

Polymer Modification

Introduction

**Polymer Performance
is determined by;**

- Composition
- Structure
- Molecular Architecture

These control the physical, chemical and other characteristics of polymer material.

Polymer modification can be accomplished by;

- Copolymerization of more than one monomer
- Control of molecular architecture
- Postpolymerization polymer reactions- **functional/reactive groups introduced into the polymer main chain or side groups**

Copolymerization

- Macromolecular design and architecture through copolymerization of monomers had led to number of commercially important polymers.
- Copolymer composition can be varied over wide limits, resulting in a wide range of property/process performance.

A copolymer may be contain;

- a) Comparable amounts of the constituents monomers – copolymer properties will be different from parent homopolymers.
- b) A small amount of one of the monomers-
 - ✓ gross physical properties of the copolymer will be similar to the homopolymer of the major constituent
 - ✓ Minor constituent confers specific chemical properties on the copolymer.

Styrene-Butadiene Copolymers (SBC)

Polystyrene

- Chemically inert
- Good resistance to alkalis, halide acids, oxidizing and reducing agents.
- Very easy to process
- Quite brittle
- Low deflection T (82 to 88 °C)

SBC provide illustration of the considerable latitude in the variation of polymer properties by;

- careful manipulation of composition
- distribution of the components

Polybutadiene

- An elastomeric material with good elastic properties
- outstanding toughness and resilience
- Poor resistance to oils, solvents, oxidation and abrasion

Styrene and butadiene can be copolymerized to produce either **random, graft, or block copolymers**.

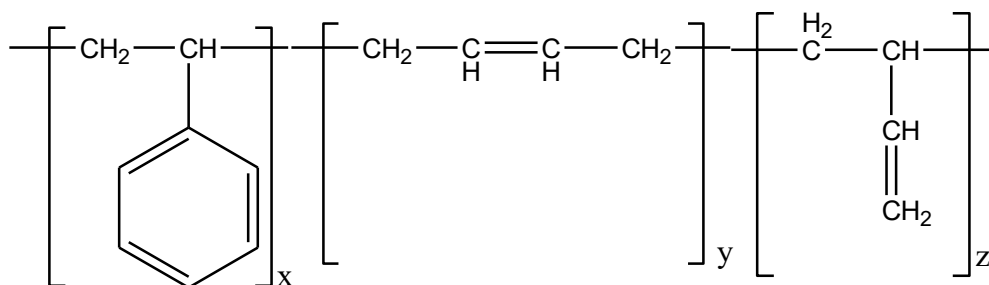
Random copolymer exhibits a homogeneous single phase and has properties intermediate to those of the parent homopolymer.

Block or graft copolymers form heterogeneous multiphase systems whose properties are not simply characteristic of each homopolymer, but are dictated by the multiphase character of the copolymer.

- ❖ Defects of polybutadiene homopolymer may be overcome by the incorporation of %25 styrene in the copolymer.
- ❖ Preferred material over natural rubber in such applications as belting, hose, molded goods, vulcanized sheets and flooring. Rubber shoe soles are made almost exclusively from SBR.
- ❖ Copolymers containing % 25 styrene are also useful adhesives (in the form of aqueous dispersion or in solution)
- ❖ If the ratio to butadiene is in the range of 60:40 and higher, the copolymer is nontacky and used in hot melt adhesives and latex paints.

Styrene-Butadiene Copolymers

Styrene-Butadiene Rubber (SBR) (Random Copolymer)



Structure of styrene-butadiene rubbers

- ❑ SBR is produced by free radical polymerization of styrene and butadiene
- ❑ The resulting polymer is random, irregular and not crystallizable.
- ❑ Butadiene can undergo 1,2 or 1,4 polymerization

Property Differences between Hot and Cold SBR

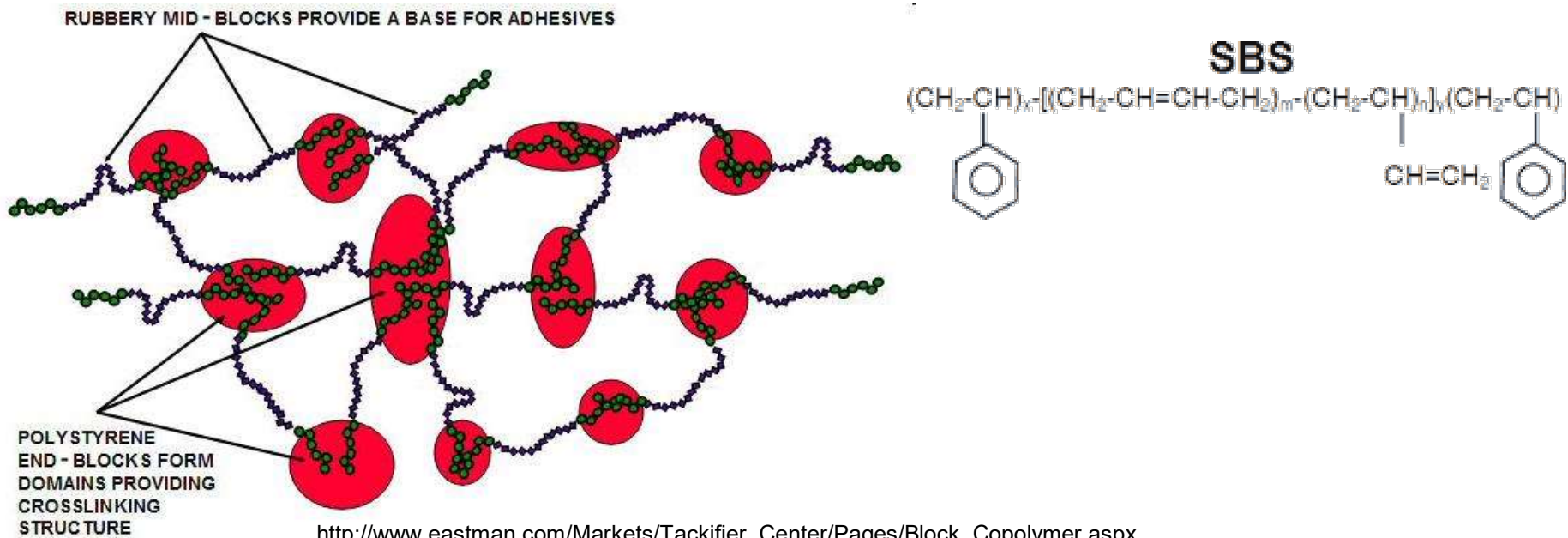
Property	Hot	Cold
Molecular weight		
Viscosity average, \overline{M}_v	150–400,000	280,000
Weight average, \overline{M}_w	250–450,000	500,000
Number average, \overline{M}_n	30–100,000	110–260,000
Microstructure (%)		
1,4 (<i>cis</i>)	15	18
1,4 (<i>trans</i>)	58	69
1,2 (vinyl)	27	23

- ❑ Commercial SBR is produced by either emulsion or solution copolymerization of butadiene and styrene.
- ❑ Emulsion copolymerization is either a cold (41°F) or hot (122°F) process.
- ❑ Solution copolymerization of SBR involves the use of an alkyl lithium catalyst.
- ❑ Solution SBR has higher MW, narrower MW distribution, and higher *cis* diene content than emulsion polymerization.

Styrene-Butadiene Copolymers

Styrene-Butadiene Block Copolymers

- Styrene-butadiene Block Copolymers belong to the family of thermoplastic elastomers (TPE).
- Products made from these polymers possess the mechanical properties of rubbers, and the processing characteristics of thermoplastics. This is related to their molecular structure.
- Like true thermoplastics, scrap from TPE can be recycled.
- Styrene-Butadiene block copolymers belongs to the A-B-A type TPE.
- The styrene-butadiene (SBS) consist of at least three blocks, namely two hard polystyrene end blocks and one soft, elastomeric (polybutadiene) midblock. It is essential that the hard and soft blocks are immiscible, so that, on a microscopic scale, the polystyrene blocks form separate domains in the rubber matrix, thereby providing physical cross links to the rubber.



Ethylene Copolymers

- ✓ Low density polyethylene (LDPE) is produced under high pressure.
- ✓ Application areas: Film and sheeting , injected molded products (such as wires and cables)
- ✓ Its physical properties are dictated by density, molecular weight and molecular weight distribution.

As density increases;

Barrier properties, hardness, abrasion, heat and chemical resistance strength, surface gloss increases

Decreasing density results in;

❖ **Enhanced Toughness, stress-crack resistance, clarity, flexibility, elongation**

❖ **Reduced creep and mold shrinkage**

Melt index (MI) is a measure of molecular weight, it decreases with increasing molecular weight.

Increasing MI improves clarity, surface gloss, and mold shrinkage.

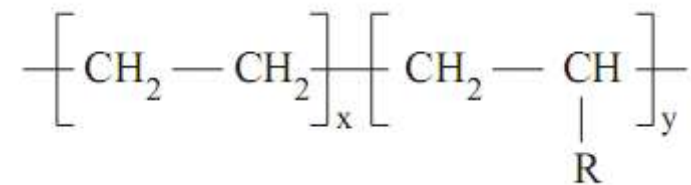
Decreasing MI leads to improved creep and heat resistance, toughness, melt strength, and stress-cracking.

Narrower molecular weight distribution gives better impact strength, but reduced resin processability.

A broader molecular weight distribution leads to shear viscosity at high shear rates and is thus easier to process.

Ethylene Copolymers

By copolymerizing ethylene with polar [α-olefins](#), it is possible to produce a variety of materials ranging from rubbery to low melting products. This class of copolymers can be represented by the general formula;



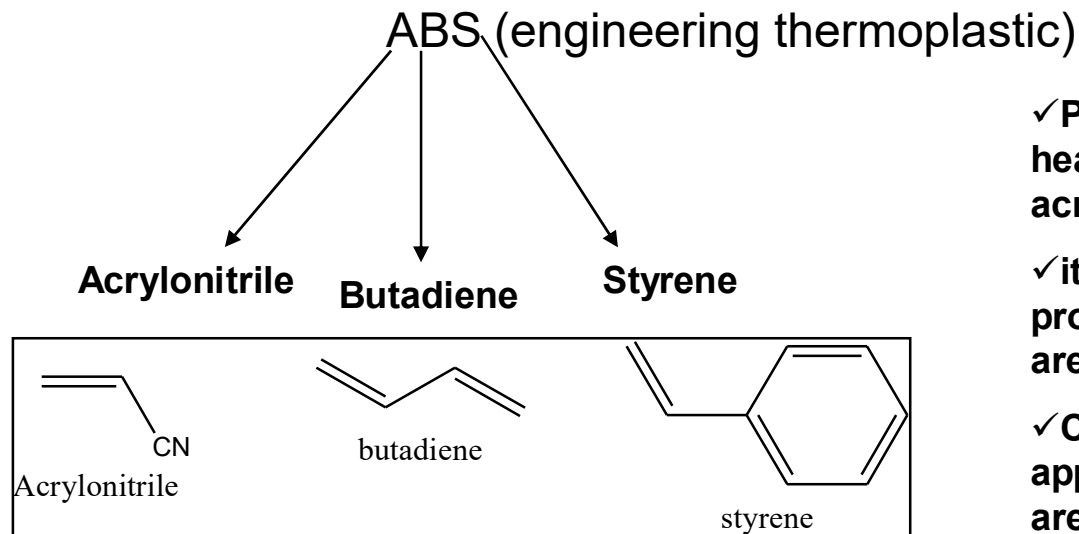
where R is a polar group The introduction of comonomers with a polar pendant group, R, produces a highly branched random copolymer but with increased interchain interaction.

These copolymers have enhanced flexibility, toughness, stress-cracking resistance, oil and grease resistance, clarity, and weatherability.

Some Ethylene Copolymers

R	Copolymer
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{Me} \end{array}$	Ethylene-methyl acrylate (EMA)
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{Et} \end{array}$	Ethylene-ethyl acrylate (EEA)
$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{C}-\text{Me} \end{array}$	Ethylene-vinyl acetate (EVAc)

Acrylonitrile-Butadiene-Styrene (ABS)



✓ Polymer chemical resistance and heat and aging stability depend on acrylonitrile

✓ its toughness, impact resistance, and property retention at low temperature are developed through butadiene.

✓ Copolymer rigidity, glossy surface appearance, and ease of processability are contributions from styrene

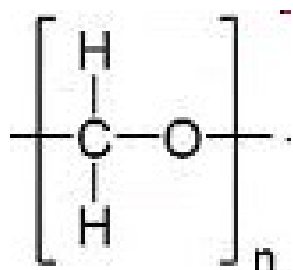
ABS resins consist essentially of two phases:

- (1) a rubbery phase dispersed in
- (2) a continuous glassy matrix of styrene–acrylonitrile copolymer (SAN) through a boundary layer of SAN graft.

The dispersed rubbery phase is rubber polymerized from butadiene.

Condensation Polymers

Acetal Copolymer



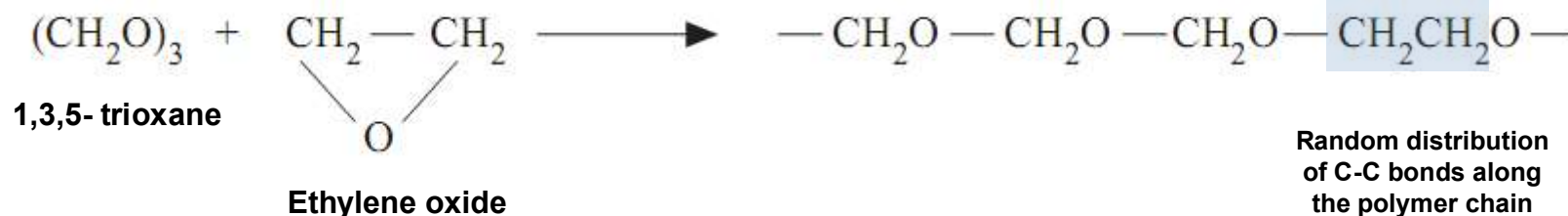
➤ Acetal homopolymer or polyoxymethylene is a formaldehyde polymer and has a good balance of physical, mechanical, chemical, and electrical properties.

➤ The polymer is thermally unstable as the polymer has hemiacetal hydroxy end groups.

➤ To stabilize the homopolymer we can use of appropriate additives or transform the unstable end groups into stable end groups by “end capping” through acetylation or methylation.

Polyoxymethylene (POM)

copolymerization of trioxane with small amounts of comonomer, usually cyclic ethers like ethylene oxide or 1,3-dioxolane.



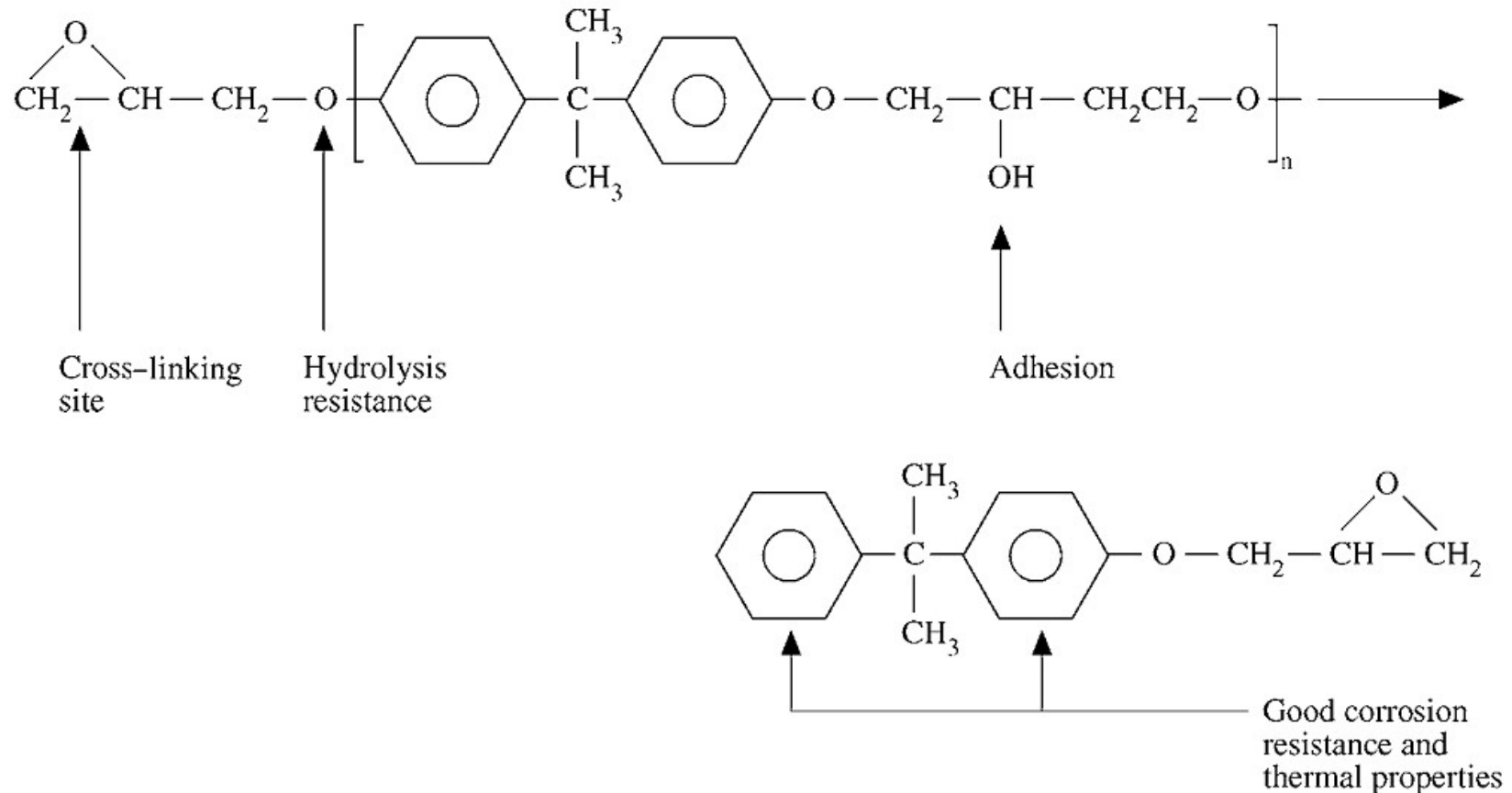
The depolymerization of ethylene oxide units is much more difficult than that of oxymethylene units.

Copolymerization confers thermal stability on the acetal copolymer.

Condensation Polymers

Epoxyes

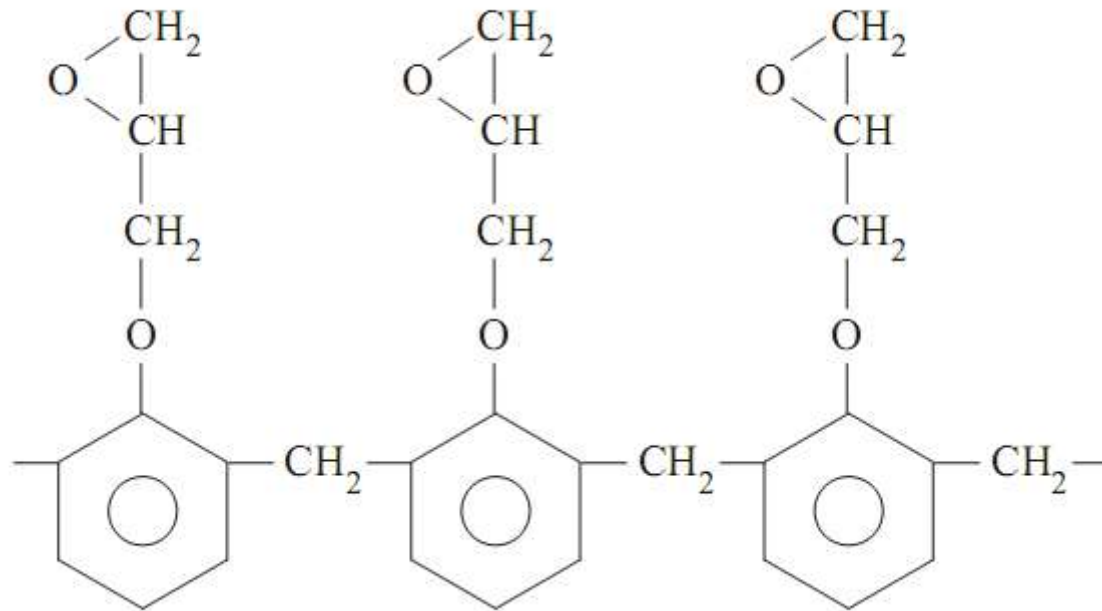
diglycidyl ether of bisphenol A (DGEBA)



- Epoxy resins, because of their versatility, are used in a variety of applications in protective coatings, adhesives, laminates, and reinforced plastics and in electrical and electronic devices.
- Epoxy resins exhibit lower heat resistance than phenolics due to the lower aromatic units in their structures.

Condensation Polymers

Epoxies

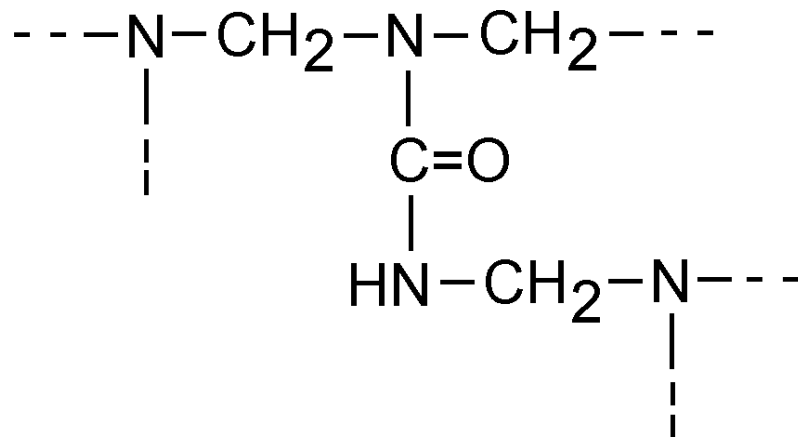


Structure of Novolak-modified epoxy resin

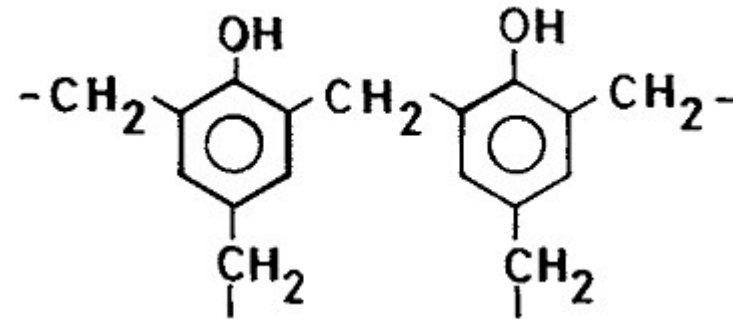
- The phenolic component confers thermal stability.
- The epoxide group provides sites for cross-linking.

Condensation Polymers

Urea-Formaldehyde (UF) resins



Phenol-formaldehyde (PF) Resin



- The wood adhesive is done with UF or PF adhesives.
- UF resins are cheaper and can be carried out under a wider variety of conditions.
- PF-bonded wood products can be employed in outdoor structural applications, whereas the poor stability of UF-bonded wood products limits their use to interior, non-structural applications. This is due to the strength losses of UF-bonded solid wood joints, irreversible swelling of UF-bonded composite panels and formaldehyde release.
- Two bond degradation processes viewed currently as responsible for the poor durability of UF are hydrolytic scission and stress rupture. (1) low and nonuniform distribution of cross-links in cured UF resins, and (2) the brittleness of the cured resin
- To minimize these defects, urea derivatives of flexible di- and trifunctional amines were incorporated into UF resin structure through copolymerization.

Postpolymerization Reactions

Postpolymerization reactions may occur on reactive sites dispersed in the polymer main chain.

- Chain extensions
 - Cross-linking
- Graft and Block copolymer formation

Reactions may occur on reactive sites dispersed in the polymer main chain.

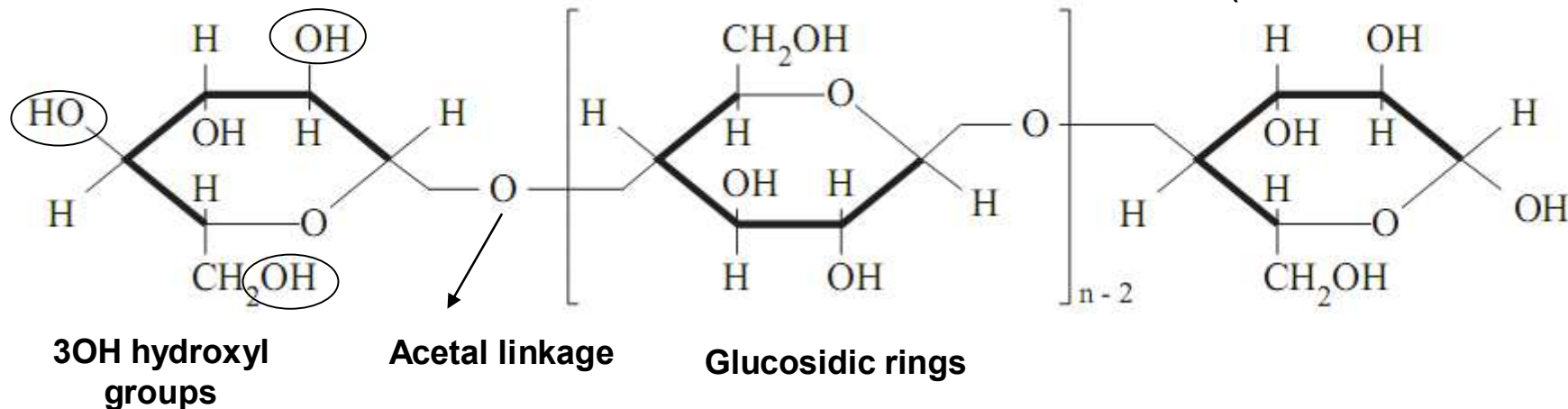
- Halogenation
 - Sulfonation
 - Hydrolysis
 - Epoxidation
- Surface reactions

In both cases these types of reactions transform existing polymers into those with new and/or improved properties.

Reaction of Polysaccharides

Cellulose Derivatives

Cellulose is a polysaccharide — a natural polymer.



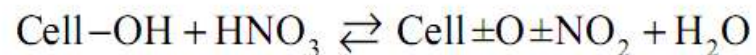
Stiff (due to cyclic nature of repeating unit)

Linear molecule (due to β - (1-4) linkage)

A highly crystalline polymer (strong hydrogen bonding)

Insoluble and infusible (it burns rather than melts)

Cellulose nitrate

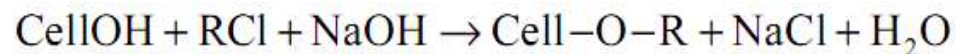


Fully nitrated product has a nitrogen content of 14.8%

Plastics and lacquer grade material contain 10-12% nitrogen

Explosives- nitrogen content greater than 12.5%

Cellulose ethers



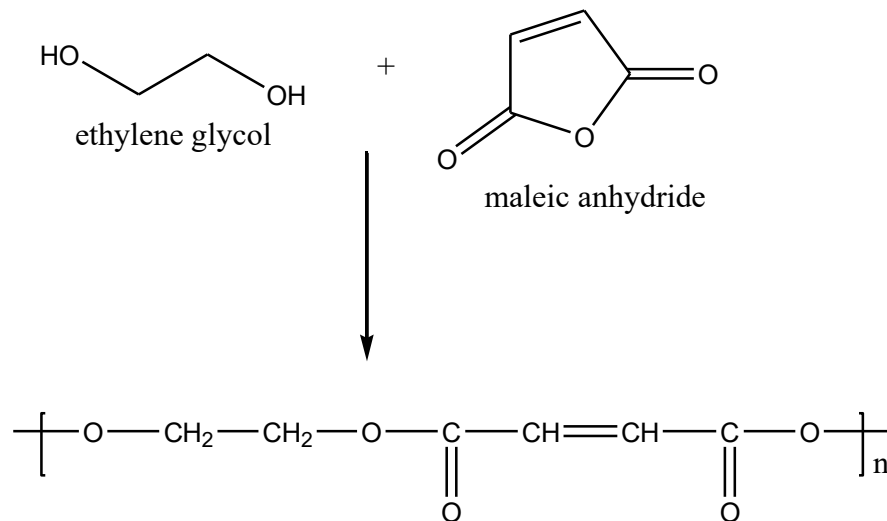
Ether content and the viscosity can be controlled by controlling the reaction conditions

Ethyl cellulose is the most important of the cellulose ethers. Commercial ethyl cellulose (about 2.4 to 2.5 ethoxy groups per glucose residue) is a molding material that is heat stable and has low flammability and high impact strength.

It is flexible and tough even at low T; it has a relatively high water absorption

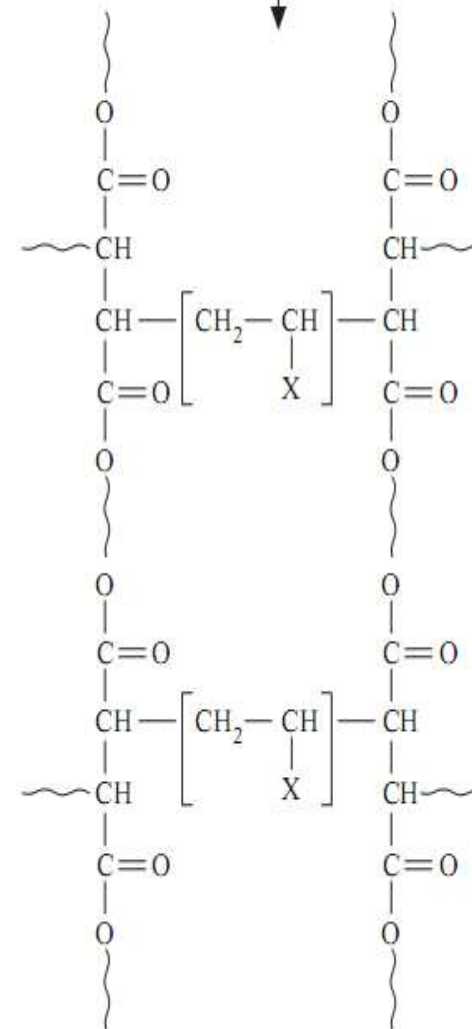
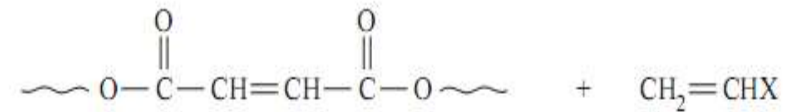
Crosslinking

Unsaturated Polyesters



unsaturated polyester

stable at room temperature



Reactive monomer

-styrene

-vinyl toluene

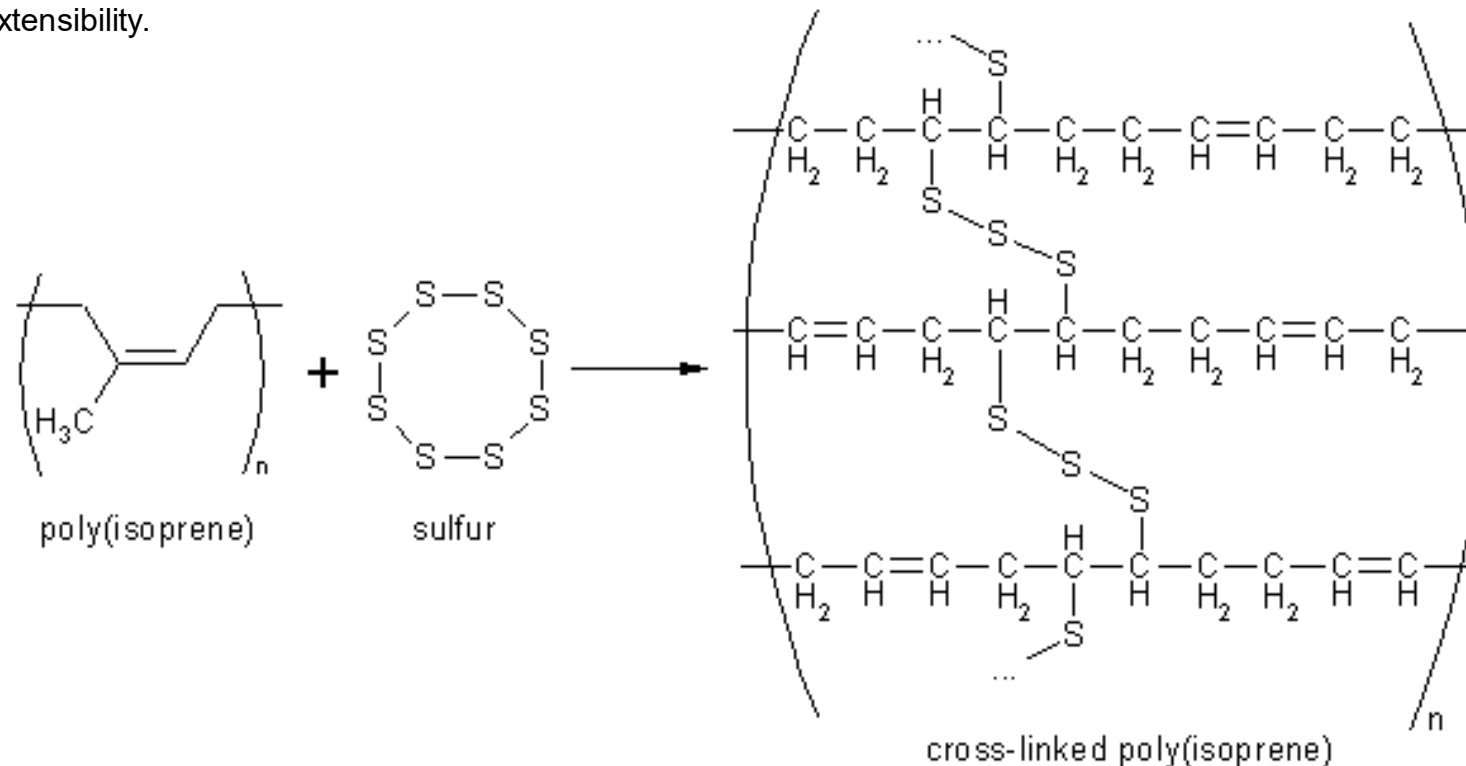
-Methyl methacrylate

-diallyl phthalate

Crosslinking reaction

Vulcanization

- The process by which such a network of cross-links is introduced into an elastomer is called vulcanization.
- It transforms an elastomer from a weak thermoplastic mass without useful properties into a strong, elastic, tough rubber.
- Vulcanization decreases the flow of an elastomer and increases its tensile strength and modulus, but preserves its extensibility.



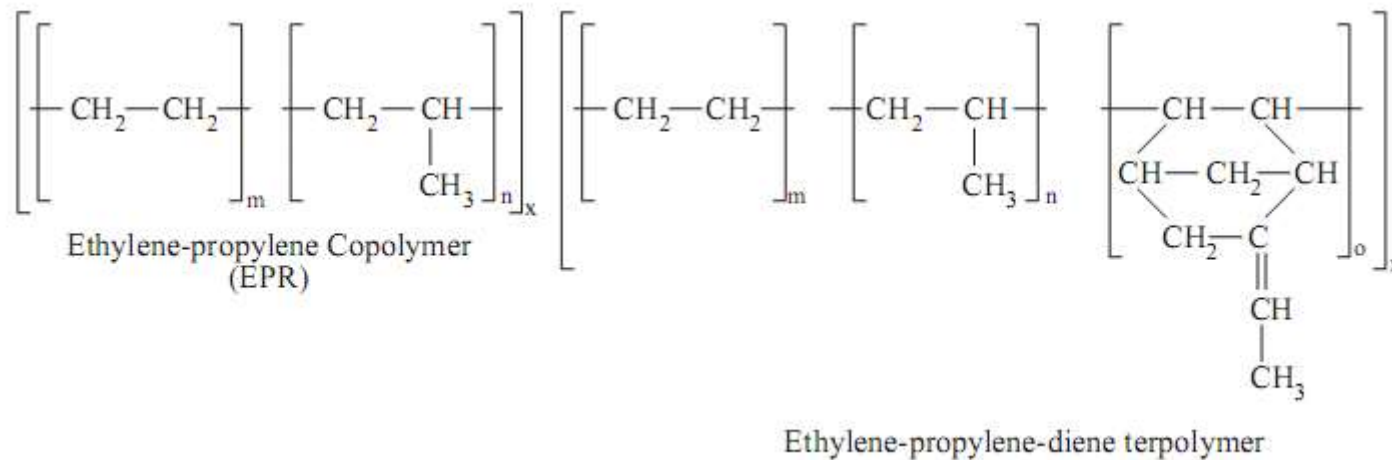
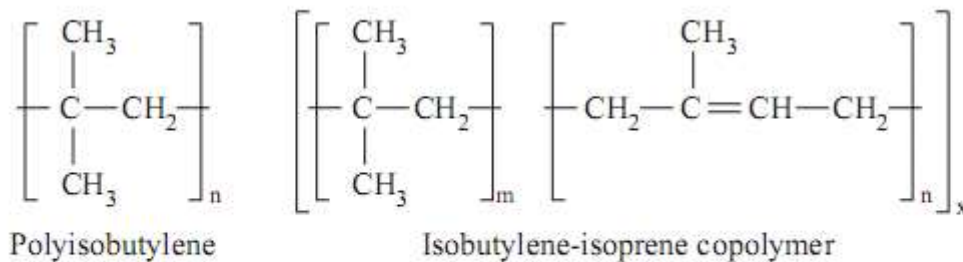
Accelerators: speed up the reaction and reduce the sulfur waste

Activators: metallic oxides such as zinc oxide

Rubbers

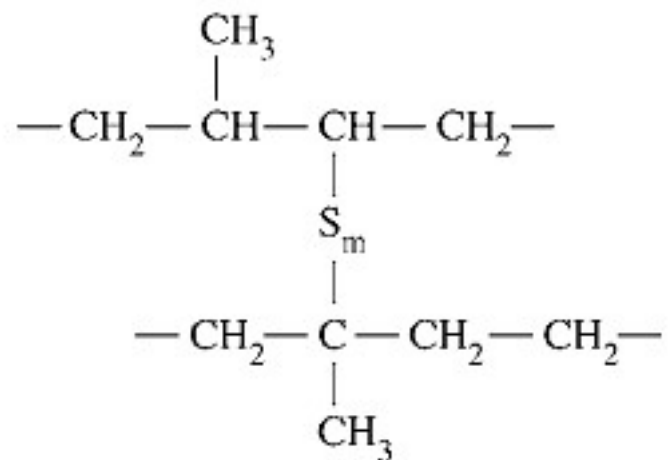
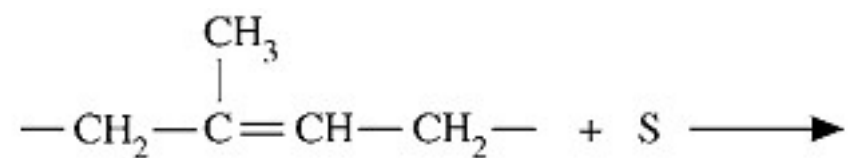
Early synthetic rubbers (diene polymers such as polybutadiene) possess a considerable degree of unsaturation (for lightly crosslink structure and elastomeric property).

The residual double bonds make diene elastomers Vulnerable to oxidative and ozone attack



Creation of vulcanization sites for butyl and ethylene-propylene rubbers through copolymerization

Rubbers

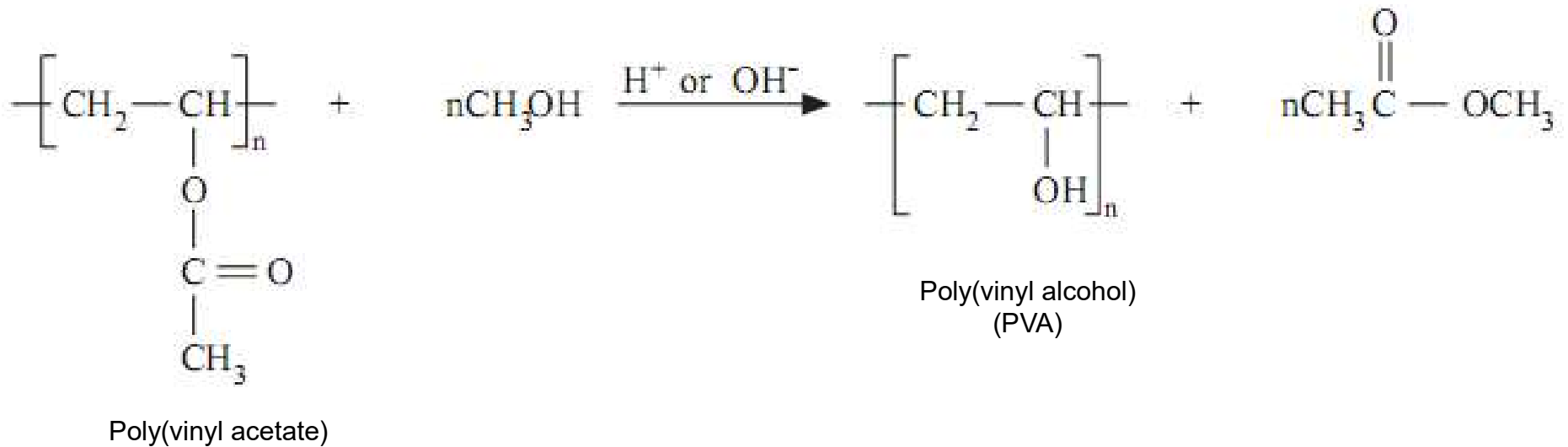


The commercial cross-linking of diene polymers is carried out almost exclusively by heating with sulfur.

Hydrolysis

Poly (vinyl acetate)- Primary use in the production of water-based emulsion paints.

- emulsion-type and hot-melt adhesives



PVA- thickening agent for various emulsion and suspension system because of its water solubility

-is used widely as water-soluble adhesive with excellent binding capacity for cellulosic material such as paper due to its high hydroxyl content

Block and Graft Polymer Formation

Block and graft copolymer formation involves the reaction of a previously formed homopolymer or copolymer with fresh monomers.

For vinyl monomers two general methods are employed:

- (1) The polymerization of a monomer in the presence of a polymer by the initiation of growth through chain transfer. (graft polymers)
- (2) Polymerization of a monomer in the presence of a polymer containing reactive sites. (block copolymers –terminal active sites or graft copolymerization occurs on active sites located on the polymer backbone or pendant groups)

Polymer results in a mixture of products:

- (1) the initial homopolymer that did not participate in the reaction
- (2) the homopolymer of the fresh monomer
- (3) the cross-linked parent homopolymer through graft polymerization or the branched block copolymer
- (4) the desired copolymer.

Block Copolymerization-1

The preparation of block copolymers requires the presence of terminal reactive groups.

A variety of techniques have been used to achieve this.

1. Butyl acrylate- styrene and acrylonitrile- styrene block copolymers: Irradiation of butyl acrylate and acrylonitrile containing photosensitive initiator with UV radiation. Then mixed it with styrene

2. In situ block polymer formation is obtained by using a mixture of water-soluble and oil soluble monomers. An example involves dissolution of acrylic acid or methacrylic acid in water followed by styrene emulsification in the water.

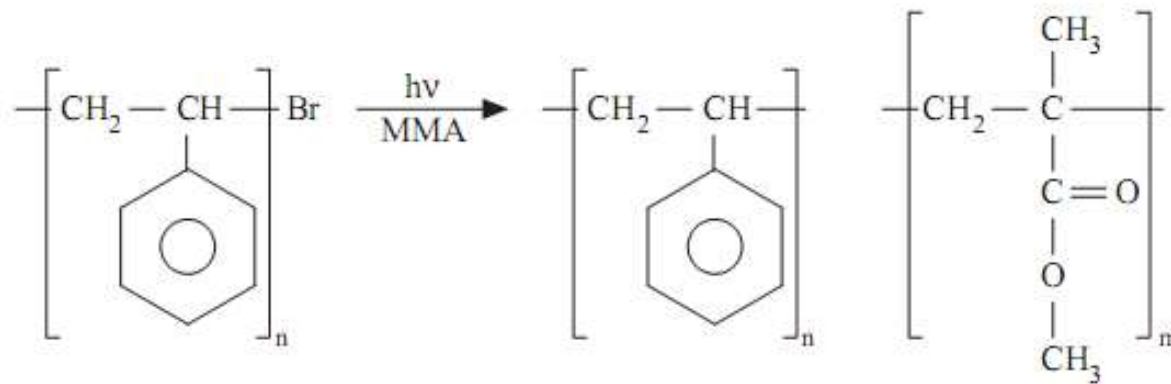
3. When a polymer chain is ruptured mechanically, terminal-free radicals can be generated, and these can be utilized to initiate block copolymerization.

Various Block Copolymers Prepared by Mechanical Rupture of Polymer Chains in Presence of Monomer

Polymer Unit	Monomer
Acrylamide	Acrylonitrile
Isobutylene	Acrylonitrile
	Styrene
	Vinylidene chloride
Methyl acrylate	Vinyl chloride
	Vinylidene chloride
Methacrylonitrile	Acrylonitrile
Methacrylonitrile-co-vinyl chloride	Methyl methacrylate
Methyl methacrylate	Methacrylonitrile
	Styrene
	Vinylidene chloride
Methyl methacrylate-co-methacrylonitrile	Styrene
Styrene	Methyl methacrylate
	Vinylidene chloride
Vinyl acetate	Vinyl chloride
Vinyl chloride	Methyl vinyl ketone

Block Copolymerization-2

4. When polymer chains are terminated by labile end groups, block polymers can be produced by irradiation.

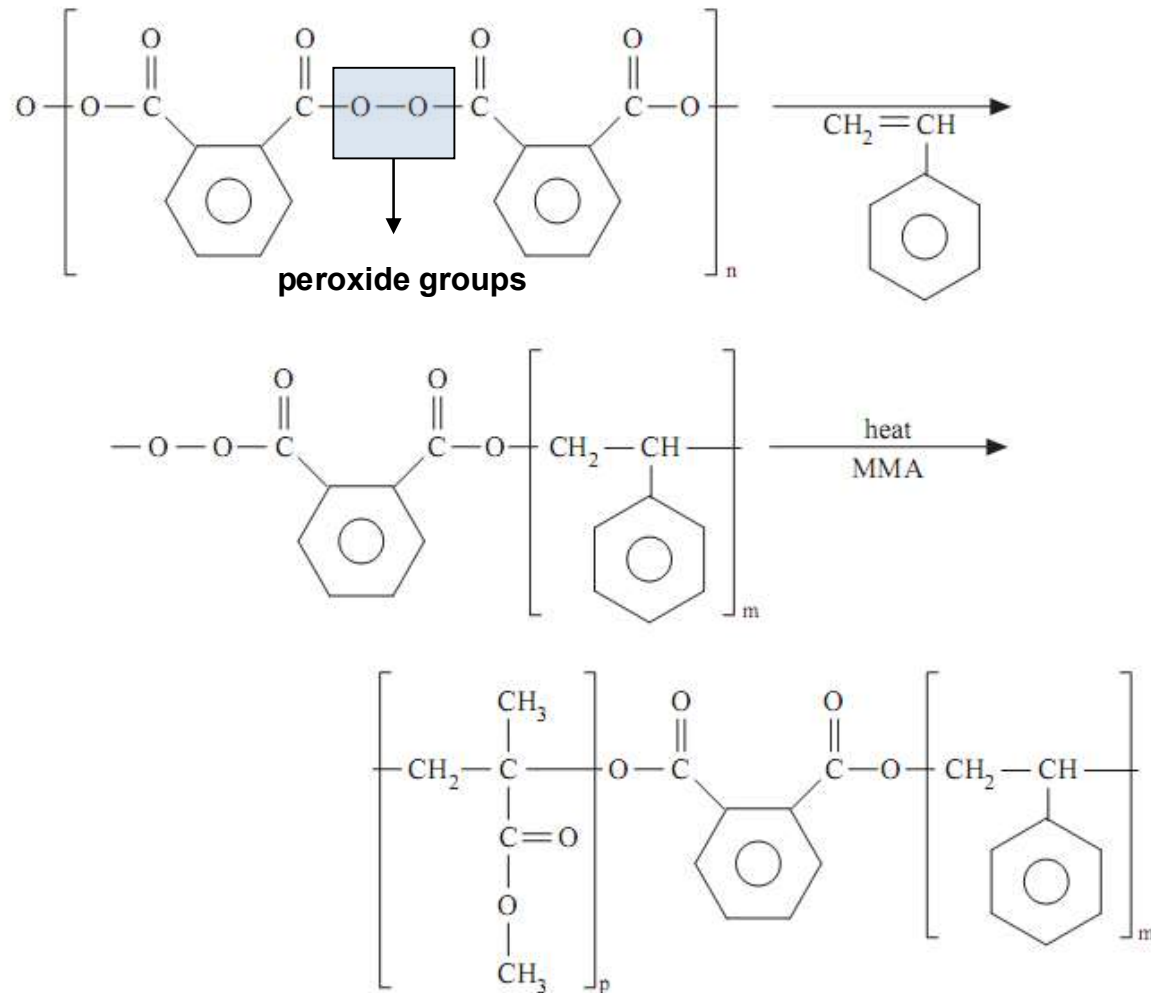


Terminal brominated styrene

Styrene- methyl methacrylate copolymer

Block Copolymerization-3

5. A common technique of preparing block copolymers is the introduction of peroxide groups into the polymer backbone or as stable end groups .



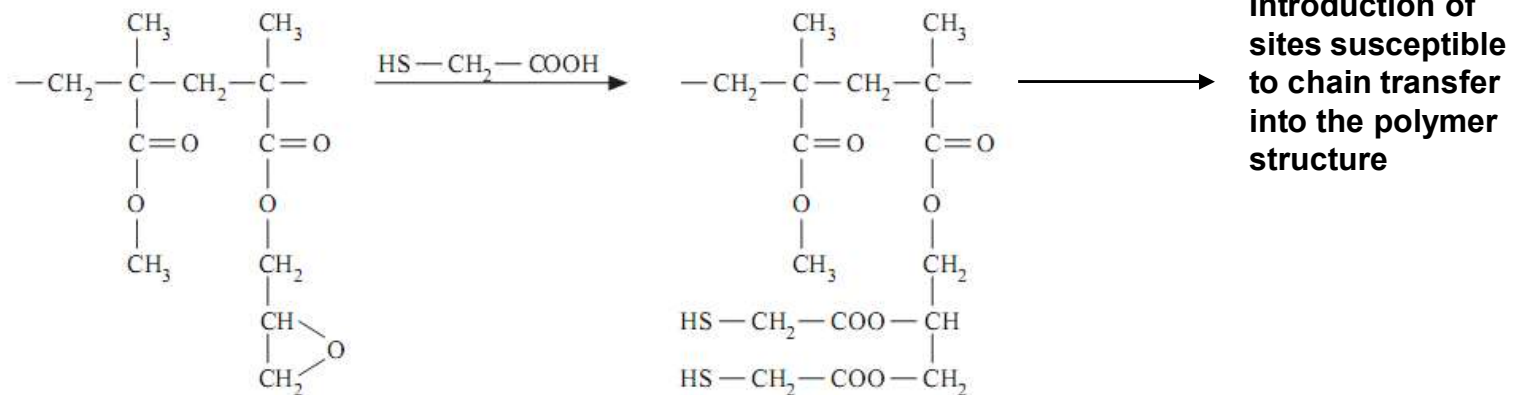
Graft Polymerization-1

There are essentially three approaches to the preparation of graft copolymers via free radical mechanism:

- 1.Chain transfer to a saturated or unsaturated polymer
- 2.Activation by photochemical or radiative methods
- 3.Introduction and subsequent activation of peroxide and hydroperoxide groups

1. Graft copolymer formation by chain transfer requires three components:
a polymerizable monomer, a polymer, and an initiator

The initiator serves to create active sites either on the polymer or on the monomer.



A commercially important graft polymer (transfer to unsaturated polymer) – Impact polystyrene (butadiene grafted to PS)

Graft Polymerization-2

Active sites can be generated on a polymer to initiate graft copolymerization by ultraviolet light and high-energy irradiation.

The process may involve

- (1) simultaneous irradiation of polymer in contact with monomer;
- (2) irradiation of polymer predipped in the monomer;
- (3) pre-irradiation of the polymer in the absence of air (O_2) followed by exposure to the monomer; and
- (4) pre-irradiation of the polymer in air to form peroxide and subsequent decomposition in the presence of the monomer. (Unstable compounds such as peroxides and hydroperoxides are usual initiators for vinyl polymerization reactions. These groups can be introduced into a solid polymer by pre-irradiation in the presence of air or oxygen)

Properties of Graft Copolymers Produced by Mutual Irradiation of Monomer

Polymer	Monomer	Property Changes
Polyethylene	Acrylonitrile	Increased solvent resistance and softening temperature; excellent adhesion to polar materials
	Vinyl chloride	Retention of superior electrical properties while increasing softening point to 215°C
	Acrylate methacrylate	Following hydrolysis, surface becomes permanently conductive; prevention of accumulation of static charges; good adhesion to materials like cellulose, glass, and metals
	Styrene	Increased melt viscosity
Polytetrafluoroethylene	Styrene	Enhanced adhesion, enhanced elimination of plastic flow, and increased ultimate strength
Polychlorotrifluoroethylene		

Surface Modification-1

Deliberate chemical modification of surface properties.

Surface reactions- **do not include bulk homogeneous reactions of polymers**

-those confined to the surface and do not significantly alter the physical properties of the substrate.

To improve

- ☐ Feel
- ☐ Washability
- ☐ Dye retention
- ☐ Antistatic properties
- ☐ Abrasion resistance of fibers

To enhance;

- ☐ Printability
- ☐ Solvent resistance
- ☐ Adhesion
- ☐ Permeability to liquids and vapors of films

Surface oxidation techniques

- ☐ Use of corona discharge
- ☐ Ozone
- ☐ Hydrogen peroxide
- ☐ Nitrous acid
- ☐ Alkaline hypochloride
- ☐ UV irradiation
- ☐ Oxidizing flame
- ☐ Chromic acid

-To increase printability of PE and PET

-to improve the adhesion of PE and PP to polar polymers and PTFE (teflon) to pressure sensitive tapes

-Greasy feel of PE is removed by surface oxidation.

-Surface-oxidized PE when coated with a thin film of vinylidene chloride, acrylonitrile, and acrylic acid terpolymer becomes impermeable to O₂ and more resistant to oil, grease, abrasion and high T

Surface Modification-2

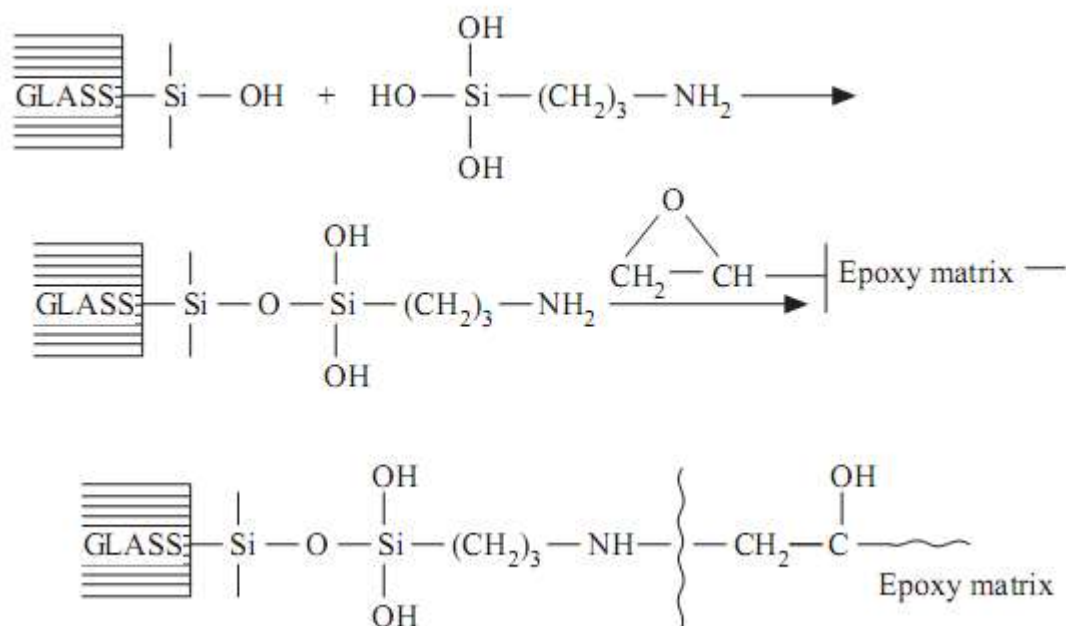
Alkali and acid treatments have also been used to modify surface properties of polymers:

- ❑ Permanently amber-colored polyethylene containers suitable for storing light-sensitive compounds have been produced by treating fluorosulfonated polyethylene with alkali.
- ❑ Poly(ethylene terephthalate) (PET) dipped into trichloroacetic/chromic acid mixture has improved adhesion to polyethylene (PE) and nylons.
- ❑ Antifogging lenses have been prepared by exposing polystyrene films to sulfonating conditions.
- ❑ Surface halogenation of the diene polymers natural rubber and polyisobutylene resulted in increased adhesion to polar surfaces.

Treatment of a large number of thermoplastics with alkyl or alkenyl halosilanes has yielded materials with improved heat, stain, and scratch resistance.

The use of silane coupling agents in a number of systems is particularly instructive.

These systems include glass- or carbon-fiber-reinforced composites, phenolic-bonded sand, grinding wheel composites of aluminum oxide, metal-filled resins for the tool and die industry, etc.



Chemical linkage between matrix resin and glass-fiber reinforcement through a silane coupling agent

Functional Polymers

Functional polymers -whose efficiency and characteristics are based on a functional group.
-give the polymer special features

A specific functional group - carefully designed and located at a proper place on the polymer chain. (dispersed along the polymer main chain (including chain ends) or attached to the main chain either directly or via spacer groups.)

Functional groups are typically chemical units that are chemically reactive, biologically active, electroactive, mesogenic (liquid crystals), photoactive, and, more commonly, ionic, polar, or optically active.

There are two general techniques used for the preparation of functional monomers:

❑ Polymerization or copolymerization of functional monomers

❑ Chemical modification of preformed polymers (enables the choice of molecular weight and the dispersity of polymer and also allows the synthesis of polymers inaccessible by direct routes)

Crosslinking, vulcanization, and grafting are the polymer reactions that take place on the functional or reactive groups located in the polymer main chain.