by further reaction of the ionic complex with another epoxy.

Tertiary amines, representative reactive Lewis bases, are highly basic compounds and catalyze the curing of epoxy. The tertiary amine approaches one of the carbon atoms of the epoxy and attaches itself. Once the alkoxide ion is available, it will then react directly with an epoxy to generate a new alkoxide ion. The process continues in a chain mechanism.

As the cationic catalyst, Lewis acid such as boron trifluoride (BF_3) is used. Usually, BF_3 is complexed with amine as a Lewis base, thereby controlling the reactivity. The complex is stable at room temperature, and works as a latent curing agent which becomes active at elevated temperatures.

5.25.5 General Properties of Epoxy Resins

Epoxy resins are available in a range of molecular structures, suitable for reaction with a large variety of different curing agents, for a multitude of end uses. At the early stages of cure of an epoxy resin, before the molecules are fully crosslinked, the resin exists as a thermoplastic or B-stage resin. It is hard but soluble in solvents such as acetone. At this stage, the cure reaction has been initiated at a number of widely separated points by the formation of branched and linear molecules. With the progress of cure, crosslinking becomes general. Epoxy resin forms network and becomes thermoset.¹⁻⁴

5.25.5.1 Glass Transition Temperature of Cured Epoxy Resins

One of the advantages of thermosets such as epoxy over the thermoplastics is thermal properties. Thermal properties are evaluated from glass transition temperature (T_g) or HDT.

A major factor that determines the T_g value is chemical structure of epoxy and curing agent. Increase of rigidity, for

example, by the higher content of aromatics, increases the T_g value, but tends to become brittle. The introduction of flexible groups, on the other hand, decreases T_g but increases toughness. Introduction of polar groups in the polymer chains increases the molecular interactions between adjacent chains and hence decreases the chain flexibility, resulting in increased T_g . Bulky side groups, such as aromatic rings, also hinder segmental motion and, therefore, reduce flexibility, resulting in increased T_g .

Another major factor that determines the T_g values is crosslink density. Crosslink density is defined as the number of effective crosslinks per unit volume. It is important to know how far apart the functional groups are located, since this determines crosslink density. In the DGEBA ($n=0$), the epoxy groups are separated by seven units (the aromatic ring being counted as one unit). In general, short spacing gives rigidity, medium spacing gives semi-rigid properties, and long spacing gives flexibility or softness.

T_g of network polymer is determined by the crosslink density (ρ) as shown in the following equation:

$$T_g = K_1 \log K_2 \rho = K_1 \log \rho + K_2$$

where K_1 is a constant that suggests how the crosslink density affect T_g , and in the range of 50–250. K_2 ($K_1 \log K_2$) is a constant that depends on various factors such as rigidity, steric hindrance, and intermolecular interaction. Aromatic polymers have high K_2 . Among the similar polymers, K_1 and K_2 are constant. Crosslink density, ρ , is estimated from the modulus at the rubbery plateau region above T_g using the following equation:

$$\rho = \frac{(dN_A)}{Mc} = \frac{E}{(3\phi RT)}$$

where E is usually the storage modulus measured from the viscoelastic analyses. N_A is Avogadro constant, d is density, R is gas constant, and $\phi = 1$ is very often used.

Various epoxy resins with improved thermal properties have been examined aiming for high-temperature applications such as matrix resin for advanced composite materials. Some of the proposed epoxy resins are shown in **Figure 11**.

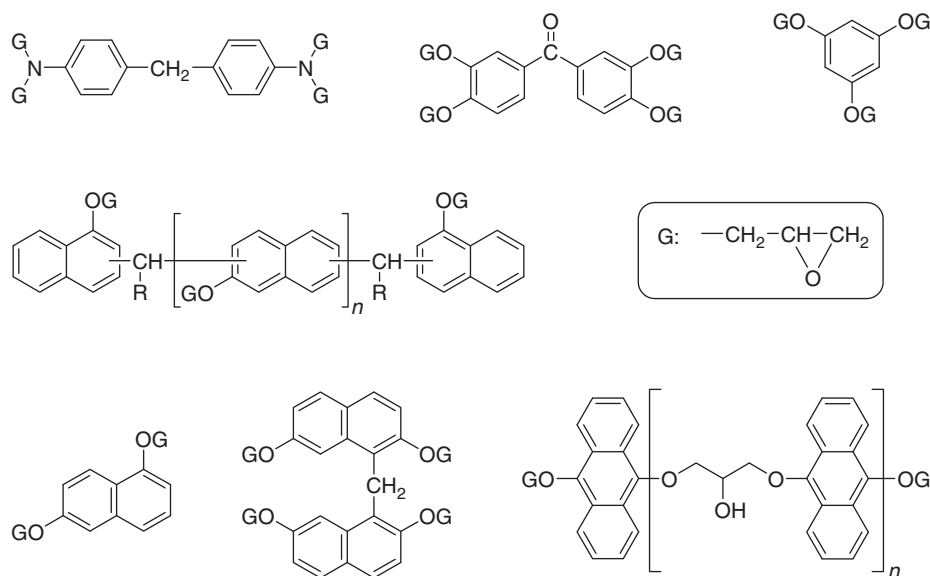


Figure 11 High-performance epoxy resins.

5.25.5.2 Thermal Degradation of Epoxy Resins

A number of epoxy resin systems have been thermally degraded, and the degradation products were studied. When epoxy resin is cured with a primary amine, the unreacted epoxy is evaporated, and the higher molecular weight fractions are degraded to release H_2 , CO, CH_4 , C_2H_6 , C_3H_6 , and C_3H_8 , the latter four possibly from decomposition of polyamine radicals. The presence of hydroxyl groups in amine-cured systems may be one of the causes for their relatively poor thermal stability, perhaps dehydration due to the cleavage. In addition, it is possible that amine hydrochloride is formed and decomposes to HCl, which initiates cleavage of bisphenol A structure. In the anhydride-cured system, the diester can undergo β -elimination to release olefin and carbon dioxide, with other decomposition products preceding through cleavage at the ether links following dehydration.

5.25.5.3 Toughening of Epoxy Resin

Epoxy resin is naturally a brittle material, and needs modification for toughening depending on the use. An effective method for this purpose is modification by rubber, especially amine- or carboxylic-terminated liquid rubber (ATBN or CTBN). The structure of ATBN is shown in Figure 12. At the initial stage, liquid rubber dissolves in epoxy. With the progress of cure of epoxy, liquid rubber is phase separated into particles. The particle size affects the mechanical properties of the cured resin. Therefore, the particle size control is very important. The terminal functional group reacts with epoxy to make strong the interface

between liquid rubber and epoxy. With the increase of liquid rubber, epoxy resin becomes tough. The toughening effect is most significant at a rubber content of around 20%. A disadvantage of using liquid rubber as a toughening agent is that T_g decreases with the addition of liquid rubber.

For the toughening of epoxy without decreasing the T_g of epoxy, the use of engineering thermoplastics shown in Figure 13 is effective.^{5–10} In the case of polyethersulfone, phase separation did not occur, and fracture toughness (K_{Ic}) did not improve. But, in the case of polyetherimide (PEI), sea-island type phase separation occurred, and fracture toughness increased linearly with the addition of PEI up to $\sim 1.5 \text{ MPa m}^{1/2}$ at 20% inclusion from $\sim 0.5 \text{ MPa m}^{1/2}$ of the pristine epoxy. End-reactive oligomers such as amine- and hydroxyl-terminated polysulfones and amine-terminated polyaryletherketones were also effective without sacrificing T_g and flexural modulus.

5.25.5.4 Liquid Crystalline Epoxy Resins

It has been reported that the liquid crystalline (LC) epoxy resins containing mesogenic groups in the backbone moiety and having controlled network structures show high thermal stability and fracture toughness.^{11–14}

Recently, Takezawa and Akatsuka used LC epoxy resins (Figure 14), and succeeded in preparing isotropic cured resins that have 5 times higher thermal conductivity than that of the conventional epoxy resins by controlling the high-ordered structure because mesogens were highly ordered to form crystal-like structure.¹⁵

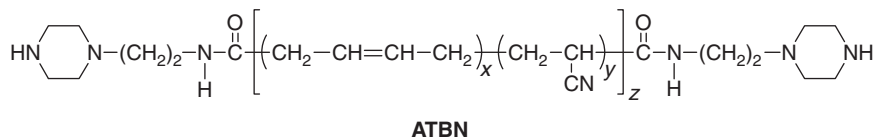


Figure 12 Structure of ATBN.

Name		Structure	T_g
Polyetherimide (PEI)			215 °C
Polyethersulfone (PES)			225 °C
Polysulfone (PSF)	Amine-terminated		—
	Hydroxy-terminated		180 ~ 183 °C
Polyaryletherketone (PAEK)			—

Figure 13 Engineering thermoplastics for toughening epoxy.

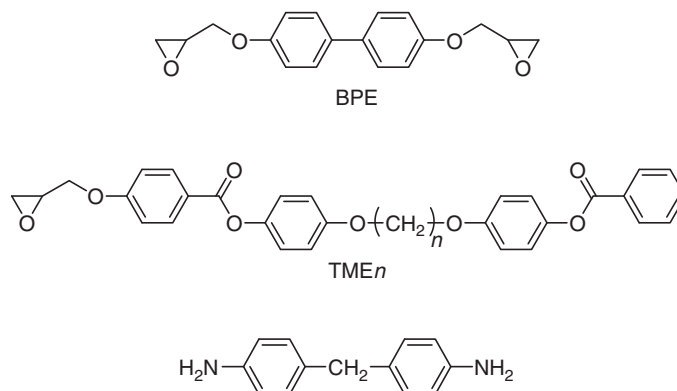


Figure 14 Liquid crystalline epoxy resin.

Harada *et al.* cured LC epoxy resin, shown in Figure 15, under a magnetic field to obtain a highly ordered network structure. They found that the thermal conductivity in the direction along the applied field had a significantly high

value ($0.89 \text{ W m}^{-1} \text{ K}$) as compared with that ($0.32 \text{ W m}^{-1} \text{ K}$) of the cross direction.¹⁶

5.25.6 Introduction of Phenolic resins

Phenolic resin was produced in 1910 as the first man-made synthetic plastic, and now has the history for more than 100 years. Phenolic resin possesses excellent characteristics such as excellent heat and flame retardance, high strength, long-term thermal and mechanical stability, excellent electrical and thermal insulating properties, good chemical resistance, low water absorption, and excellent cost-performance characteristics due to the inexpensive raw materials and fabricating processes. Therefore, phenolic resin is widely used in various applications from commodity and construction materials to the high-technology aerospace industry in the form of electric

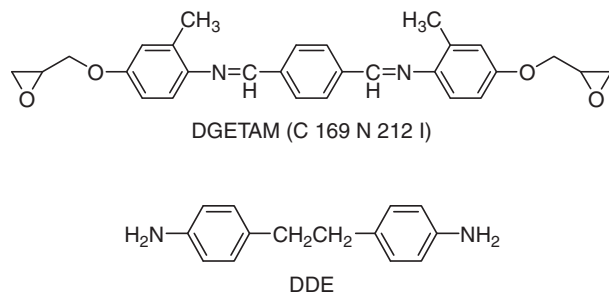


Figure 15 Liquid crystalline epoxy resin and curing agent.

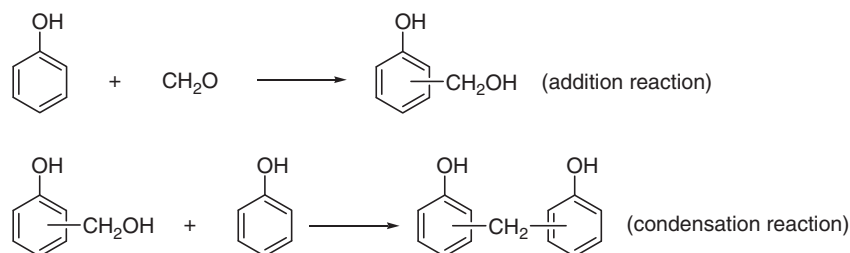


Figure 16 Addition and condensation reactions of phenol and formaldehyde.

laminates, adhesives, molding compounds, fiber-reinforced composites, glass fiber or rock wool insulation, honeycomb paneling, acid-resistant coatings, wood panels, binder in friction linings, or automobile brakes.

Phenolic resin is prepared from phenols and aldehydes using various organic and inorganic acids and alkalis or their salts as catalysts. Two types of reactions, addition and condensation reactions (Figure 16), take place depending on the reaction conditions, such as the type of catalyst or pH, and molar ratio of aldehyde to phenol. The obtained materials with low to medium molecular weight are reactive intermediates that can be cured, or can undergo various transformations utilizing phenolic hydroxyl group that have new utility. These transformations include epoxy, cyanate ester, and benzoxazine.

For the production of phenolic resins, mono-hydroxybenzenes, especially phenol, are of greatest importance. Alkylphenols such as cresols (monomethyl derivatives of phenol) and xylenols (dimethyl derivatives) are also important. Resorcinol (1,3-dihydroxybenzene) has a very high reaction rate toward formaldehyde. Bisphenol A is used for the production of special resins.

Formaldehyde is practically the only carbonyl component used in the synthesis of industrial phenolic resins. It is highly reactive, and commonly handled in aqueous solutions containing variable amounts of methanol. Paraformaldehyde, obtained by the distillation of formaldehyde solutions, is a polycondensation product whose degree of polymerization ranges between 10 and 100. Commercial grades contain up to 6% water. Paraformaldehyde is seldom used in resin production because of the high costs compared to aqueous formaldehyde solution, and problems with the high heat evolution. Paraformaldehyde is used for resins with a high solids content or to avoid distillation of waste water. Trioxane, a cyclic trimer of formaldehyde, is a colorless solid, and can be used as a source of formaldehyde in prepolymer formation or as a resin curing agent. Hexamethylenetetramine (HMTA or very often called hexa), prepared from formaldehyde and ammonia, is stable white crystal at room temperature (Figure 17). Hexa is soluble in water, and is by far the most important compound to cure novolac resin. Special resins are made with other

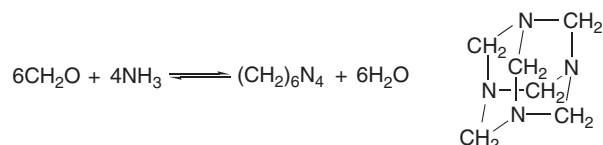


Figure 17 Hexa as the source of formaldehyde.

aldehydes such as acetaldehyde, butylaldehyde, furfural, glyoxal, and benzaldehyde.

The reaction of formaldehyde (F) with phenol (P) leads to either novolac (or novolak) or resol (or resole) depending on the mode of catalyst and molar ratio of F to P.

Under acidic conditions, the reaction rate of condensation reaction is faster than the addition reactions. Therefore, by feeding an excess amount of P against F, linear or branched condensation products in which phenolic moieties are linked together through methylene linkages are obtained (Figure 18). These products are called 'novolac'. Novolac is normally solid at room temperature, having number average molecular weight between 500 and 800. It is soluble in organic solvents such as acetone and tetrahydrofuran (THF), and melts on heating. But novolac is stable, is not curable as it is, and is 'thermoplastic'.

On the other hand, under basic conditions, the reaction rate of the addition reaction is faster than the condensation reaction. Therefore, by feeding an excess amount of F to P, addition of aldehydes to phenols occurs preferentially, and eventually, hydroxymethylphenols called 'resols' are formed as viscous liquid at room temperature. The number average molecular weights of resols are generally as low as 200–500, and resols are soluble in alcohols and acetone.

Different curing conditions are necessary to crosslink novolacs and resols. Novolacs require a source of formaldehyde, which is commonly hexa as a latent source of formaldehyde. Other curing methods of novolac besides hexa consist of solid resol, bismethylol cresol, bisoxazolines, and bisbenzoxazines.

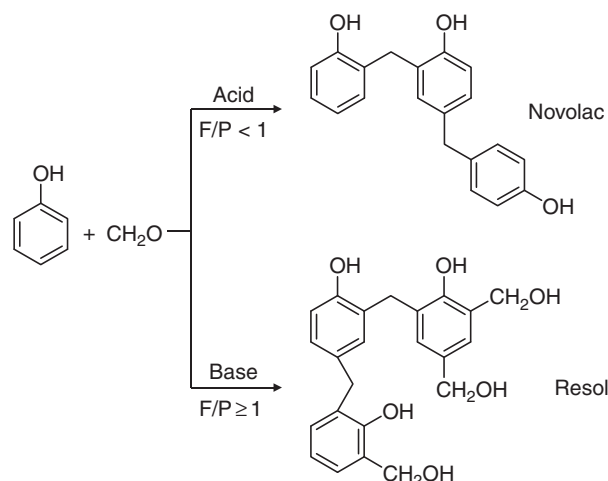


Figure 18 Chemical structures of typical novolac and resol.

Resols are readily cured on heating or even at room temperature under acidic or special basic conditions, through condensation reactions between methylol groups and phenolic core at *ortho* and *para* positions, affording intractable network polymers.

5.25.7 Novolac

5.25.7.1 Bisphenol F

The simplest novolac, bisphenol F, is prepared by conducting the reaction of phenol (P) and formaldehyde (F) with a large excess of P under acidic conditions. The mechanism of formation involves initial protonation of methylol glycol, which reacts with phenol at the *ortho* and *para* positions (Figure 19). Among the mixtures of isomers obtained, *o,p'* isomer predominates, followed by *p,p'*, and *o,o'* the lowest.

Recently, synthesis of bisphenol F was examined over microporous H-beta zeolites, with different Si/Al ratios.¹⁷ With an increase in the aluminum content in beta zeolite, the

acidity is increased gradually. The catalyst with Si/Al ratio of 75.0 mol mol⁻¹ showed the highest yield and selectivity at 90 °C (yield of 68% with 91% Bis F selectivity). Isomer distribution was considerably different, and *p,p'* isomer ratio was as high as 54%, with *o,p'* 35%, and *o,o'* 11%.

5.25.7.2 Random Novolac

Novolacs with varying molecular weight can be prepared under acidic conditions using an excess amount of P to F in a typical ratio of P:F = 1.0:0.75–0.85. The overall reaction scheme showing isomeric structural changes that occur during oligomerization is shown in Figure 20. Beyond bisphenol F, the number of isomeric structural oligomers increases significantly.

As the acid catalyst, oxalic acid is preferably used rather than the strong acid like HCl or H₂SO₄. When low reactive phenols and aldehydes are used, strong acid like *p*-toluenesulfonic acid or H₃PO₄ will be used.

Novolac synthesis was studied by conducting the oxalic acid-catalyzed reaction in an NMR tube.¹⁸ *o*-Methylolphenol

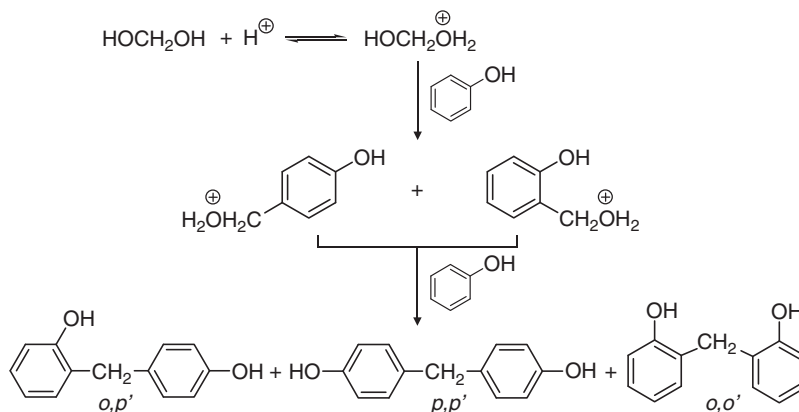


Figure 19 Preparation of bisphenol F.

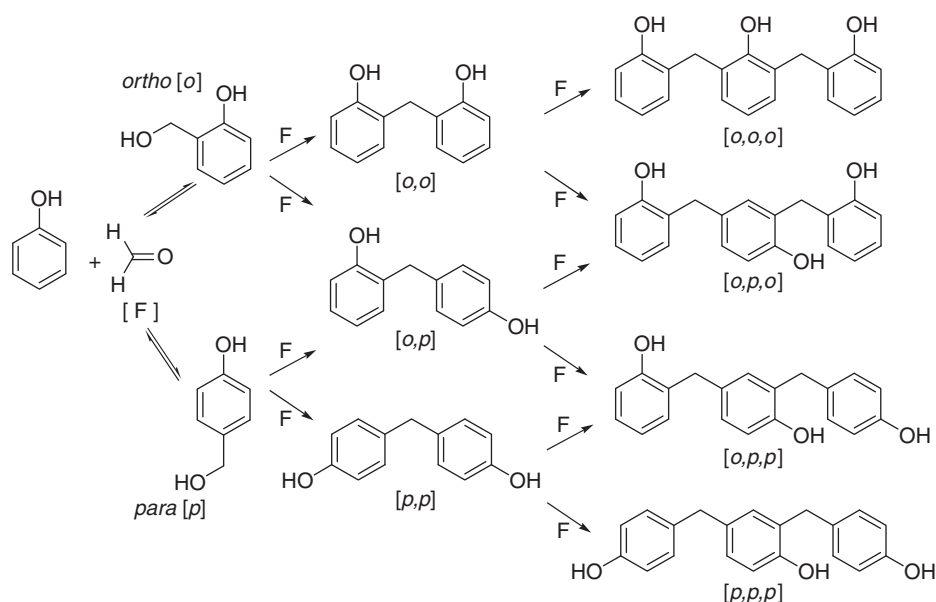


Figure 20 Preparation of novolac.

Table 2 Isomeric content of various novolacs

Novolak	% Methylene bridges		
	<i>p-p'</i>	<i>o-p'</i>	<i>o-o'</i>
Random	25.8	49.1	25.1
Oxalic acid	27.6	49.1	23.3
Phosphoric acid	25.4	51.1	23.5
Sulfuric acid	25.6	48.5	25.9
High <i>ortho</i>	2.3	40.2	57.5
PAPS	40.1	45.3	14.6

was identified, but *p*-methylolphenol was not identified. It was proposed that *o*-CH₂OH is more stable than *p*-CH₂OH due to the intramolecular H-bonding of methylol group and adjacent phenolic group. It should be noted that, in the latter stage of reaction, *p*, *p'* and *o*, *p'* methylene linkages were observed, which proves the existence of *p*-methylolphenol.

In the random novolac, the ratio of *ortho* and *para* is almost 1:1. This means that *para* position is twice more reactive than *ortho* position because there are two *ortho* positions and only one *para* position in phenol. Various factors affect *ortho:para* ratio (Table 2). There is a tendency that, under weakly acidic conditions, high *ortho* resin is obtained, and under strong acidic condition, high *para* resin is obtained. Reaction media also affects the ratio, and at high concentrations of water, high *para* resin is obtained. Whilst the use of paraformaldehyde, instead of formalin, results in high *ortho* resin, because of the small content of water and high reaction temperature. Higher reaction temperature gives high *ortho* resin. Heterogeneous two-phase method yields a high *para* resin.

5.25.7.3 High-Molecular-Weight Novolac

In order to improve thermal and mechanical properties of phenolic resins, various approaches have been examined to obtain high-molecular-weight novolac. As the molar ratio of F to P is increased, higher melting novolacs are obtained (Table 3), which is due to the increase of higher molecular weight materials. When the ratio increases above 0.9, the reaction tends to cause gelation.

In an attempt to prepare higher molecular weight novolacs, Yamagishi *et al.*^{19,20} conducted an acid-catalyzed reaction in polar organic solvents. Using equimolar amounts of F (paraformaldehyde) to P, reactions were carried out using HCl in solvents such as isopropanol, ethyl propionate, 2-methoxy ethanol, 4-methyl-2-pentanone, dioxane, and acetic acid (Table 4). It was found that relatively high-molecular-weight

Table 3 Relationship of F/P ratio to novolac softening point

F:P	Softening point (°C)
0.65:1	60–70
0.75:1	70–75
0.85:1	80–100

Table 4 Reaction condition and the molecular weight of novolac

No.	Solvent	Reaction time (h)	<i>M_n</i>	<i>M_w</i>
1	2-Propanol	4	2990	16 700
2	Ethyl propionate	2.5	2830	18 600
3	2-Methoxyethanol	8	3870	22 900
4	water	5	2550	12 100
5	4-Methyl-2-pentanone	5	3030	24 100
6	Dioxane	22	3580	75 700

novolacs with weight-average molecular weight greater than 1×10^6 were obtained. It was also indicated from ¹³C NMR that this solution-based novolac gives higher branching with the progress of the reaction.

Konishi *et al.* have been preparing various types of phenolic resins using polycondensation from phenols whose phenolic OH was protected.²¹ The kinds of protecting groups for the phenolic OH affords variation of monomers and solvents usable for the reaction, and the control of reactive sites became possible. As a result, it became possible to control the structures of the obtained polymers including main chain structure, molecular weight, and stereochemistry. When anisole was used as the most simple protected phenol, by using sulfuric acid as the catalyst in acetic acid, anisole reacted with formaldehyde as a bifunctional monomer, and linear polymer was obtained without branching, though the methylene linkage was random (Figure 21). The use of large excess formaldehyde did not cause gelation, and molecular weight of the polymer reached as high as 5×10^6 in only 10 min.

The reaction of trimethyl ether of 1,3,5-trihydroxybenzene with formaldehyde using HCl as a catalyst gave completely different products depending on the solvents (Figure 22). Linear polymer was obtained in THF, highly branched polymer in chloroform, and crosslinked nanoparticle in acetic acid/chloroform. The result indicates that the kind of solvent controlled the number of reactive sites of monomer.

5.25.7.4 High *Ortho* Novolac

Under weak acidic conditions (pH 4–6) with an excess of P to F, the use of divalent metal salt such as Zn, Mg, Cd, Pb, Cu, Co, and Ni, preferably acetate, yields a uniformly structured phenolic resin known as high *ortho* novolac. The initial reaction is proposed to occur through chelation of P and F through metal carboxylate (Figure 23). The chelated intermediate is then transformed into *o*-methylol phenol.

Huang *et al.* described many different catalysts for high *ortho* novolac and confirmed the use of divalent salts as the preferred catalyst.²² Optimum reaction conditions required a molar ratio of 1.25 for P/F, 4% zinc acetate, 5 as pH, xylene as a solvent, and 5 h at 125 °C. *Ortho* content was greater than 90%.

Solution properties of all *ortho* linear oligomer (Figure 24) were examined by Yamagishi *et al.*²³ All the oligomers (*n* = 2–7) were highly solvated in acetone and molecularly dispersed, while strong H-bonding was observed in chloroform. Both inter- and intramolecular H-bonding facilitated bimolecular aggregation of dimer and trimer into tetramer and hexamer-like

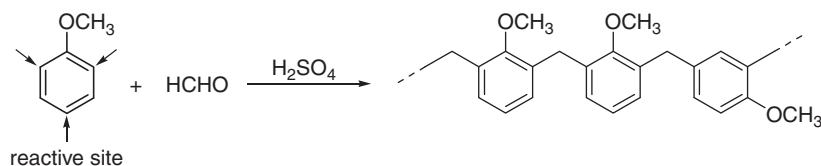


Figure 21 Preparation of linear polymer from anisole.

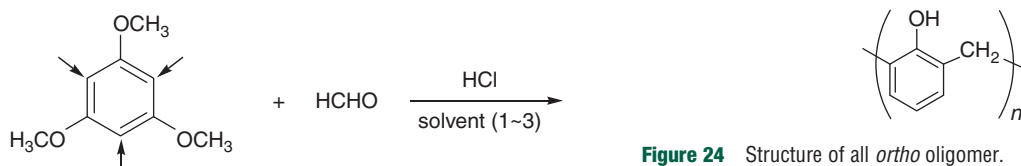


Figure 24 Structure of all *ortho* oligomer.

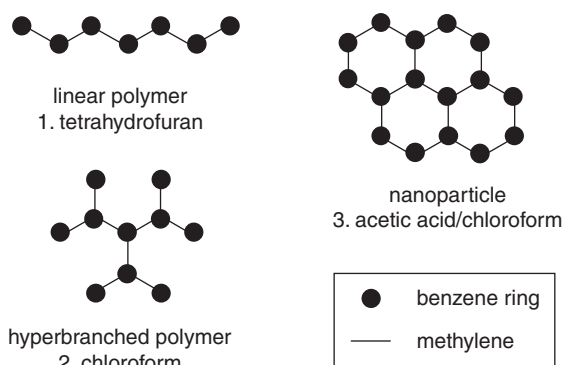


Figure 22 Reaction of protected phenol with formaldehyde.

calixarene structure (Figure 25). Tetramer ($n=4$) and hexamer ($n=6$) formed pseudo-calixarene structures by intramolecular H-bonding.

5.25.7.5 Heterogeneous Two-Phase Process

A unique heterogeneous two-phase process was reported by Sumitomo Bakelite for the production of novolacs.²⁴ In the process, large quantities of an organophosphonic acid (usually 20–100 wt.% based on phenol) was used with molar ratios of P/F = 0.5–1.0 at 110–200 °C. 1-Hydroxyethylidene-1,1'-diphosphonic acid, known as Ferriox 115, is a preferred acid. The resulting novolac is obtained in virtually 100% yield with less free phenol (about 1%) and a narrower molecular weight

distribution (MWD) of 1.3–3 than a comparable novolac prepared under oxalic acid conditions.

The organophosphonic acid is highly water soluble, whereas phenol has lower water solubility followed by an even lower water solubility of novolac. These different water solubility characteristics result in a heterogeneous two-phase reaction process, in which P and F and low-molecular-weight materials are within the aqueous organophosphonic phase and react rapidly and go out of the aqueous phase as the molecular weight of novolac increases. Due to these factors, a novolac-type resin with less unreacted P and a narrow MWD is obtained in high yield.

Another unique heterogeneous two-phase novolac process, known as 'phosphoric acid phase-separation' (PAPS) process, was developed by Asahi.^{25,26} The heterogeneous two-phase process uses a high amount of phosphoric acid as catalyst/phase reactant by reacting P with 0.4–0.93 mol of F. Molar ratios between 0.4 and 0.8 are for lower molecular weight novolac, and molar ratios between 0.8 and 0.93 are for high-molecular-weight novolac. The high-molecular-weight novolac has extremely low amount of free P, low amount of dimers (~5%), and an MWD between 1.5 and 2.0. The low-molecular-weight novolac has less than 3% of free P, higher amount of dimer (20–60%), and a narrow MWD between 1.1 and 1.8.

A comparison of PAPS resins with current resins (oxalic acid catalyzed) is shown in Table 5. It is clearly shown that PAPS resin has very low MWD, lower amount of dimer, and lower bulk viscosity with similar softening point as well as higher softening point for similar bulk viscosity. Gel permeation chromatography (GPC) shows a significantly narrow MWD for the

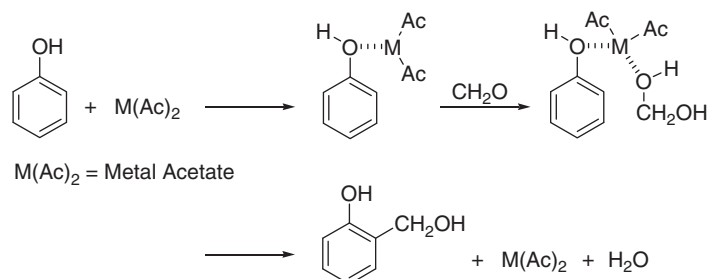


Figure 23 Mechanism for the high *ortho* novolac.

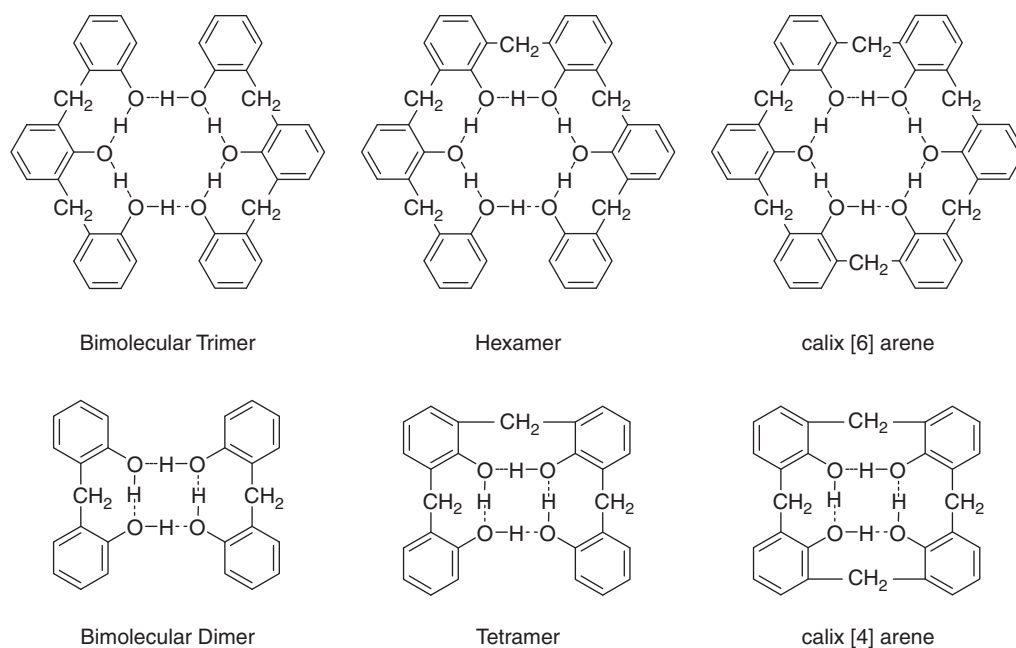


Figure 25 Aggregation of *ortho* oligomers through H-bonding.

Table 5 Comparison of PAPS resins with current resins

Novolaks		M_n^a	M_w^a	M_w/M_n	Dimer (GPC)	Softening point (°C)	Melt viscosity at 150 °C (Pa s)
PAPS resins	Low (1)	340	412	1.21	45	49	0.04
	Middle (2)	615	720	1.17	6	83	0.21
	High (3)	688	1035	1.50	1	111	3.03
	Ultra high (4)	1535	7696	5.01	1	150	–
Current resins	Middle (5)	631	2028	3.22	12	85	0.97
	High (6)	864	2623	3.04	11	105	1.38
	Ultra high (7)	950	7926	8.34	8	120	–

^a Reduced value (polystyrene).

PAPS resin, while the peak for dimer is substantially reduced (Figure 26). An overview of the types of PAPS resin that can be obtained by controlling F/P ratios is shown in Figure 27.

The PAPS yields a high *para* resin as was shown in Table 1. The higher *p,p'* functionality affects the reactivity with hexa, and PAPS resins are slower in cure than standard resins. The PAPS

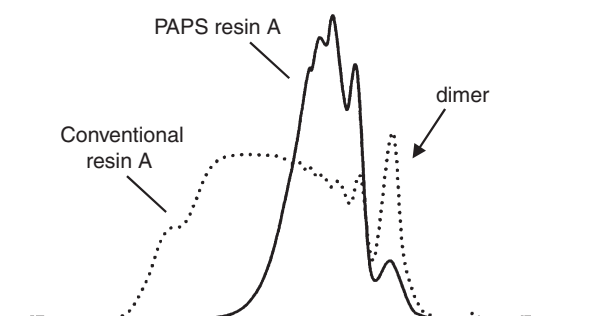


Figure 26 Molecular weight distribution of PAPS and conventional novolac.

resin also exhibit improved thermal stability because of the lower amount of free phenol and low-molecular-weight components.

5.25.7.6 Curing of Novolac

Hexamethylenetetramine (HMTA or hexa) is by far the most important curing agent for novolac. Typically, about 10% of hexa will be added to novolac. The hydrolysis of hexa by the water in novolac affords, via aminoalcohols (Figure 28), methylene carbocations which attack phenol moieties. A complete understanding of the mechanism of hexa-cured novolac has been lacking due to the crosslinking and intractability of the product.

In 1987, Hatfield and Maciel identified 15 possible intermediates involved in hexa-cured novolac.²⁷ They used ¹³C-labeled and ¹⁵N-labeled hexa for the study of the curing reaction, and presented solid state ¹³C and ¹⁵N CS/MAS spectra.

More recently, Solomon and co-workers expanded Maciel's proposed mechanistic scheme by undertaking a study on the novolac/hexa curing mechanism by synthesizing many phenolic oligomers with known configuration.^{28,29} They studied

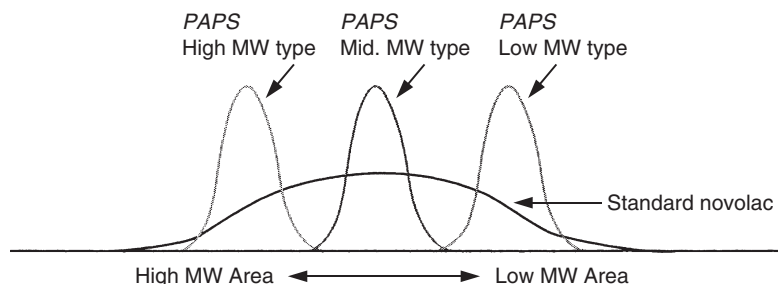


Figure 27 An overview of PAPS and standard novolac.

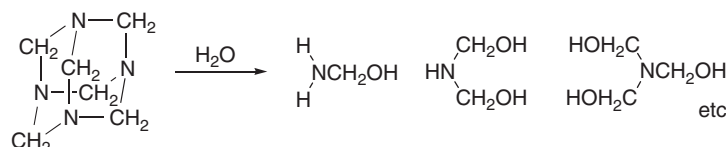


Figure 28 Hydrolysis of hexa.

reaction of hexa with model compounds,³⁰ studied the fate of novolac/hexa intermediates generated from model compounds/hexa,³¹ and analyzed the novolac/hexa cure reaction by ¹³C and ¹⁵N NMR.³²

Individual reactions of hexa with xylenols, cresols, and phenol showed that when an *ortho* site is unoccupied, a benzoxazine structure is formed. Benzoxazines formed with 2,4-xyleneol, *o*- and *p*-cresol, and phenol, whereas 2,6-xyleneol led to benzyl amines. The model studies by Solomon *et al.* established the intermediacy of benzoxazine by attack of hexa at vacant *ortho* position. But if *ortho* positions are occupied, benzyl amine is formed by the reaction of hexa at the open *para* site. The curing reaction of novolac with hexa was also conducted with a conventional novolac with novolac/hexa weight ratios of 80/20, 88/12, and 94/6. Accordingly, the curing reaction was proposed to occur in two stages (Figure 29). At the first stage, benzoxazine and benzyl amines form as the initial intermediates. Other intermediates such as triazine, diamine-, and ether-type structures are also formed. At the second stage, by the decomposition, oxidation, and/or further reactions, these initial intermediates are transformed into methylene bridges between phenol rings. At this stage, various amines, amides/imides, imines, methyl phenols, benzaldehydes, and other trace species also forms. Some of the boiling species are considered to remain in the final cure products. The chemical structure of the final cured novolac was proposed to be controlled by the amount of initial hexa introduced and the ratio of *ortho/para* sites of the starting resin.

5.25.7.7 Non-Hexa Cure

Other than hexa, methylol derivatives of phenol, bisoxazines, bisbenzoxazines, and solid resol are used as the non-hexa curing agents.

Sergeev *et al.* reported the use of methylol derivatives of phenols as curing agents for novolacs.³³ Besides bismethylol cresol (1), other bismethylol compounds based on cresol trimer (2), cresol novolac (3), and bisphenol A tetramethylol

(4) were evaluated (Figure 30). Curing behavior of methylol derivatives and hexa with novolac is compared in Table 6. All methylol materials were satisfactory curing agents for novolac with low extractibles as hexa. Mechanical properties such as impact strengths and ultimate bonding strengths of the methylol-cured novolac were higher than those of the hexa-cured novolac.

Bisoxazolines (A), known as 1,3-PBOX, is reported to co-react with novolac using triphenyl phosphine catalyst³⁴ (Figure 31). The ring-opening reaction of the bisoxazoline is facilitated by the phenolic hydroxyl group without evolving volatiles. As will be described in detail, benzoaxazines also co-react with novolacs. At low cure temperature, the use of benzoxazines for the cure of novolac does not emit ammonia, and yields cured product with lower weight loss. Solid resol is also a curing agent for novolacs. Special formulations based on solid novolac/resol systems are used in molding compounds for electrical applications and others.

5.25.8 Resol

The reaction of F and P using excess amount of F to P under basic condition gives the mixture of products named 'Resol'.

5.25.8.1 Methylol Phenols

Under basic conditions, the reaction of P with F is the addition of F to phenolate (Figure 32), leading to *ortho*- or *para*-methylol phenol, the simplest phenolic components that can be cured into a phenolic resin.

Preparation of *o*- and *p*-methylol phenol has been studied using complexation with cyclodextrin.^{35,36} The base-catalyzed reaction of P with F using β -cyclodextrin increased the ratio of *para* isomer to 3:1. Mechanism of selective synthesis of *para* isomer is shown in Figure 33. Phenolate anion is located in the β -cyclodextrin cavity, and approach of F from the bottom of the cavity is more facile to react with the *para* position of the phenolate. Approach of F to the *ortho* position is hindered by

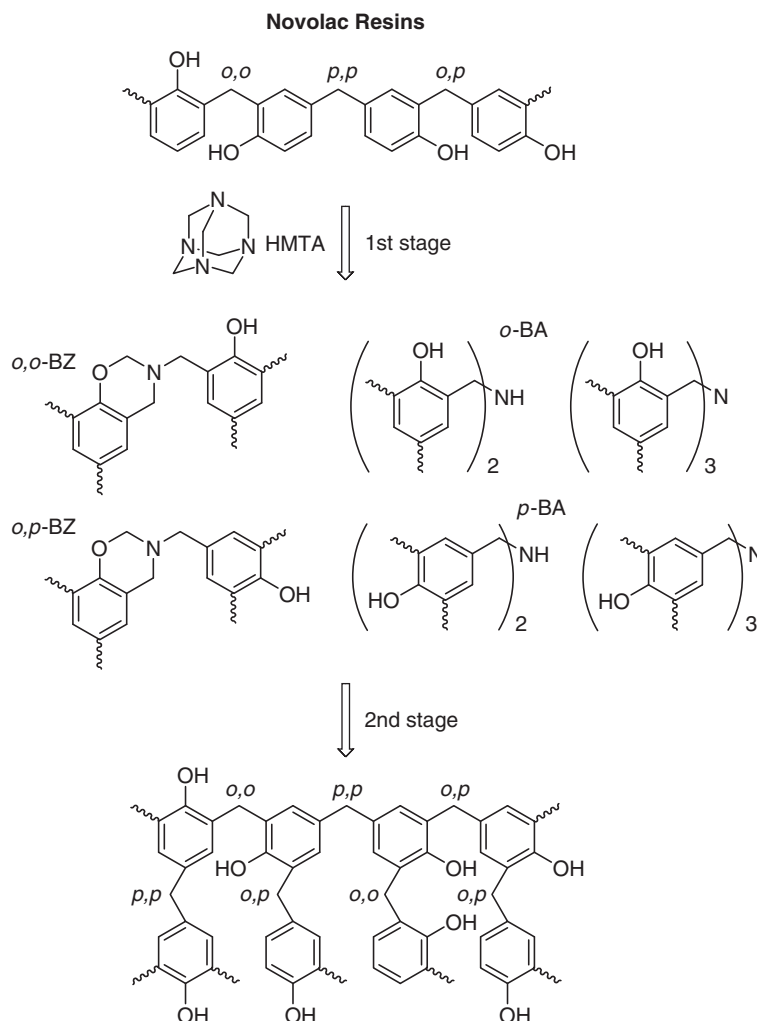


Figure 29 Curing reaction of novolac by hexa.

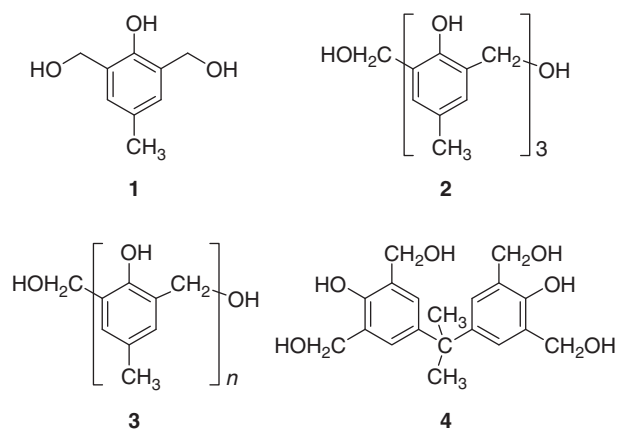


Figure 30 Methylol derivatives of phenols as curing agents for novolac.

the complexation of phenolate and β -cyclodextrin. With a 2-hydroxypropyl group on the bottom side of the cavity, the selectivity of *para* over *ortho* was increased up to 94%. Use of crown ether, 18 crown 6, also led to a high selectivity of *p*-methylol phenol of up to 88%.

Besides the monomethylol phenols, some di- and tri-methylol phenols are formed when the reaction is carried out with more than an equimolar amount of F (**Figure 34**). These mono-, di-, and tri-methylolated phenols act as transient intermediates and undergo oligomerization into dimeric, trimeric, and higher oligomers depending on F content, reaction basicity, and temperature during reaction.

5.25.8.2 Oligomers

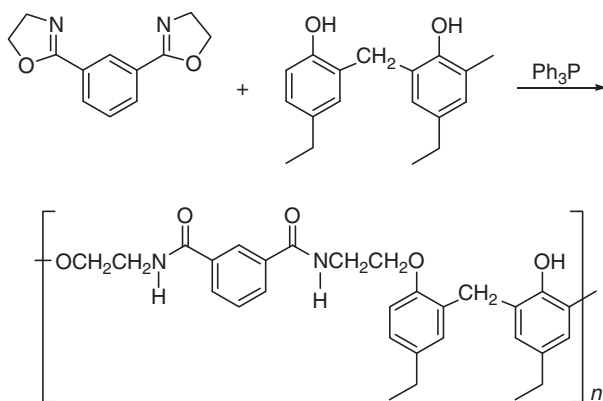
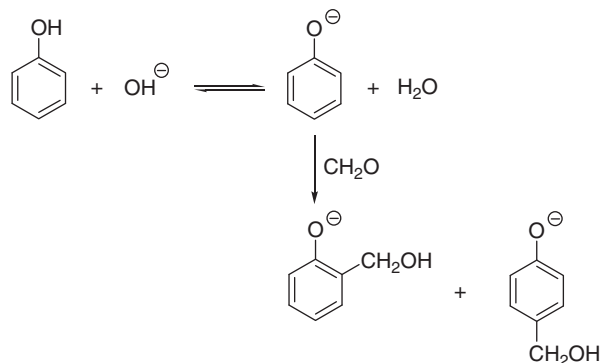
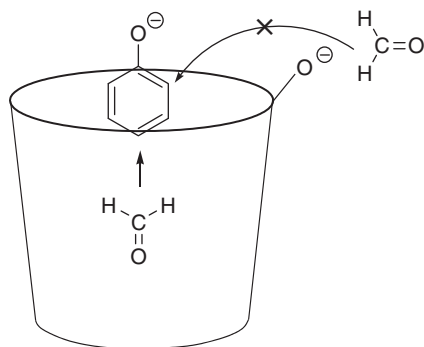
At low temperatures below 60 °C, only addition of F to P occurs. Above 60 °C, condensation reactions of methylol phenols with P and/or methylol phenol occur, and leads to resol resin (**Figure 35**). Resols are a mixture of the monomethylol phenols, oligomers, residual-free P and F.

The structure of resol depends strongly on the ratio of P and F, the kind of catalyst, and reaction conditions. The ratio of F/P is usually between 1 and 3. The catalysts used are NaOH, Na_2CO_3 , oxide and hydroxide of alkali earth metals, aqueous ammonia, hexa, and tertiary amines.

Grenier-Loustalot *et al.* analyzed the resol resin.³⁷ They showed that resol resin structure depends on reaction

Table 6 Comparison of methylol derivatives of phenol and hexa on cure of novolacs

Curing agent	% Wt ^a	Cure time ^b	% Extractibles ^c	Impact strength (kJ m ⁻²)	Ultimate bending strength (MPa)
1	36	6.0	2.8	6.2	108.0
2	87	7.5	2.6	2.6	41.5
3	100	6.5	2.9	5.0	64.5
4	38	7.0	2.6	3.6	69.3
Hexa	10	5.5	2.7	1.8	38.9

^a Comparable amount of reactive groups as hexa.^b 180 °C min⁻¹.^c Acetone extraction/1 h.**Figure 31** Curing of novolac by bisoxazolines.**Figure 32** Reaction of phenol and formaldehyde under basic condition.**Figure 33** Reaction profile of phenol and formaldehyde in cyclodextrin.

conditions and that all the methylol phenols shown in **Figure 34** were formed along with dimers and trimers. Analyses of the dimers (**Figure 36**) indicated that the dimers were linked by *p,p* methylene bridges.

They also studied catalytic activity at F/P = 1.5 and at pH = 8 from the decrease of F.³⁸ It was found out that activity was in the following order:



This result concludes that divalent alkali earth metals have higher catalytic activity than monovalent alkali metals and that cations with larger ionic radius have higher catalytic activity. *Ortho/para* ratio of resol has been examined from the ratio of *o*- and *p*-methylol phenol, and found to increase by using metals that have higher chelation ability³⁹ (**Table 7**).

5.25.8.3 Curing of Resol

Resols are readily cured by thermal conditions or even at room temperatures by the help of acid or base. The reactions involved in the curing of resol are shown in **Figure 37**. As the cure of resol proceeds, molecular weight increases, leading to a gel state. Complete cure of phenolic resol leads to a highly cross-linked material exhibiting high modulus, excellent moisture and heat resistance, and high *T_g* (~150 °C).

There are some other special systems that accelerate the cure of resol resins, such as anhydrides, amides, carboxylic acid esters, and carbonates.

5.25.9 Transformation of Phenolics

Selective reactions can be directed to the hydroxyl functionality of the phenolic group whereby the transformed product has a new utility in applications that are not attainable by the phenolic resin. Moreover, in many instances, these transformations eliminate evolution of by-product such as water and minimize void formation. These transformations are preferably conducted on the stable novolac system. The new functional groups include epoxy, cyanate ester, and benzoxazine. Introduction of epoxy is the most important transformation of phenolics. Cyanate ester and benzoxazine offer promise in many high-temperature applications such as electronics and primary structural components for aircrafts.

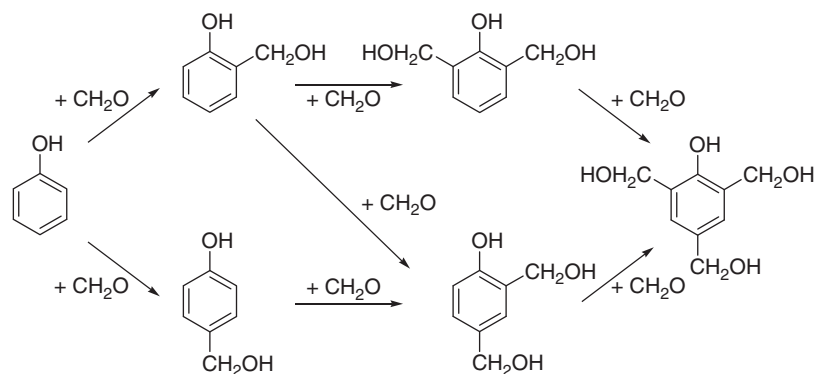
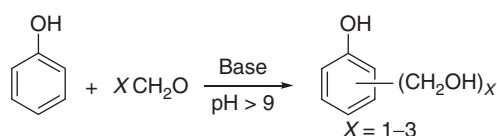


Figure 34 Addition of formaldehyde with phenol.

Addition (<60 °C)



Condensation (60–100 °C)

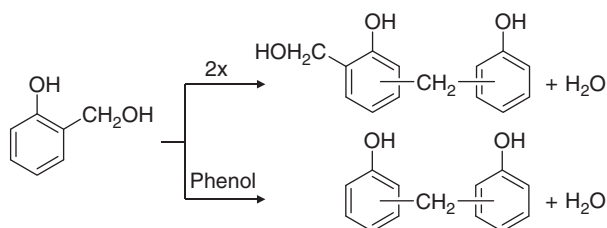


Figure 35 Addition and condensation reactions for resol.

5.25.9.1 Epoxy

By introducing epoxy groups onto the phenolic hydroxyl groups, transformation of phenolic to epoxy is achieved, and a variety of epoxy compounds are obtained. A commodity epoxy resin,

bisphenol A epoxy resin, is prepared by the reaction of epichlorohydrin with bisphenol A (Figure 38). The average degree of polymerization, n , changes depending on the ratio of the reagents. The simplest novolac, bisphenol F, is transformed into the corresponding epoxy resin as a low-viscosity epoxy resin system. Details on epoxy were described before.

5.25.9.2 Cyanate Esters

The cyanate esters were developed in a manner analogous to epoxy resins. Bisphenol A dicyanate ester is obtained in high yield from bisphenol A by using cyanogens chloride and base (Figure 39). The cyanate ester trimerizes into a cyanurate ring structure at elevated temperature catalyzed by metal salts, affording crosslinked resin having T_g above 250 °C, excellent thermal stability, low water absorption, low dielectric constant (D_k), and dissipation factor (D_f).^{40,41} Only Teflon and polyethylene possess lower D_k and D_f values than cyanate esters.

The problem with this material is its brittleness. Toughening by high-performance thermoplastics such as PES, PSF, PPO, PEI, and PI was successful without sacrificing high T_g .^{42,43} Iijima *et al.* studied the effect of *N*-phenylmaleimide-styrene copolymers (PMSs) for the toughening of cyanate ester, and found that cocontinuous phase is effective for the toughening.⁴⁴ It was found out that *in situ* polymerization of PMS was

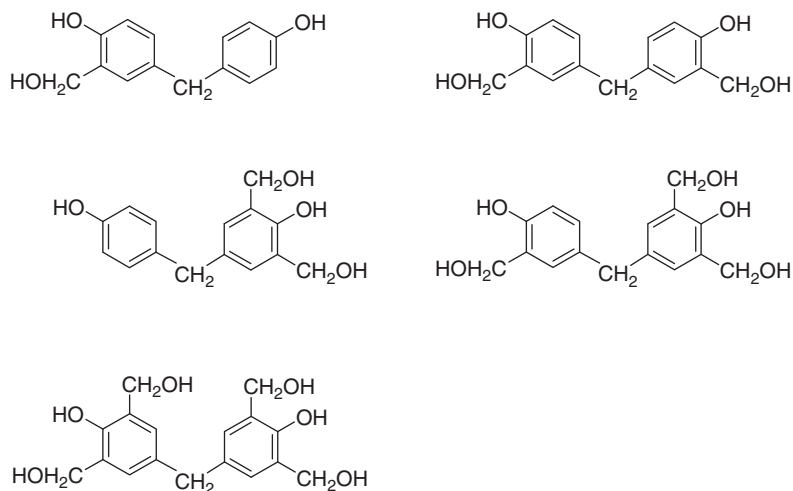
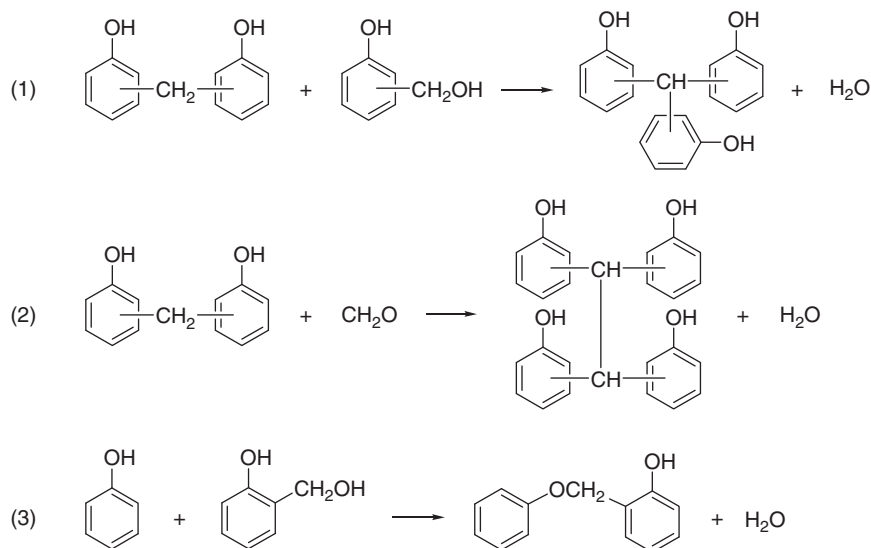
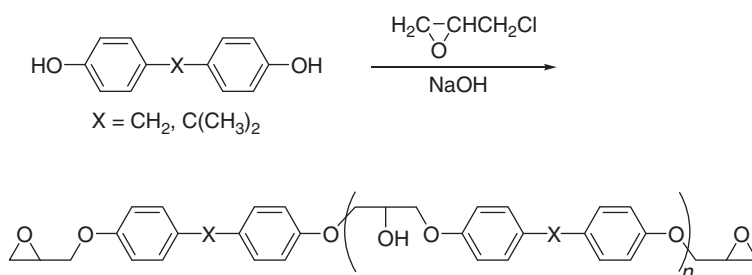
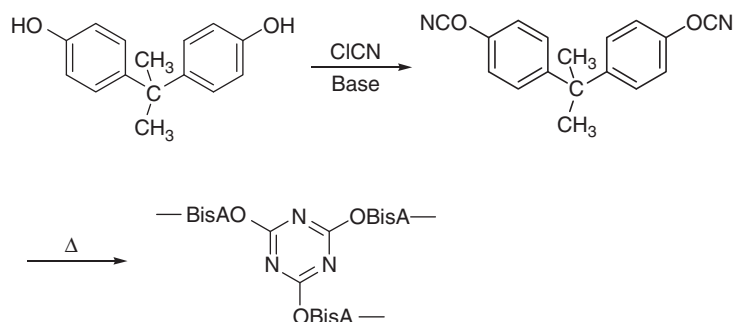


Figure 36 Dimer structures.

Table 7 Effect of catalyst on the *o/p* ratio of hydroxymethylphenols

Catalyst	Mg(OH) ₂	Ca(OH) ₂	Sr(OH) ₂	Ba(OH) ₂	LiOH	NaOH	KOH	(CH ₃) ₄ NOH
<i>o</i> -/ <i>p</i> - ratio	4.39	3.08	2.68	2.52	1.75	1.56	1.33	0.88

**Figure 37** Curing reactions of resol.**Figure 38** Preparation of epoxy from phenols.**Figure 39** Preparation of cyanate ester and the cure reaction.

effective for the toughening of cyanate esters keeping the flexural properties and T_g .

As a family of cyanate ester, 'BT resin' that consists of bisphenol A dicyanate and bismaleimide is an important resin that is used in high T_g electrical laminates.

5.25.9.3 Benzoxazines

Benzoxazine has been known as the intermediate of the hexa-cured novolac. But, detailed study on benzoxazine was not performed until Ning and Ishida showed that benzoxazines

are obtained from the reaction of phenols, amines, and formaldehyde.⁴⁵ They reported that the ring-opening polymerization of benzoxazine is facilitated by active hydrogen-containing chemicals such as unreacted starting phenolics and oligomeric phenolics^{46,47} and that the cured resin shows various interesting features.⁴⁸ Now, benzoxazines are emerging as a novel type of phenolic resin. Review papers^{49–51} reveal the synthesis and interesting properties of benzoxazines. The first book on polybenzoxazine will be published in 2011.⁵²

5.25.9.3.1 Typical benzoxazines

Benzoxazines are easily prepared from phenols, primary amines, and formaldehyde. The wide variations of raw materials, phenols and amines, allow tremendous molecular design flexibility for the cyclic monomers. Formation of one of the typical benzoxazines, B-a, and the structure of the ring-opened resin is shown in Figure 40.

Benzoxazines are typically prepared in one step using phenols, amines, and formaldehyde as starting materials with or without solvent. It is reported that in the benzoxazine formation, triazine is an intermediate.⁵³ Benzoxazines can be prepared through a two step reaction, in which triazine will be formed first from the reaction of amine and formaldehyde, and in the second step the triazine will be reacted with phenols to give benzoxazine (Figure 41).⁵⁴

Benzoxazines undergo ring opening only by heat treatment without the need of catalysts and without emitting volatiles during cure, and thus offering an excellent dimensional stability for the cured products. The ring-opening reaction is autocatalytic and can be catalyzed by organic and inorganic acids, bases, and metal compounds to lower the cure temperature. Polymerization occurs with near zero shrinkage or slight

expansion.⁴⁷ The uniqueness of expansion of benzoxazine on polymerization is attributed to molecular packing via H-bond formation.⁴⁸ Benzoxazine is a six-membered ring and very stable at ambient atmosphere. This outstanding stability of the monomer makes the curing by the ring-opening polymerization occur at relatively high temperature.

On the mechanism of the ring-opening polymerization, from the detailed study using model compounds, the reaction pathway is proposed as shown in Figure 42: (1) formation of an intermediate polymer having *N,O*-acetal-type linkage in the main chain, and (2) its rearrangement into Mannich-type linkage in the solid state.⁵⁶ The mechanism explains that when formation of polymer A in Figure 42 is hindered, weight loss through evolution of imines increases. Therefore, the use of small aliphatic amine such as methylamine is advantageous in

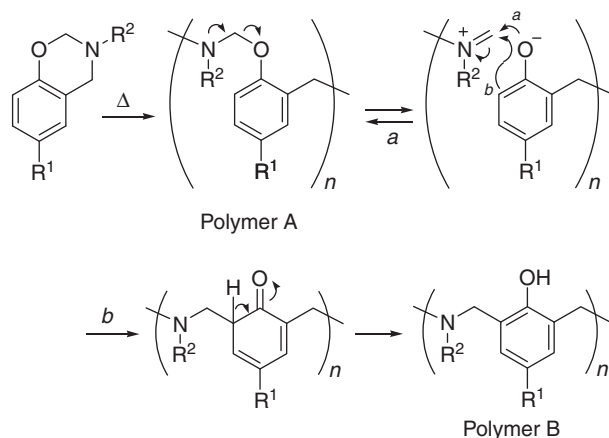


Figure 42 Mechanism of ring-opening reaction of benzoxazine.

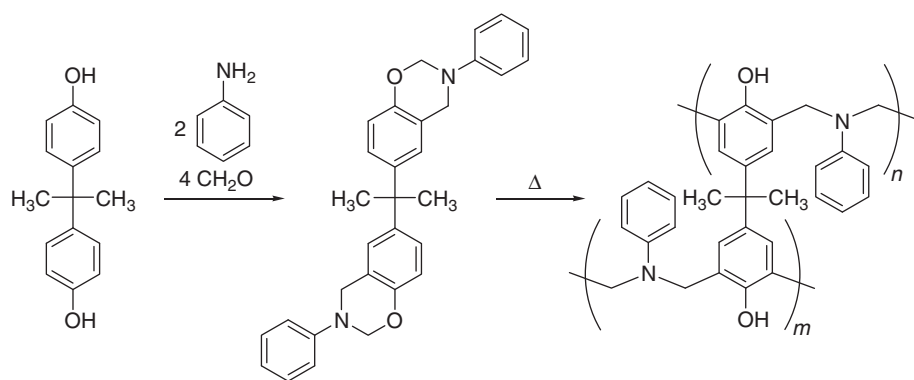


Figure 40 Preparation of typical benzoxazine and the structure of cured product.

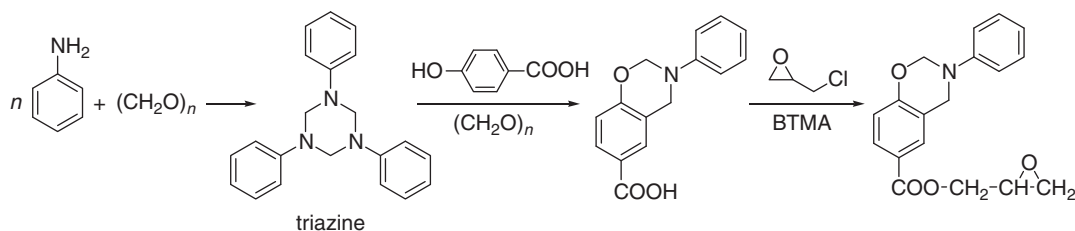


Figure 41 Preparation of benzoxazine through triazine intermediate.

lowering the ring-opening temperature and reducing the amount of volatiles at the cure.

Benzoxazines differ from the traditional phenolics in that the phenolic moieties are connected by a Mannich base bridge $[-CH_2-N(R)-CH_2-]$ instead of methylene $(-CH_2-)$ bridge. Polybenzoxazines provide characteristics found in the traditional phenolic resins such as excellent heat resistance and flame retardance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption, and stable low dielectric properties. Therefore, it is considered that polybenzoxazines have overcome the disadvantages of the traditional phenolic resins including poor shelf life of the precursors, the use of harsh catalyst for polymerization, evolution of volatiles during the cure leading to a large volumetric shrinkage upon cure, and formation of voids. These attractive features are responsible for its large volume use in electronics and Fiber Reinforced Plastics (FPR). It was also reported that polybenzoxazine has very low surface free energy.⁵⁷ The surface free energy is as low as 16.4 mJ m^{-2} , which is even lower than that of pure Teflon (21 mJ m^{-2}).

A comparison of thermal properties of benzoxazines with other important thermosetting resins is shown in Table 8.⁵⁸ Both polybenzoxazine and phenolic are favorable based on T_g and char yield as compared to expensive BMI.

However, polybenzoxazines are brittle as is common for thermosets. They also need relatively high temperature

($\sim 200^\circ\text{C}$) for the ring-opening polymerization. The typical polybenzoxazine, PB-a, has T_g at $\sim 160^\circ\text{C}$ and storage modulus drops considerably at around T_g due to the low crosslink density. Therefore, further enhancement of the thermal properties is also expected. Another shortcoming is the difficulty to process into thin films from the typical monomers. Aiming for performance enhancement and lowering the polymerization temperature, various approaches have been developed.

5.25.9.3.2 Molecular design of benzoxazines

Taking advantage of the tremendous molecular design flexibility, various types of benzoxazine can be prepared, and properties of polybenzoxazines are easily tuned from the combination of raw materials. Benzoxazines with improved properties are prepared. Such properties include toughness, thermal properties, flame retardant properties, and so on.

For the toughness enhancement, the inclusion of flexible linkages into the backbone of benzoxazine is effective. Such linkages include long alkylene groups⁵⁹ and siloxane groups.⁶⁰ In some cases, however, the introduction of flexible linkage lowers the thermal properties of the cured polymer.

For the enhancement of thermal properties, introduction of crosslinkable units into the benzoxazine moiety is very effective. It is proposed that polybenzoxazines decompose by volatilizing aniline fragments during the thermal degradation.⁶¹ Therefore, the introduction of crosslink sites into an aniline moiety is expected to enhance thermal properties of polybenzoxazine.

Various double and triple bonds have been found to be effective as crosslink sites. For example, an allyl group is an effective crosslink site that works at moderate temperature.⁶² The allyl-containing monomers, P-ala and B-ala, were prepared from phenol and bisphenol A with allylamine and formaldehyde (Figure 43). Differential scanning calorimetry (DSC) of P-ala showed two separate exotherms with maxima at 207°C and 260°C , which correspond to the polymerization of the allyl groups and the ring opening of benzoxazines, respectively. The obtained thermosets exhibit much higher T_g ($\sim 300^\circ\text{C}$), which is nearly 150°C enhancement. Another series of allyl-containing monofunctional benzoxazine, prepared by reacting various cresols with allylamine and paraformaldehyde,

Table 8 Comparison of benzoxazines with thermosetting resins

Resin family	T_g ($^\circ\text{C}$)	T_d^a ($^\circ\text{C}$)	Char yield (%)
Polybenzoxazines	150–260	250–400	45–65
Phenolics	~ 175		40–50
Epoxyes	150–261		≤ 40
Bismaleimides	250–300	450–500	50–70

^aTemperatures when 5% weight loss during TGA in N_2 , $20^\circ\text{C min}^{-1}$ heat rate.

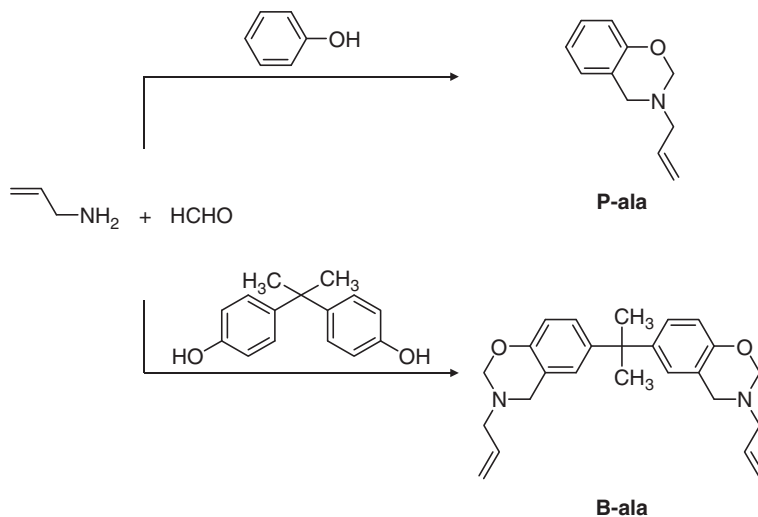


Figure 43 Preparation of allyl-containing benzoxazine.

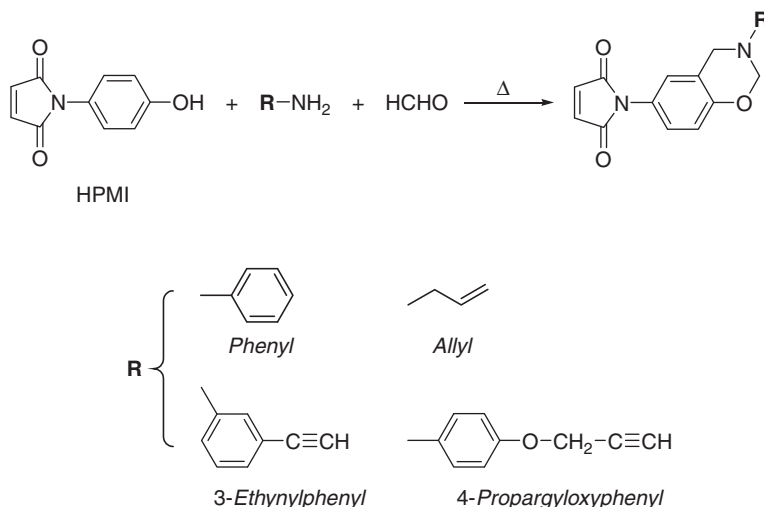


Figure 44 Preparation of novel benzoxazines containing crosslink sites.

also showed increased thermal properties.⁶³ The *ortho* position in cresol was more reactive than the *para* position.

Other double and triple bonds attached to amine moieties were similarly effective to enhance the thermal properties of polybenzoxazines. The examples are propargyl,⁶⁴ ethynyl,⁶⁵ and nitrile groups.⁶⁶

Crosslink sites can also be introduced into phenol moiety. An example is the introduction of maleimide double bond through the use of hydroxyphenylmaleimide (HPMI). By reacting HPMI with formalin and various amines (e.g., aniline, allylamine, and aminophenyl propargyl ether), a series of maleimide-containing benzoxazines are obtained (Figure 44).⁶⁷ The thermal cure of the monomers at 250 °C afforded polybenzoxazine having novel network structures. The T_g s were as high as 241–335 °C with improved thermal stability and higher char yield (62–70%). Other than the double and triple bond, epoxy group was introduced as another crosslink site of benzoxazine as shown in Figure 41.⁵⁴

The introduction of a mesogenic group in benzoxazines was attempted to provide LC benzoxazines, which give, upon cure, polybenzoxazine resins with enhanced thermal conductivity as well as improved thermal and mechanical properties. In the first report on LC benzoxazines, a cyanobiphenyl unit was used as the mesogen. The LC benzoxazine showed a nematic phase only upon cooling and did not show any LC phase upon heating, indicating a monotropic LC phase.⁶⁸ Another type of LC benzoxazines was recently reported, in which ester and azomethine linkages were used as the mesogenic unit. The benzoxazine showed an LC phase not only upon cooling down but also upon heating.⁶⁹

5.25.9.3.3 High-molecular-weight benzoxazine precursors

As the precursors of polybenzoxazines, only low-molecular-weight cyclic benzoxazines, prepared by the reaction of bisphenol, amine, and formaldehyde, have been studied in detail. The yield of monomer is ~80%, and the reaction mixture contains ring-opened oligomers. The combination of diamine and bisphenols with formaldehyde could give polymers that contain benzoxazine in the backbone. Though Ishida reported the modification of polyphenol with a

monofunctional amine to get a benzoxazine-functional polymer,⁷⁰ a high-molecular-weight polymer containing the cyclic benzoxazine structure as a repeating unit in the main chain has not yet been prepared.

Takeichi *et al.* reported the first successful synthesis of high-molecular-weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone.^{71,72} The reaction of bisphenol A, various diamines, and paraformaldehyde (Figure 45) afforded various precursors in the range of 77–87% yield after purification. The M_w was in the range of 6000–8900 and M_n was 2200–2600, showing that the molecular weight is not so high. But, it should be emphasized that self-standing thin films were easily obtained by casting the precursor solutions. All the polybenzoxazine films cured by the heat treatment up to 240 °C gave remarkably improved tough films (Figure 46). They also had much improved tensile strength and the elongation at break. The T_g values of the polybenzoxazines from the high-molecular-weight precursors were as high as 238–260 °C, much higher than the T_g of the typical polybenzoxazine. The significant increase in T_g indicates the beneficial effect of the linear long backbone and the high crosslink density.

High-molecular-weight precursors were also synthesized from aminophenols and formaldehyde (Figure 47).⁷³ The precursors also gave self-standing thin films. Upon a gradual thermal cure up to 250 °C, they afforded polybenzoxazine films, having T_g as high as 260–300 °C. Decomposition temperature and char yield of the thermosets were higher than those of the typical polybenzoxazine.

The above approach to prepare high-molecular-weight polybenzoxazine precursors employs the benzoxazine formation as the method of polymerization. The reaction to make benzoxazine is known to give benzoxazine only in 70–80% yield. It is therefore not a good reaction to be used for polymer formation. But because of this unique reaction feature, the obtained high-molecular-weight benzoxazines have various advantageous unique properties as follows: (1) the oligomers are low molecular weight, (2) the solubility in the ordinary solvents is excellent, (3) the uncured films can be obtained as self-standing films, and (4) cured films are very tough with much improved thermal

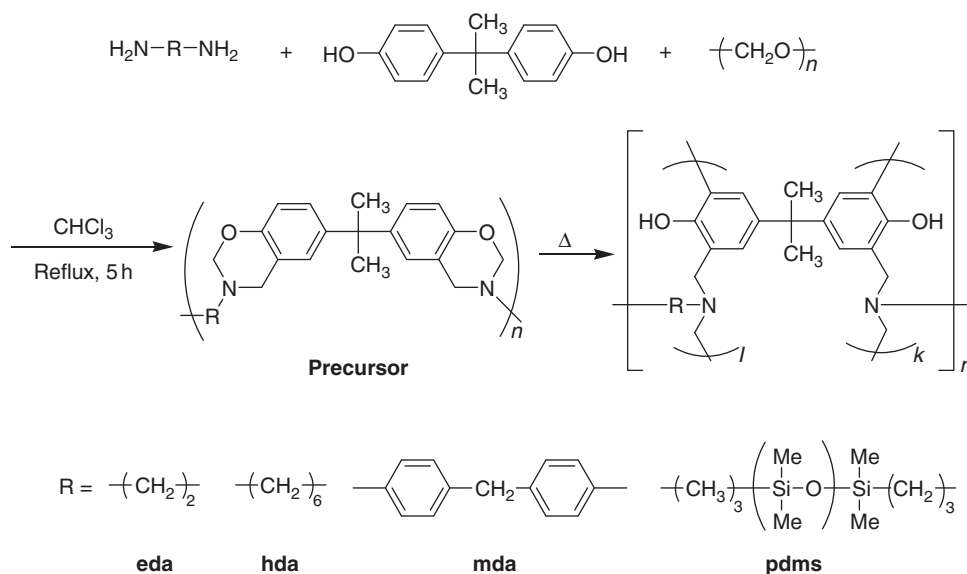


Figure 45 Preparation of high-molecular-weight polybenzoxazine precursor.

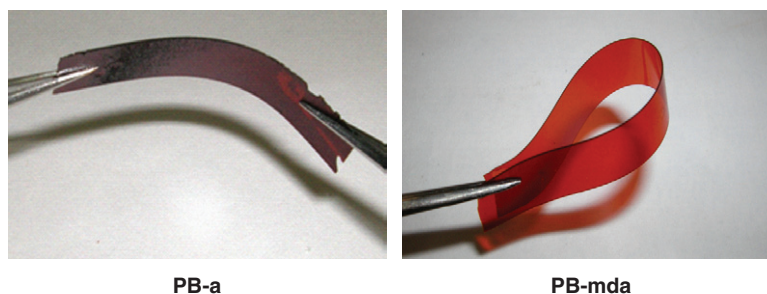


Figure 46 Appearance of polybenzoxazine films.

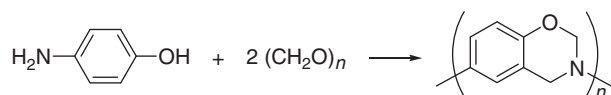


Figure 47 Preparation of polybenzoxazine from aminophenols and formaldehyde.

properties (T_g s are around 250 °C). Other research groups also employed the same chemistry and examined the structure and properties of the obtained polymers.^{74–77}

The disadvantage of the above method is that the chemical structure is not well defined. Various attempts have been examined to prepare high-molecular-weight polybenzoxazine precursors with well-defined structure, having benzoxazine in the polymer backbone or as a pendant. For that purpose, difunctional monomer containing benzoxazine in the backbone (main-chain type) will be first prepared, and then reacted to give a polymer containing benzoxazine. Various reactions have been employed for the polymerization of benzoxazine-containing monomers such as ester formation between diol and adipoyl chloride,⁷⁸ Diels–Alder reaction,⁷⁹ click reaction,⁸⁰ and hydrosilylation⁸¹ (Figure 48). These approaches give well-characterized polymer. But one of the problems of the approach is that the solubility of the polymers is generally low and that it is often difficult to get soluble high-molecular-

weight polymers. Side-chain or pendant-type polybenzoxazines have also been prepared using similar chemistry.^{82–87}

5.25.10 Natural Products as Phenolics

Various natural products are known to contain phenolic groups within their structure such as lignin, tannin, and cashew nut shell liquid. These natural products undergo similar reactions as were shown for novolacs. An epoxy group has been introduced into lignin,⁸⁸ and hydroxymethylation was examined with lignin⁸⁹ and tannin.⁹⁰ The chemistry of cashew nut shell liquid was reviewed.⁹¹

Lignin is actually a naturally occurring phenolic compound, but phenolic activity is rather low. Funaoka *et al.* developed a method to isolate lignin from cellulose and hemicellulose mixtures and convert them into ligninophenol by the cleavage of benzyl aryl ether through the phase-separation system.^{92–94}

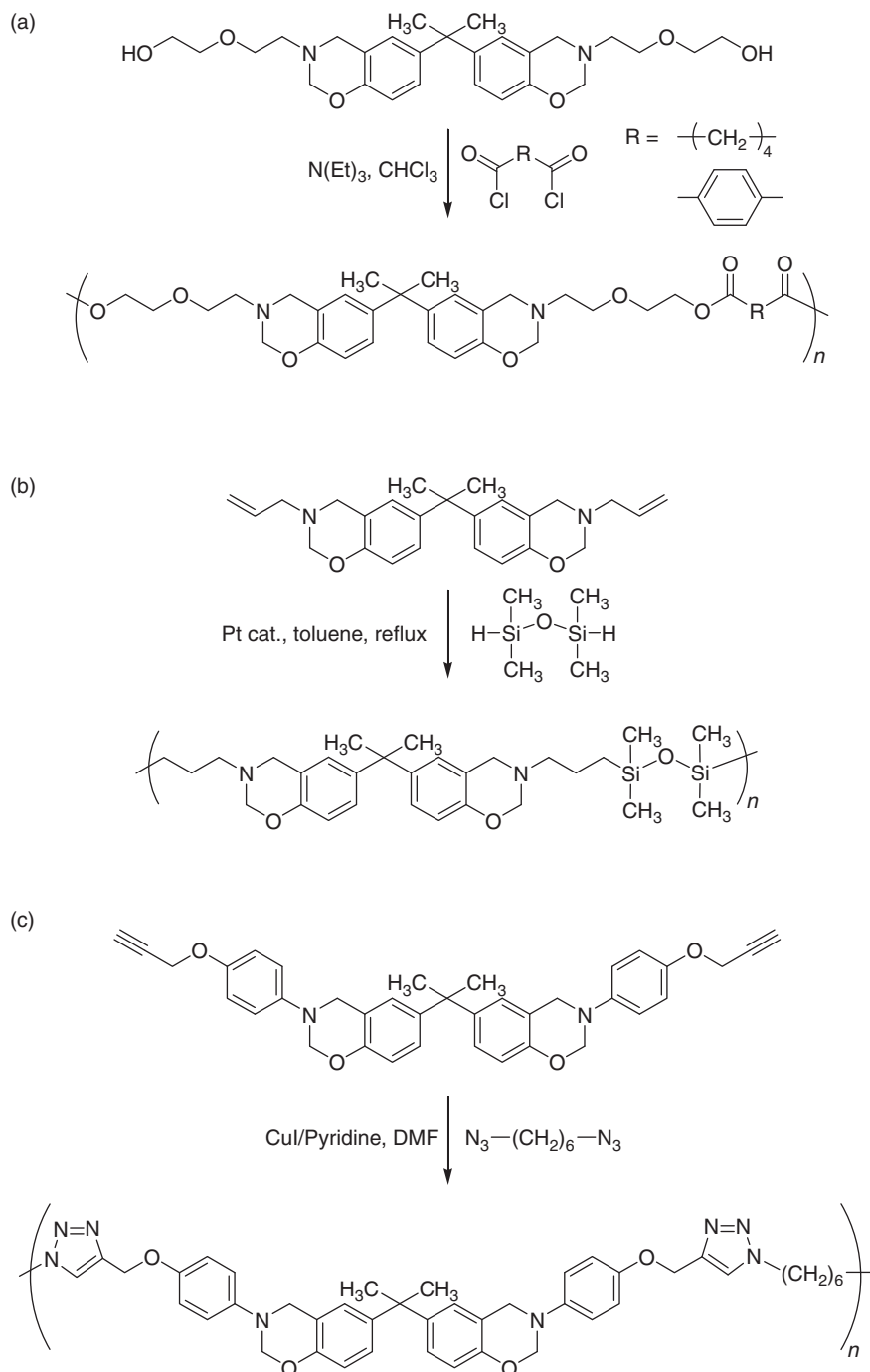


Figure 48 Preparation of polymers containing benzoxazine in the main chain.

The lignophenols have improved activity as phenolic compounds, and various studies to utilize the lignophenol are being carried out.⁹⁵

5.25.11 Modification by Alloys and Co-curing

5.25.11.1 Modification of Phenolics by Alloying

Brittle characteristics have been always a problem for thermosets. Several methods have been used to toughen the phenolics. A method that has been mainly applied to novolac

is the introduction of rubber modifiers. Rubber emulsion or latex is added to crude novolac and then dehydrated so that the rubber component is uniformly dispersed in the novolac. These rubber-modified novolac are used by curing with hexa. They exhibited marginal toughness.

Another method which is mainly applicable to resols consists of a co-reaction of resol methylol with the double bond/acid end group of nitrile butadiene rubber or resol methylol reacting with polyol/isocyanate (PUR rubbery phase). The flexible rubbery phase is introduced into the resol phase by the proposed co-reaction.

An interpenetrating network system (IPN) is reported on phenolic resin combined with oligomeric silanol or siloxane leading to a toughened phenolic resin system.⁹⁶ The phenolic resin modified with siloxane showed better impact and burst strength than phenolic control.

A technique that has been successful in enhancing the toughness of thermosets is the introduction of thermoplastic, ductile phase into matrix resin.⁹⁷ High-performance, high T_g engineering plastics are co-reacted or uniformly dispersed in the thermoset. Poly(aryl ether)s are high T_g ($\sim 200^\circ\text{C}$), high modulus/strength polymers, and poly(aryl ether)s with and without hydroxyl end group were evaluated in hexa-cured novolac.⁹⁸

5.25.11.2 Modification of Benzoxazine by Alloying

The performance of polybenzoxazines can be improved much more easily than novolac or resol by alloying with various polymers. Also, benzoxazines appear to be versatile in that they can undergo co-reaction with a variety of materials such as epoxy, isocyanates, and bismaleimide (BMI).

Alloying with epoxy and/or phenolic resins has been one of the well-studied examples.^{47,99,100} Epoxy reacts with polybenzoxazine through its phenolic OH, and the traditional phenolic resin works as an acid catalyst for the ring-opening polymerization of benzoxazine. Addition of the low viscous epoxy resin is also advantageous in processing.

Toughness of the brittle polybenzoxazine can be remarkably improved by alloying with elastomers like liquid rubber and polyurethane (PU). Jang and Seo evaluated the effect of amine-terminated butadiene acrylonitrile (ATBN)

and carboxyl-terminated butadiene acrylonitrile (CTBN) rubbers, and reported that ATBN exhibited better distribution of rubber particles in the matrix phase than CTBN.¹⁰¹ Higher fracture toughness and smaller rubber particle size was observed in benzoxazine modified with ATBN than that modified with CTBN.

The performance of the ATBN-modified polybenzoxazines can be further improved by the addition of HPMI.⁶⁴ HPMI is activated by its OH group and copolymerize with benzoxazine (Figure 49). The blend with HPMI effectively lowers the cure temperature of B-a as large as $40\text{--}60^\circ\text{C}$. The maleimide double bond in HPMI further crosslinks to give a cured resin having improved properties such as higher T_g , tensile modulus, and thermal stabilities. Thus, the combination of HPMI and ATBN was effective to lower the curing temperature, to increase toughness, T_g , and degradation temperature at the same time.

PU is one of the most important functional polymers that are being used in various applications. Alloying of PU with polybenzoxazine can be considered as a novel polymer alloy of PU and phenolic resin, in which improvement of both the thermal properties of PU and the toughness of polybenzoxazine can be achieved. The blend of an NCO-terminated PU prepolymer and a benzoxazine was thermally treated at $190\text{--}200^\circ\text{C}$ to give yellow, transparent films.^{103,104} The network structure is formed by the reaction of the NCO functionality with the phenolic OH that was formed through the ring-opening polymerization of the benzoxazine (Figure 50). Films became a plastic or an elastomer depending on the ratio of the benzoxazine and the PU prepolymer. Only one T_g was observed, and the T_g value increased with the increase of the

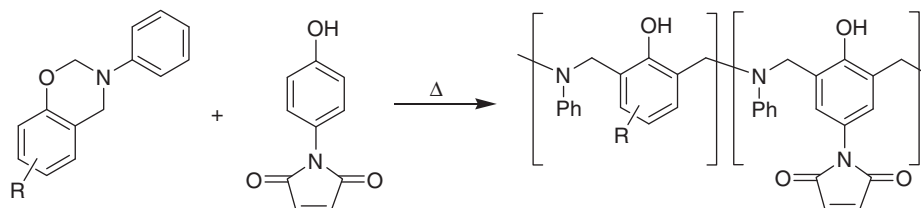


Figure 49 Reaction of benzoxazine and hydroxyphenylmaleimide.

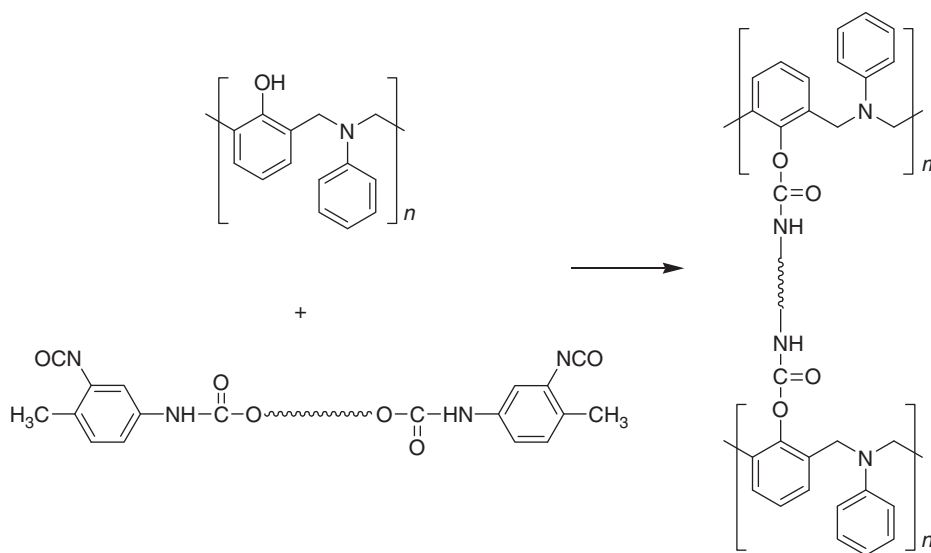


Figure 50 Reaction scheme of benzoxazine and polyurethane prepolymer.

benzoxazine content. By the introduction of PU, the toughness of benzoxazine was improved. On the other hand, the thermal stability of the PU was improved by the addition of a small amount of the benzoxazine.

5.25.11.3 Alloying of Benzoxazine with Polyimide

Polyimide is the most important thermally stable polymers. Wide variations of the monomers and the precursors make polyimide a suitable candidate to be used as one component of a polymer alloy.

Polymer alloys of a polybenzoxazine and a polyimide was prepared by blending B-a as a benzoxazine with a poly(amide acid), PAA, as a precursor of polyimide, followed by film casting and thermal treatment for the ring-opening polymerization

of the benzoxazine and imidization.¹⁰⁵ Various types of PAA were prepared as shown in Figure 51. It was observed that the onset temperature of the exotherm due to the ring-opening polymerization decreased by as much as $\sim 80^\circ\text{C}$ by blending B-a with a PAA because of the catalytic effect of the carboxylic group in the PAA. The resulting alloy films are considered to form a semi-interpenetrating polymer network (semi-IPN) consisting of a linear polyimide and a crosslinked polybenzoxazine or to form an AB-co-crosslinked polymer network by the copolymerization of benzoxazine with polyimide containing a pendent phenolic hydroxyl (Figure 52).¹²² The semi-IPN polymers gave two T_g s, while the AB-co-crosslinked polymers gave only one T_g . Both types of polymer alloys were effective to improve the brittleness, the T_g and the thermal degradation temperature of polybenzoxazine. The semi-IPN formation

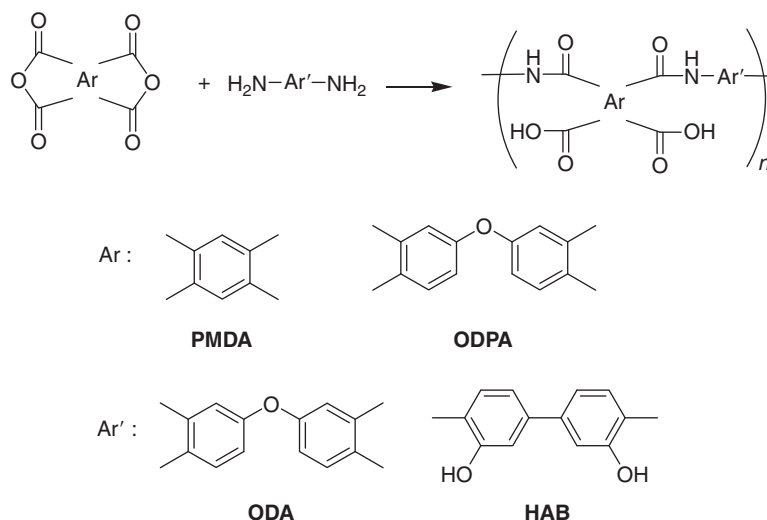


Figure 51 Preparation of various poly(amide acid) as polyimide precursor.

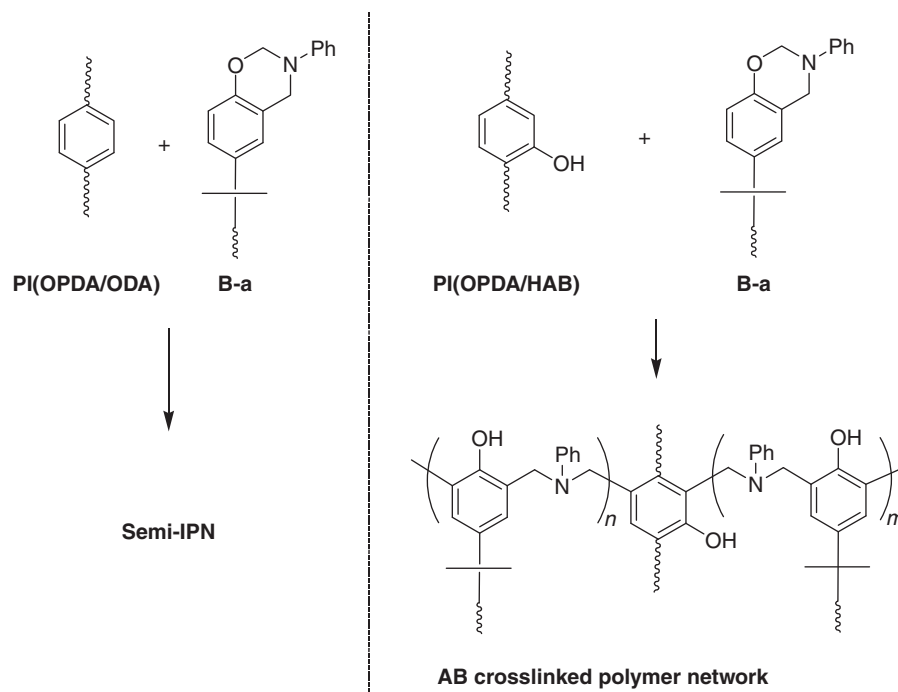


Figure 52 Scheme of reaction between polyimide and benzoxazine.

was especially effective for toughening the polybenzoxazine, while the AB-co-crosslinked polymer network was effective for increasing T_g .¹²³

5.25.11.4 Alloying of Benzoxazine with Bismaleimide

Another type of polymer alloy was prepared by mixing a typical benzoxazine, such as P-a and B-a, and a typical bismaleimide, 4,4-bismaleimidodiphenyl methane (BMI), followed by a thermal cure.^{51,124} IR and DSC analyses indicated the thermal reaction between the hydroxyl group of the polybenzoxazine and the double bond of BMI, forming an AB-co-crosslinked structure as supported by the model reaction of phenol and *N*-phenylmaleimide. Dynamic mechanical analysis (DMA) of the polymer alloys showed only one T_g , also suggesting the formation of the AB-co-crosslinked structure. Interestingly, T_g of the polymer alloys shifted to higher temperature by the increase of the BMI content, and were even higher than those of each resin due to the formation of the AB-co-crosslinking (Figure 53). The thermal stability also increased with the increase of the BMI content.

5.25.12 Hybrids and Composites

Nanotechnology has been applied to phenolic resins, benzoxazines, and cyanate esters using various nanomaterials such as nanoclay, carbon nanofiber, carbon nanotubes, nanosilica, POSS, and metal oxide nanoparticles by the sol-gel process.

5.25.12.1 Preparation of Hybrids by Layered Clay

Polymer-clay hybrid is a new class of composite material, in which a clay, a layered silicate, is dispersed in a polymeric matrix in nanoscale size.^{106,107}

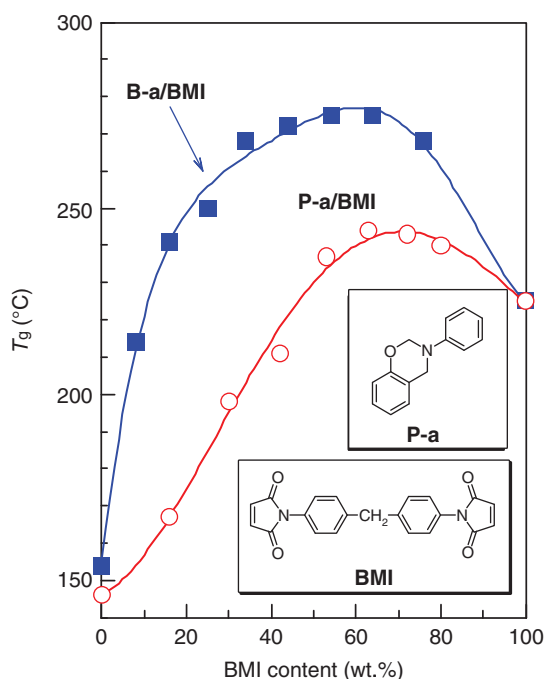


Figure 53 T_g profile of benzoxazine/bismaleimide blend.

The first study on the successful preparation of polybenzoxazine/clay hybrids was reported by Takeichi *et al.*, in which the inclusion of an organically modified-montmorillonite (OMMT) into a polybenzoxazine matrix led to a considerable improvement of its properties.^{108,109} Polybenzoxazine/clay hybrids were prepared by two different methods; a melt method and a solvent method. X-ray diffraction (XRD) measurements of the hybrids showed that the blending method and the kind of solvent play crucial roles for the dispersion of OMMT in the polybenzoxazine matrix. In the melt method and in the solvent method using NMP as a solvent, a complete exfoliation of clay nanolayers into the polybenzoxazine matrix was achieved. Interestingly, the inclusion of any type of OMMT significantly lowered the curing exotherm of the benzoxazines, suggesting a catalytic effect of the onium ions of the clay surface and/or the silanol groups at the edge of the clay on the ring-opening polymerization of the benzoxazines. The hybrids exhibited higher T_g (for 25–30 °C) and increased storage moduli than the pristine resins. Dynamic and isothermal TGA clearly showed the improvement of the thermal stability by the inclusion of the clay. The effect of the clay was most significant at around 2–5 wt.% of inclusion for the improvement of various properties.

The effect of OMMT inclusion was also examined in the epoxy/polybenzoxazine^{110,111} and the PU/polybenzoxazine¹¹² alloys. In both cases, lowering of the cure temperature and the enhancement of the thermo-mechanical properties were achieved.

Polybenzoxazine-clay hybrids were also prepared using a synthetic mica.¹¹³ The storage moduli of the hybrids were much enhanced because of the reinforcing effect of the mica nanolayers that have large aspect ratio. The hybrids also showed an improved thermal and thermoxidative stability with higher char yield.

5.25.12.2 Preparation of Hybrid by Sol-Gel Process

The sol-gel process is a common and a convenient technique to develop a homogeneous and high-purity metal oxide (Figure 54). Therefore, it is convenient to grow an inorganic ceramic network within a polymer matrix through the sol-gel process, thus producing organic-inorganic hybrids.

Polybenzoxazine/silica hybrids were prepared by blending various content of tetraethoxysilane (TEOS) with B-a using THF, followed by the curing up to 240 °C for 1 h.¹¹⁴ Polybenzoxazine/titania hybrids were similarly prepared by using titanium isopropoxide (TIPO).¹¹⁵ The hybrid films were optically transparent with loading of silica or titania up to 10–20%, and the transparency decreased at higher loading. In the blends of B-a and TEOS or TIPO, the onset and the maximum of the exotherm due to the ring opening of the benzoxazine was shifted to lower temperature at small loading of the metal oxide precursor. This implies that the acidity of the residual Si–OH and Ti–OH group in silica or titania network is high enough to initiate the ring-opening polymerization of B-a. The morphology study of the hybrids indicates that the inorganic domains are homogeneously dispersed into the organic matrix in a nanoscale. The viscoelastic analyses revealed that the inclusion of silica or titania shifted the T_g to higher temperature than the neat resin. The decomposition temperatures and the char yield of PB-a considerably increased by the

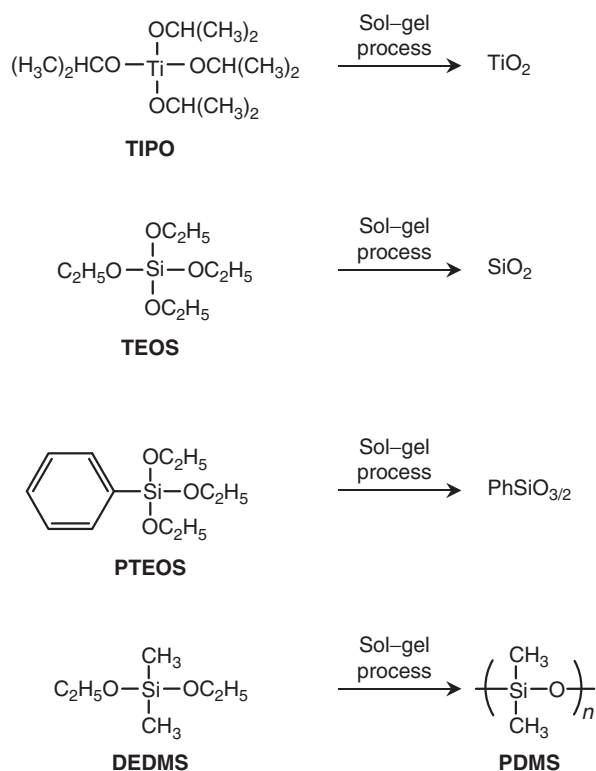


Figure 54 Sol-gel reactions of various precursors.

inclusion of a small amount of silica or titania, demonstrating that the metal oxide dispersed into the matrix acts as a thermal insulator to protect the polybenzoxazine network.

Polydimethylsiloxane (PDMS) is an inorganic polymer that shows not only flexibility but also unique properties such as good thermoxidative stability, low surface energy, high hydrophobicity, and high gas permeability. Polybenzoxazine/PDMS hybrids were successfully prepared by blending a benzoxazine and diethoxydimethylsilane (DEDMS), followed by the thermal curing that induce the ring-opening polymerization of the benzoxazine and the sol-gel process of DEDMS (Figure 54).¹¹⁶ The introduction of PDMS improved the tensile strength and the elongation at break of the pristine PB-a, because of the toughening effect of the PDMS. Surprisingly, in spite of the introduction of the flexible and low T_g PDMS, T_g of the polybenzoxazine shifted to higher temperature (Figure 55). The decrease of the storage modulus above T_g was also suppressed by the hybridization with PDMS. These results suggest that the *in situ* formed PDMS behaves as a plasticizer for the polymerization of benzoxazine accompanied with the increase of the crosslink density. Moreover, the decomposition temperature and the weight residue at 850 °C increased with an increase in the PDMS content.

5.25.13 Conclusion

Epoxy and phenolic resins are the most important thermosets widely used in various fields such as electronics and aerospace industries. These thermosets are indispensable because of the excellent thermal and mechanical properties, and creep

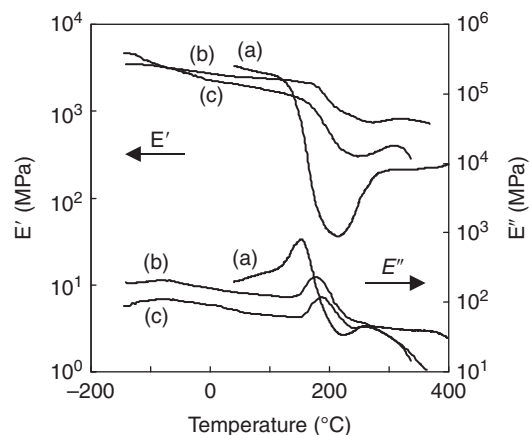


Figure 55 Dynamic mechanical properties of polybenzoxazine/PDMS hybrids.

resistance. Thermosetting materials are becoming more and more important as evidenced by the recent increasing application in commercial airplanes such as the Airbus A380 and Boeing B787.

It is true that thermosets are old polymers, but there continues to be new developments. For epoxy resins, toughening without sacrificing thermal properties is always expected. The enhancement of thermal conductivity is also a challenge nowadays. For phenolic resins, PAPS resin is a promising new material. Remarkable development can be seen in the progress of benzoxazine resin as an emerging high-performance thermoset. The designing of novel monomers and high-molecular-weight precursors of benzoxazines are a promising approach for obtaining polybenzoxazines for specific applications, taking advantage of the wide selection of mono- and diamines and mono- and bisphenols. Polymer alloys and organic-inorganic hybrids are also promising approaches for the design of benzoxazine-based materials with required performance.

References

- Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw Hill Book Company: New York, 1972.
- Sultan, J. N. *Handbook of Composites*; Van Nostrand-Reinhold: New York, 1982.
- Shechte, L.; Wynstra, J. *Ind. Eng. Chem.* **1956**.
- Ward, R. J.; Bobalek, E. J. *Some Correlation between Thermal, Electrical, and Mechanical Properties of Alkyl-Epoxy Copolymer Adhesives*. ACS Symposium: Atlantic City, NJ, September, 1962.
- Bucknall, C. B.; Gilbert, A. H. *Polymer* **1989**, *30*, 213.
- Hedrick, J. H.; Yilgor, I.; Wilkens, G. L.; McGrath, J. E. *Polym. Bull.* **1985**, *13*, 201.
- Hedrick, J. H.; Yilgor, I.; Jerek, M.; *et al.* *Polymer* **1991**, *32*, 2020.
- Hourston, D. J.; Lane, J. M. *Polymer* **1992**, *33*, 1379.
- Murakami, A.; Saunder, D.; Oishi, K.; *et al.* *Nippon Setchaku Gakkaishi* **1991**, *27*, 364.
- Pak, S. J.; Lyle, G. D.; Mercier, R.; McGrath, J. E. *Polymer* **1993**, *34*, 885.
- Barklay, G. G.; McNamee, S. G.; Ober, C. K.; *et al.* *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1845.
- Ochi, M.; Shimizu, Y.; Nakanishi, Y.; Murata, Y. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 397.
- Ortiz, C.; Kim, R.; Rodighiero, E.; *et al.* *Macromolecules* **1998**, *31*, 4074.
- Shiraishi, T.; Motobe, H.; Ochi, M.; *et al.* *Polymer* **1992**, *33*, 2975.
- Akatsuka, M.; Takezawa, Y. *J. Appl. Polym. Sci.* **2003**, *89*, 2463.
- Harada, M.; Ochi, M.; Tobita, M.; *et al.* *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1739.

17. Jana, S. K.; Okamoto, T.; Kugita, T.; Namba, S. *Appl. Catal. A: General* **2005**, *288*, 80.
18. Pethrick, R. A.; Thomson, B. *Br. Polym. J.* **1986**, *18*(6), 380.
19. Yamagishi, T.-A.; Nomoto, M.; Ito, S.; et al. *Polym. Bull.* **1994**, *32*, 501.
20. Yamagishi, T.-A.; Nomoto, M.; Yamashita, S.; et al. *Macromol. Chem. Phys.* **1998**, *199*, 423.
21. Konishi, G.; Yamagishi, T.; Nakamoto, Y. *Secchaku* (in Japanese) **2004**, *48*, 74.
22. Huang, J.; Xu, M.; Ge, Q.; et al. *J. Appl. Polym. Sci.* **2005**, *97*, 652–658.
23. Yamagishi, T.-A.; Enoki, M.; Inui, M.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 675.
24. Asami, M.; Kobayashi, Y. US Patent 6,326,453, 2001.
25. Inatomi, S.; Tanoue, N.; Yokoyama, M.; et al. US Patent 0,241,276, 2006.
26. Inatomi, S.; Tanoue, N. US Patent 7,241,833, 2007.
27. Hatfield, R.; Maciel, G. E. *Macromolecules* **1987**, *20*, 608.
28. Dargaville, T. R.; Guerzoni, F. N.; Looney, M. G.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1399.
29. de Bruyn, P. J.; Foo, L. M.; Lim, A. S. C.; et al. *Tetrahedron* **1997**, *53*(40), 13915.
30. Looney, M. G.; Solomon, D. H. *Aust. J. Chem.* **1995**, *48*, 323.
31. Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, *39*(2), 399.
32. Zhang, X.; Looney, M. G.; Solomon, D. H.; Whittaker, A. K. *Polymer* **1997**, *38*(23), 5835.
33. Sergeev, V. A.; et al. *Poly. Sci. Ser. B* **1995**, *37*(5/6), 273.
34. Cuthbertson, B. M.; Tilsa, O.; Devinney, M. L.; Tufts, T. A. *SAMPE* **1989**, *34*, 2483.
35. Komiyama, M. *J. Chem. Soc. Perkin Trans.* **1989**, *1*, 2031.
36. Komiyama, M. *Prog. Polym. Sci.* **1993**, *18*, 871.
37. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; et al. *Polymer* **1994**, *35*(14), 3046.
38. Grenier-Loustalot, M.-F.; Larroque, S.; Grande, D.; et al. *Polymer* **1996**, *37*(8), 1363.
39. Eapen, K. C. *Makromol. Chem.* **1968**, *119*, 4.
40. Fang, T.; Shimp, D. *Prog. Polym. Sci.* **1995**, *20*, 61.
41. Shimp, D. *Polym. Mat. Sci. Eng.* **1994**, *70*, 561.
42. Srinivasan, S. A.; McGrath, J. E. *High Perform. Polym.* **1993**, *5*, 259.
43. Woo, E. M.; Shimp, D. A.; Seferis, J. C. *Polymer* **1994**, *35*, 1658.
44. Iijima, T.; Maeda, T.; Tomoji, M. *J. Appl. Polym. Sci.* **1999**, *74*, 2931.
45. Ning, X.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1121.
46. Dunkers, J. P.; Zarate, A.; Ishida, H. *J. Phys. Chem.* **1996**, *100*, 13514.
47. Ishida, H.; Allen, D. J. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1019.
48. Shen, S. B.; Ishida, H.; Allen, D. J. *Polym. Comp.* **1996**, *17*(6), 710.
49. Ghosh, N. N.; Kiskan, B.; Yagci, Y. *Prog. Polym. Sci.* **2007**, *1344*.
50. Nair, C. P. R. *Prog. Polym. Sci.* **2004**, *29*, 401.
51. Takeichi, T.; Saito, Y.; Agag, T.; et al. *Polymer* **2008**, *49*, 1173.
52. Ishida, H.; Agag, T. *Handbook of Benzoxazine Resins*; Elsevier: Amsterdam, The Netherlands, 2011.
53. Brunovska, Z.; Liu, J. P.; Ishida, H. *Macromol. Chem. Phys.* **1999**, *200*(7), 1745–1752.
54. Andreu, R.; Espinosa, M. A.; Galià, M.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*(4), 1529–1540.
55. Ishida, H.; Allen, D. J. *Polymer* **1996**, *37*, 4487.
56. Sudo, A.; Kudoh, R.; Hayakawa, H.; et al. *Macromolecules* **2008**, *41*, 9030.
57. Wang, C. F.; Su, Y. C.; Kuo, S. W.; et al. *Angew. Chem., Int. Ed.* **2006**, *45*, 2248.
58. Shen, S. B.; Ishida, H. *J. Appl. Polym. Sci.* **1996**, *61*, 1595.
59. Allen, D. J.; Ishida, H. *J. Appl. Polym. Sci.* **2006**, *101*, 2798.
60. Liu, Y.-L.; Hsu, C.-W.; Chou, C.-I. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1007.
61. Low, H. Y.; Ishida, H. *Polymer* **1999**, *40*, 4365.
62. Agag, T.; Takeichi, T. *Macromolecules* **2003**, *36*, 6010.
63. Takeichi, T.; Nakamura, K.; Agag, T. *Des. Monom. Polym.* **2004**, *7*, 727.
64. Agag, T.; Takeichi, T. *High Perform. Polym.* **2001**, *13*, S327.
65. Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999**, *40*, 1815.
66. Brunovska, Z.; Ishida, H. *J. Appl. Polym. Sci.* **1999**, *73*, 2937.
67. Agag, T.; Takeichi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1424.
68. Velez-Herrera, P.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5871.
69. Kawauchi, T.; Murai, Y.; Hashimoto, K.; et al. *Polymer* **2011**, *52*, 2150.
70. Ishida, H. US Patent 5, 543,516, 1996.
71. Takeichi, T.; Kano, T.; Agag, T. *Polymer* **2005**, *46*, 12172.
72. Takeichi, T.; Kano, T.; Agag, T.; et al. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 5945.
73. Agag, T.; Takeichi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1878.
74. Chernykh, A.; Liu, J. P.; Ishida, H. *Polymer* **2006**, *47*, 7664–7669.
75. Gong, W.; Zeng, K.; Wang, L.; Zheng, S. X. *Polymer* **2008**, *49*, 3318–3326.
76. Li, Y.; Zheng, S. X. *J. Polym. Sci., Part B: Polym. Phys.* **2010**, *48*, 1148–1159.
77. Wang, L.; Gong, W.; Zheng, S. X. *Polym. Int.* **2009**, *58*, 124–132.
78. Kiskan, B.; Yagci, Y.; Ishida, H. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 414.
79. Chou, C. I.; Liu, Y. L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6509–6517.
80. Chernykh, A.; Agag, T.; Ishida, H. *Polymer* **2009**, *50*, 382–390.
81. Kiskan, B.; Aydogan, B.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 804–811.
82. Ergin, M.; Kiskan, B.; Gacal, B.; Yagci, Y. *Macromolecules* **2007**, *40*, 4724.
83. Kimura, H.; Matsumoto, A.; Sugito, H.; et al. *J. Appl. Polym. Sci.* **2001**, *79*, 555–565.
84. Kiskan, B.; Colak, D.; Muftuoglu, A. E.; et al. *Macromol. Rapid Commun.* **2005**, *26*, 819–824.
85. Kiskan, B.; Demiray, G.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3512–3518.
86. Kukut, M.; Kiskan, B.; Yagci, Y. *Des. Monomers Polym.* **2009**, *12*, 167–176.
87. Liu, Y. L.; Lin, G. C.; Wu, C. S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 949–954.
88. Wang, J.; St. John Manley, R.; Feldman, D. *Prog. Polym. Sci.* **1992**, *17*, 611.
89. Peng, W.; Riedl, B.; Barry, A. O. *J. Appl. Polym. Sci.* **1993**, *48*, 1757.
90. Pizzi, A. *Advanced Wood Adhesives Technology*; Dekker: New York, 1994; Chapter 5.
91. Gedam, P. H.; Sampathkumaran, P. S. *Prog. Org. Coat.* **1986**, *14*, 115.
92. Funaoka, M.; Matsubara, M.; Seki, N.; Fukatsu, S. *Biotechnol. Bioeng.* **1995**, *46*, 545.
93. Funaoka, M. *Polym. Int.* **1998**, *47*, 277.
94. Mikame, K.; Funaoka, M. *Polym. J.* **2006**, *38*, 694.
95. Funaoka, M. *Macromol. Symp.* **2003**, *201*, 213.
96. Folkers, J. L.; Friedrich, R. S. *Proceedings International Composites Expo'97*, January 27–29, Nashville, TN, 22A, 1997.
97. Pilato, L. A.; Michno, M. J. *Advanced Composite Materials*; Springer: Berlin, Heidelberg, New York, 1994.
98. McGrail, P. T.; Street, A. C. *Makromol. Chem. Macromol. Symp.* **1992**, *64*, 75.
99. Kimura, H.; Matsumoto, A.; Hasegawa, K.; et al. *J. Appl. Polym. Sci.* **1998**, *68*, 1903.
100. Rimdusit, S.; Ishida, H. *Polymer* **2000**, *41*, 7941.
101. Jang, J.; Seo, D. J. *J. Appl. Polym. Sci.* **1998**, *67*, 1.
102. Agag, T.; Takeichi, T. *Macromolecules* **2001**, *34*, 7257.
103. Takeichi, T.; Guo, Y.; Agag, T. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4165.
104. Takeichi, T.; Guo, Y. *Polym. J.* **2001**, *33*, 437.
105. Takeichi, T.; Kusakabe, Y. *J. Network Polym. Jpn.* **2002**, *23*, 195.
106. Usuki, A.; Kawasumi, M.; Kojima, Y.; et al. *J. Mater. Res.* **1993**, *8*, 1174.
107. Yano, K.; Usuki, A.; Okada, A.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2493.
108. Agag, T.; Takeichi, T. *Polymer* **2000**, *41*, 7083.
109. Takeichi, T.; Zeidam, R.; Agag, T. *Polymer* **2002**, *43*, 45.
110. Agag, T.; Takeichi, T.; Toda, H.; Kobayashi, T. *Int. J. Mater. Prod. Technol.* **2001**, *2*, 706.
111. Agag, T.; Takeichi, T. *High Perform. Polym.* **2002**, *14*, 115.
112. Takeichi, T.; Guo, Y. *J. Appl. Polym. Sci.* **2003**, *90*, 4075.
113. Agag, T.; Taepaisitphongse, V.; Takeichi, T. *Polym. Compos.* **2007**, *28*, 680.
114. Agag, T.; Takeichi, T. *Mater. Sci. Forum.* **2004**, *449–452*, 1157.
115. Agag, T.; Tsuchiya, H.; Takeichi, T. *Polymer* **2004**, *45*, 7903.
116. Ardyananta, H.; Wahid, M. H.; Sasaki, M.; Agag, T.; Kawauchi, T.; Ismail, H.; Takeichi, T. *Polymer* **2008**, *49*, 4585–4591.
117. Ardyananta, H.; Wahid, M. H.; Kawauchi, T.; Takeichi, T. *Polym. Prepr. Jpn.* **2007**, *56*, 4932.
118. Barklay, G. G.; Ober, C. K.; Papathomas, K. I.; Wang, D. W. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1831.
119. Kim, H. J.; Brunovska, Z.; Ishida, H. *Polymer* **1999**, *40*, 6565.
120. Kim, H. J.; Brunovska, Z.; Ishida, H. *J. Appl. Polym. Sci.* **1999**, *73*, 857.
121. Ning, X.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 921.
122. Takeichi, T.; Agag, T.; Zeidam, R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2633.
123. Takeichi, T.; Guo, Y.; Rimdusit, S. *Polymer* **2005**, *46*, 4909.
124. Takeichi, T.; Kawauchi, T.; Agag, T. *Polym. J.* **2008**, *40*, 1121.
125. Takeichi, T.; Kano, T.; Agag, T.; et al. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 5945.
126. Zhang, X.; Solomon, D. H. *Polymer* **1998**, *39*(2), 405.

Biographical Sketches



Tsutomu Takeichi received his PhD degree in 1979 from The University of Tokyo under the direction of Professor Teiji Tsuruta. He joined Toyohashi University of Technology and was promoted to Professor in 2002. Meanwhile, he spent 2 years from 1984 to 1986 at Colorado State University in the USA as a postdoctoral fellow with Professor J. K. Stille, where he started research on polyimide. His current research interests include designing of novel high-performance polymers based on polyimide and polybenzoxazine.



Nobuyuki Furukawa received his Master degree from Kyoto University in 1982 and joined Nippon Steel Chemical Co., Ltd., Japan. He received his PhD degree from Kyoto Institute of Technology in 1999 under the supervision of Professor Yoshiharu Kimura. In 2005, he moved to Sasebo National College of Technology as a Professor. His current research interests include development of functional network polymers, polymer alloys, molecular composites, and composite materials especially for the application in the microelectronic applications.