

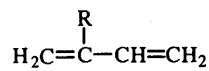
Chapter 9. Network Polymers : Elastomers & Thermosets

Network -- formed by covalent (or physical) links that connect individual molecules

9.1 Elastomers

. Diene elastomers

"Diene" -- monomers containing two sequential double bonds



where R : H (polybutadiene)

CH₃ (polyisoprene)

Cl (polychloroprene)

diene copolymers : SBR (copolymer of styrene-butadiene),

nitrile rubber (copolymer of butadiene & acrylonitrile)

TABLE 9.1 U.S. PRODUCTION OF SYNTHETIC RUBBER IN 1993

Synthetic Rubber	Billions of lb	% Total Rubber Production
SBR rubber	1.89	37.8
Polybutadiene	1.03	20.6
EP rubber	0.58	11.6
Nitrile rubber	0.14	2.8
Other (neoprene, butyl rubber, polyisoprene)	1.37	27.4
TOTAL	5.00	

Source: *Chemical and Engineering News*, April 11, 1994.

. Nondiene elastomers -- no unsaturated sites

(polyisobutylene, polysiloxane(silicone rubber), PUR, fluoroelastomers)

따라서 crosslinking 시에 trifunctional monomers를 도입, or free radical initiators를 사용, 적은 양의 diene monomer와 copolymerization

. Thermoplastic elastomers -- contain rigid("glassy") and soft("rubbery") segments

(SBS terpolymer: PS-block-PBD-block-PS)

공중합 후 cooling하면 soft and rigid segments 상이 상분리

==> rigid domain에 soft chain이 연결된 꼴

9.1.1 Diene elastomers

(See Fig. 9.1)

중합방법, 온도조절, 촉매 등의 선택에 따라 vinyl, cis, trans structure의 content가 조절됨

* Butadiene-based elastomers

SBR (styrene-butadiene) copolymers -- largest volume synthetic rubber

: BD에 St를 10-25% 첨가한 random copolymer

cf.) BD -- good resilience, abrasion resistance, low heat buildup

St -- low price, good wearing, strength and abrasion resistance

==> tire applications

NBR (nitrile rubber) -- BD에 15-40% acrylonitrile 첨가

oil & aromatic solvent resistance

==> gaskets, tubing, O-ring, gasoline hose

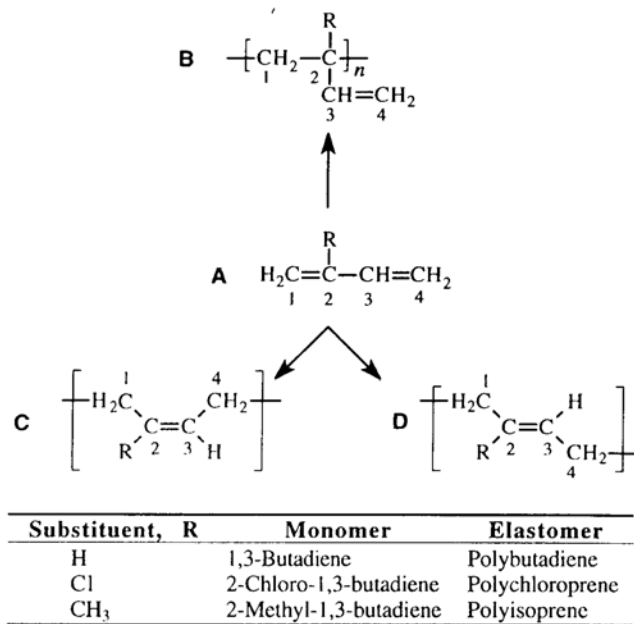


Figure 9.1. Polymerization of diene monomer (A) to yield a 1,2- (B), *cis*-1,4- (C), and *trans*-1,4-structures (D). Different elastomers are obtained depending upon the substituent group, R.

* Polyisoprene

NR (natural rubber) : *cis*-1,4-polyisoprene

rubber tree 대략 200여종, 상업성 있는 것 : *Hevea brasiliensis* (*Hevea* rubber)

현재 Malaysia, Indonesia, 태국 3국이 전세계 생산량의 80% 생산

latex (35% rubber & 5% solids) ==> dry rubber contents로 농축,

centrifugation, evaporation, coagulation & drying

vulcanization --- loose (<5%) ==> typical elastomers

hard (30-40%) ==> ebonite(pipe, valve, 만년필 축)

(See Fig. 9.3)

Synthetic *cis*-1,4-polyisoprene (IR)

-- high resilience, strength, abrasion resistance

poor resistance to attack by ozone, organic solvents

cf.) gutta percha (*trans*-1,4-polyisoprene)

: nonelastomeric materials (해저 cable 피복용, 치과용 보철재 등, ...)

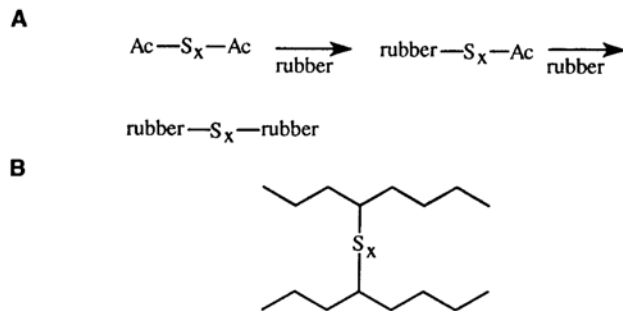


Figure 9.3. **A.** Illustration of steps in a vulcanization process where monomeric polysulfides formed by reaction of elemental sulfur with an accelerator reacts with individual polymer chains to form a polysulfide bridge. **B.** Illustration of a polysulfide bridge forming a crosslink between two chains.

9.1.2 Nondiene elastomers

: butyl rubber, silicone rubber, fluoroelastomer, PUR, EPDM

Butyl rubber & EPDM rubber -- 약간의 diene monomer 첨가, vulcanization site 제공

Others -- network 형성시키기 위해 initiator or polyfunctional monomer 사용

9.1.3 Thermoplastic elastomers

: elastomers without permanent crosslinks created through vulcanization

. absence of a separate vulcanization step

. easy recycling (possible fabrication by molding techniques)

ex) SBS elastomers -- ABA block copolymers

high MW PS & low MW PBD

cooling the melt below T_g --> PS-blocks phase separate to form rigid glassy

domains --> physical crosslinks

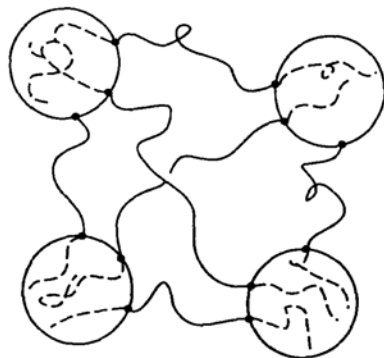


Figure 9.7. Representation of glassy domains in a thermoplastic elastomer such as SBS, polystyrene-*block*-polybutadiene-*block*-polystyrene. Circles represent physically separated domains of high glassy-polymer (e.g., polystyrene) content that serve as physical crosslinks. Glassy domains are interconnected by the elastomeric (e.g., polybutadiene) segments. (Adapted from L. H. Sperling, *Introduction to Physical Polymer Science*. Copyright ©1986. Reprinted by permission of John Wiley & Sons, Inc.)

Urethane elastomers -- coatings, adhesives, sealants

: "soft" or flexible (low T_g) blocks of a long-chain polyester

and "hard" blocks formed by reacting isocyanates and short-chain diols

good abrasion resistance, stable to attack by hydrocarbons & O_2 , susceptible to strong acids

9.2 Thermosets

TABLE 9.4 U.S. THERMOSET PRODUCTION
(billions of pounds)

	1993	1992
Thermosetting Resins		
Phenol resins	3.08	2.92
Urea resins	1.74	1.55
Polyesters (unsaturated)	1.26	1.18
Epoxies	0.51	0.46
Melamine resins	0.27	0.23
TOTAL	6.87	6.34

Source: *Chemical and Engineering News*, April 11, 1994.

9.2.1 Epoxies

bisphenol A & epichlorohydrin \rightarrow prepolymer

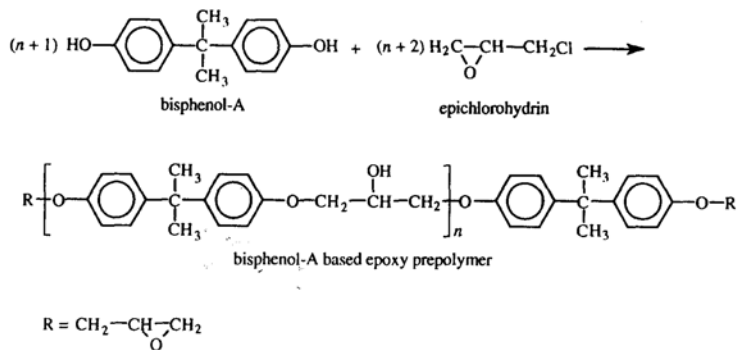


Figure 9.8. Formation of an epoxy prepolymer by reaction of bisphenol-A and epichlorohydrin.

curing with aromatic amines

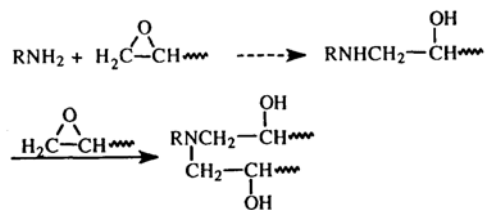


Figure 9.9. Cure of an epoxy resin by reaction of the prepolymer with an amine.

Uses : coatings, laminates, adhesives and composites

Properties : high chemical and corrosion resistance, adhesion properties,
low shrinkage, electrical properties

9.2.2 Unsaturated polyesters

used in construction and marine applications,

FRP (fiber reinforced plastics) resin

. Polyesters

saturated polyester resin

difunctional groups of alcohol & acid

--> linear polyester (thermoplastics)

ex. PET (ethylene glycol + terephthalic acid)

polyfunctional groups of alcohol & acid

--> glyptal resin (network) : used as adhesives or coatings

(See Fig. 9.11) <-- polyol + diacid

unsaturated polyester resin : copolymerization of both

saturated acid (phthalic anhydride) & unsaturated acid (maleic anhydride)

with diol (ex, propylene glycol, diethylene glycol)

==> low MW prepolymer (soluble in styrene: curing agent)

(peroxide를 촉매로 반응 개시하여 중합)

==> unsaturated polyester resin

(See Fig. 9.12)

saturated acid --> crosslink density ↓ & resin brittleness ↓

fumaric acid in place of maleic acid --> impact resistance ↑

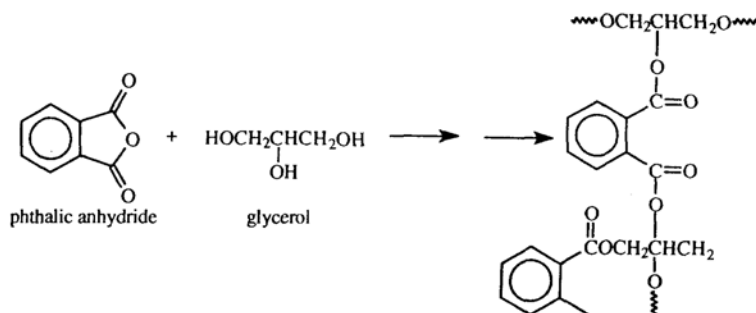


Figure 9.11. Formation of glyptal resin by the reaction of phthalic anhydride and glycerol.

9.2.3 Formaldehyde resins

Formalin 수지 :

Phenolic resins (phenoplasts) & Amino resins (aminoplasts)

used as unmodified compounds or compounded with additives such as wood flour
or glass fibers

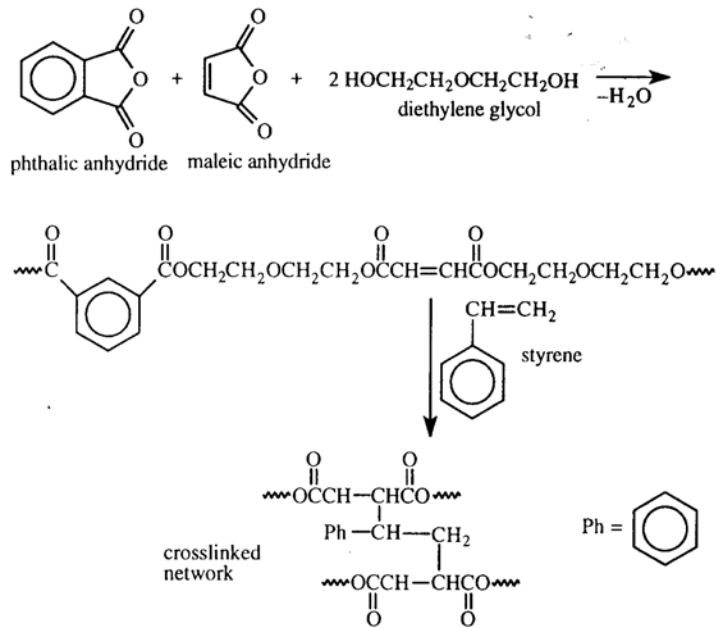


Figure 9.12. Formation of an unsaturated polyester resin.

* Phenolic resins (PF)

by condensation polymerization of phenol (or resorcinol) & formaldehyde used in plywood manufacture(41%), insulation(14%), lacquers, varnishes, molding compounds, and laminates

by a base-catalyzed reaction ==> resole

reaction of phenol with excess formaldehyde under basic conditions --> mono-, di-, and trimethylphenols (ortho & para 위치에 결합)

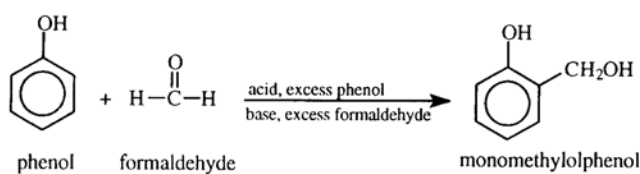


Figure 9.13. Example of the reaction of phenol and formaldehyde to yield a monomethylphenol. Formation of dimethylphenols and trimethylphenols also is possible. Either acidic or basic conditions can be used.

가열에 의해 축합반응 ==> low MW prepolymer called "resole"

(See Fig. 9.14)

더 높은 온도에서 가열하여 축합 경화 ==> high MW network called "resite"

by an acid-catalyzed reaction ==> novolac

reaction of formaldehyde with excess phenol under acidic conditions

--> mono-, di-, and trimethylphenols (ortho & para 위치에 결합)

반응 진행(산성조건) ==> low MW fusible, insoluble prepolymer called "novolac"

(See Fig. 9.15)

Novolac은 hydroxymethyl groups이 없어 자발적으로 경화는 일어나지 않음.
 경화제로 formaldehyde, paraformaldehyde, hexamethylenetetramine 등을 사용,
 경화반응시켜 high MW network "resite"를 얻음.

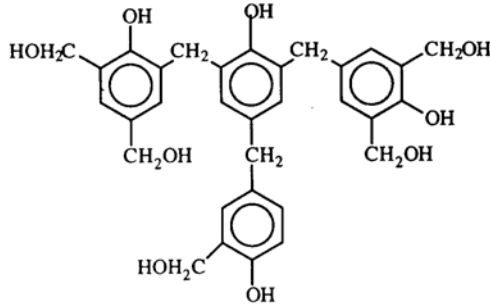


Figure 9.14. Representative structure of a resole.

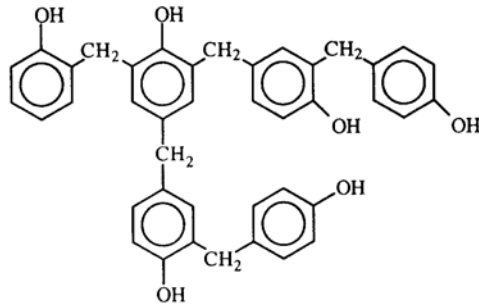


Figure 9.15. Representative structure of a novolac.

* Amino resins

by condensation polymerization of either urea with formaldehyde (UF)
 or melamine with formaldehyde (MF)

- UF

used in molding, laminating, adhesive applications(for interior-grade plywood),
 electrical switches & plugs, and insulating foam

nucleophilic addition of urea to formaldehyde -->

methylol derivatives (monomethylol urea + dimethylol urea)

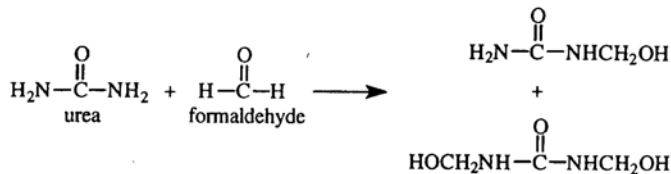


Figure 9.16. Reaction of urea and formaldehyde to yield methylol derivatives as the first step in the production of urea-formaldehyde resins.

축합반응을 더 진행 ==> high MW UF resin (두 가지 형태의 구조로 추정)

(See Fig. 9.17) -- B 형태는 formaldehyde 추가해 경화함

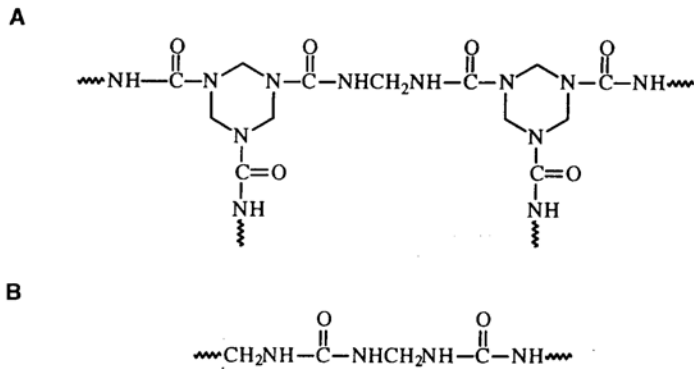


Figure 9.17. Proposed structures of a fully cured UF resin formed by the condensation of methylol derivatives. **A.** Network model. **B.** Oligomeric UF condensates in the colloidal dispersion mode.

- MF

harder and more chemical, temperature, and moisture resistant than UF, expensive used in decorative plastic dinnerware, laminated worktops, and electrical fittings

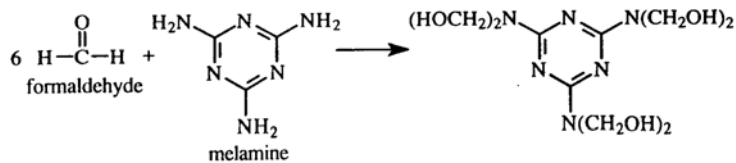


Figure 9.18. Condensation of melamine and formaldehyde to yield the dimethylol derivative of melamine.

Majority of amino groups of melamine form dimethylol derivatives rather than monomethylol derivatives.

최종단계에서는 methylol group과 amino group이 축합, methylene bridge를 형성하여 rigid network structure 속에 prepolymer chain을 연결시킨다.

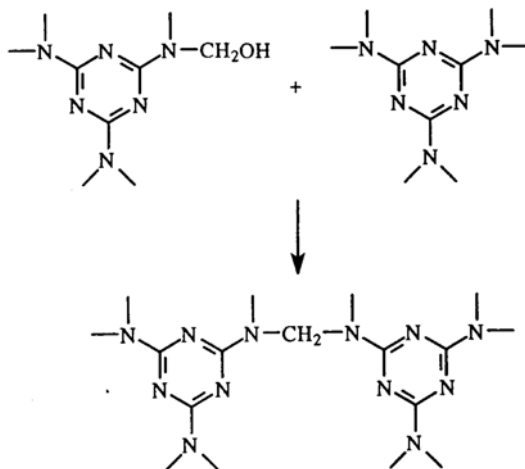


Figure 9.19. Formation of MF-resin network.