Chapter 15-3

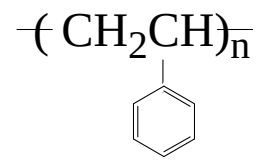
• PVC 는 점도를 낮추기 위하여 가소제 (Plasitcizer)와 함께 사용됨. 가소제로서는 dioctyl phthalate (DOP) 등이 있다.

- 용도 : (i) flexible grade :
  - calendered sheet (장판), film
  - table cloth, shower curtain
  - furniture, wire and cable 등

  (ii) rigid grade
  - pipe, fitting, roofing 등
  - blow - molded bottles
  - automobile parts 등
  - foam 으로 제조하여 단열재로 이용

    (ex) LNG 저장 tank 용 단열재 foam

• Polystyrene (PS) and styrene copolymers

- PS,  (free - radical 반응에 의해서 얻어짐)

- clear, transparent
- good electrical insulator (전기 절연체)
- brittle 함, 즉 잘 부러짐
- 용도 : packaging and containers, appliance parts (가전제품)

• Styrene - acrylonitrile (SAN) copolymer

- has better chemical resistance than PS,
- higher heat resistance
- stiffer than PS
- not as clear as PS

• Acrylonitrile - butadiene - styrene (ABS) copolymer
  - tough plastic
  - good mechanical property
  - chemical resistance 가 좋음
  - good electrical property (전기절연체)

○ Thermosetting and Engineering Resins

(1) Thermosetting Resins (열경화성수지)

- 열을 가하면 경화가 일어나고, 계속 열을 가하면 flow가 일어나지 않고 분해(degradation)가 일어남.
- a network of long chain molecules that are crosslinked which gives the polymer a three -dimensional, infusible structure.

(ex) Epoxy resin, phenol resin, polyurethane, unsaturated polyester resin

(2) Engineering Thermoplastics -(열가소성수지)

- high thermal property(stability), 내열성이 좋음
- good chemical and weather resistance (내화학성 및 내후성이 좋음)
- good electrical property (전기절연성이 좋음)

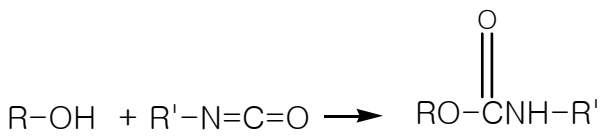
(ex) Nylon, PET, PBT, Polycarbonate, polyacetal, PMMA 등

(1) Themosets

(a) Polyurethanes (PU)

- reaction between alchol (or diol) and isocyanates
- produced by condensation reaction.

(반응)



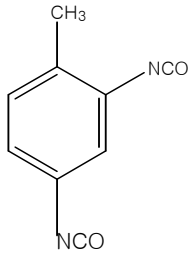
urethane linkage

- polyurethane 합성에 많이 이용되는 isocyanate 는 주로 MDI 및 TDI가 사용됨

. MDI (4,4 -methylene bis(phenyl isocyanate)

구조식 : $CH_2(C_6H_4NCO)_2$

. TDI (2,4 -and 2,6 -toluene diisocyanate)



(용도)

rigid foam (경질 폴리우레탄 폼)

flexible foam (연질 폴리우레탄 폼)

adhesive (접착제)

surface coating

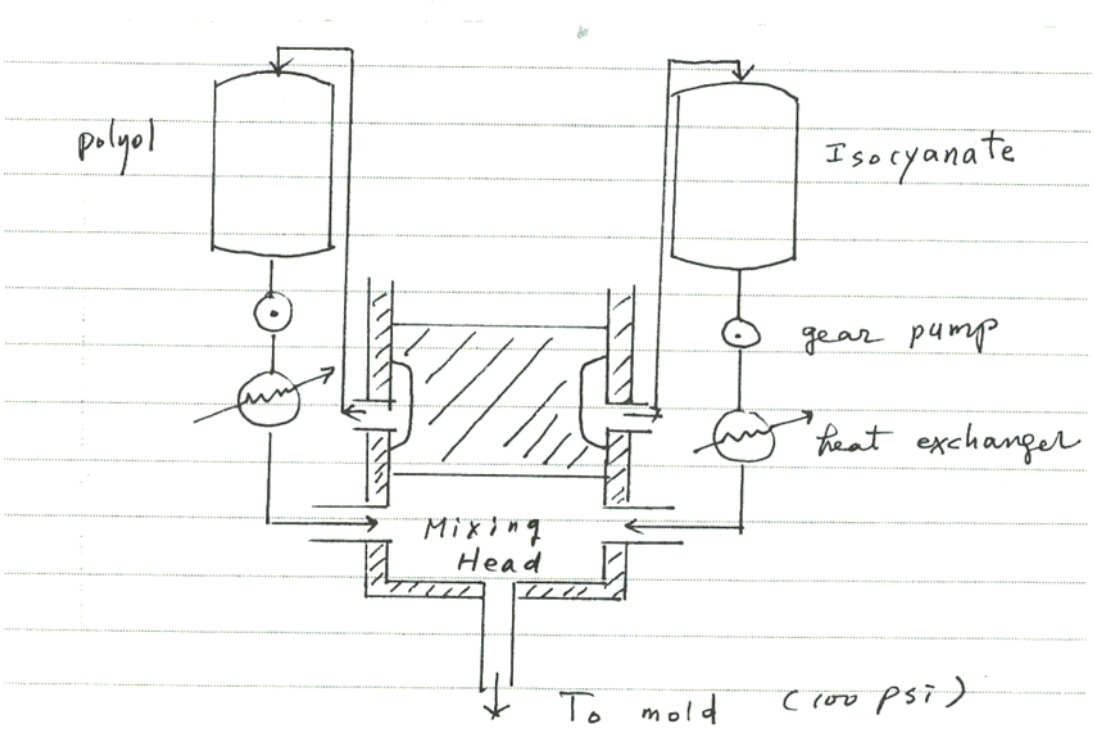
elastomer 등

○ Reaction Injection Molding(RIM)

- 반응사출성형
- a process developed recently to mold large polyurethane directly from the starting chemicals.
- the mixed stream begins to react as it flows into the mold, where the polymerization reaction is completed.

(예) highly reactive polyol 과 isocyanate.

- 위의 두 반응물이 nozzle 을 통하여 mixing head로 전달됨.



. The polyurethane maybe formulated – flexible 또는 rigid PU, solid 또는 foamed PU.

. 용도 : energy – absorbing front and rear panels for automobiles.

Insulating materials(예로서 냉장고, 건축용)

: polyurethane foam

LNG 저장 tank 용 단열재 (rigid PU foam)등

○ Reinforced RIM (RRIM)

- reinforced materials, in which short reinforcing fibers (예로서 glass fiber : 유리섬유) are incorporated or both of the

reactants.

- 사용되어지는 유리 섬유는 단 섬유
  (약 1cm정도 길이 또는 장 섬유).

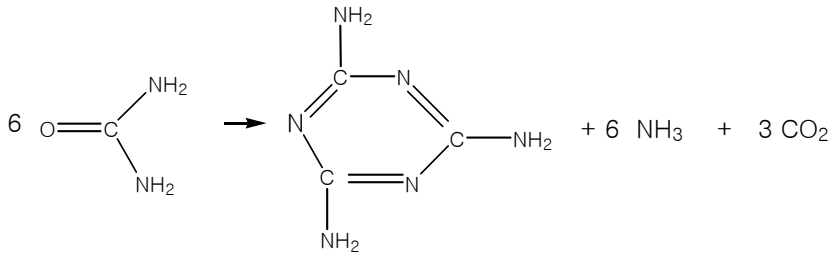
○ Urea $(H_2N\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2)$

- produced by the reaction between ammonia and carbon dioxide.

○ Urea-formaldehyde resins : the condensation reaction between urea and formaldehyde.

○ Melamine – formaldehyde resins :

- melamine is a heterocyclic aromatic condensation product of urea



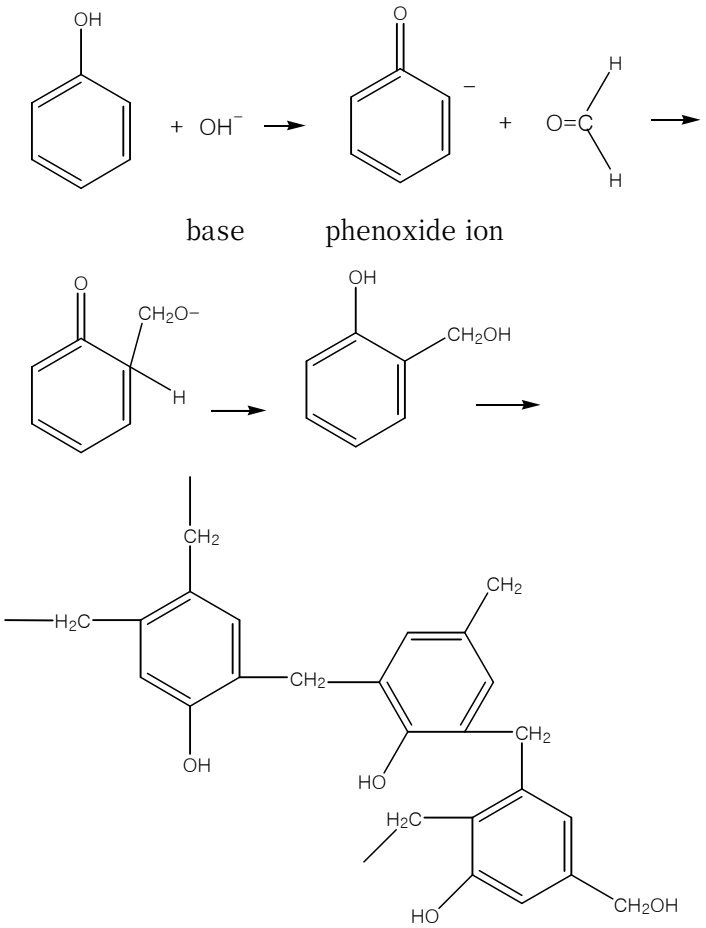
urea Melamine

(용도) 합판 등의 접착제로 이용

○ Phenolic Resins

- phenol 과 formaldehyde를 이용하여 phenol 수지로 생산, 중요한 열경화성 수지 중 하나임,
- condensation 반응임.

(반응)



○ 성질 및 용도

(a) hardness and rigidity

(b) acid and water hydrolysis resistance

(c) 단열재

(d) 150℃ 까지 사용가능

(e) 값이 싸고, 가공이 쉬움

(f) 유리섬유를 보강제로 사용하여 강도를 높힐 수 있음

○ Epoxy Resins

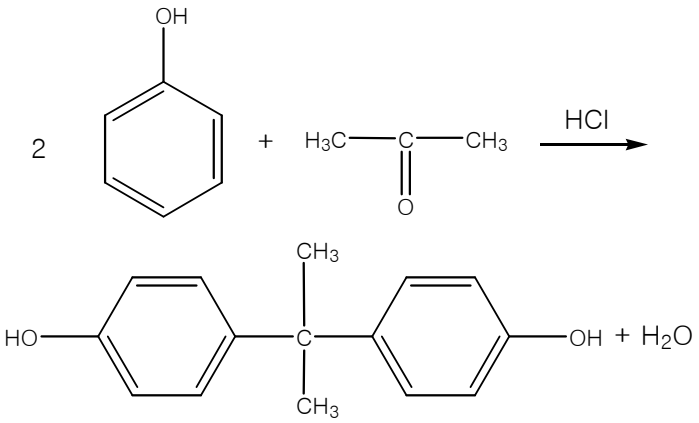
(반응1) Phenol 과 acetone으로부터 bisphenol-A 제조

(반응2) Bisphenol-A와 epichlorohydrin 과 반응하여
diglycidyl ether of bisphenol-A(DGEBA) 제조

(반응3) DGEBA (epoxy resin)과 amine 등 경화제를 이용하여
crosslinked epoxy를 제조.

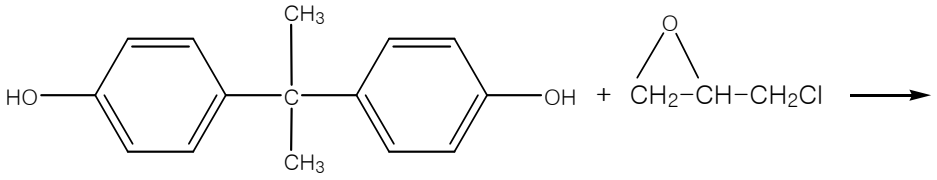
- 열경화성 고분자중 가장 많이 이용되는 수지임

(반응1)

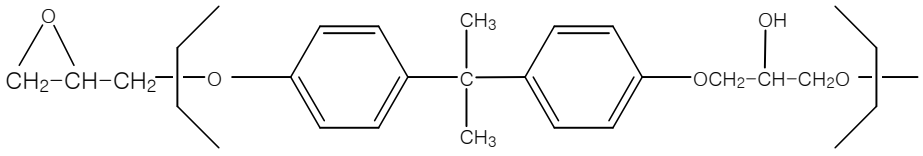


Bisphenol-A

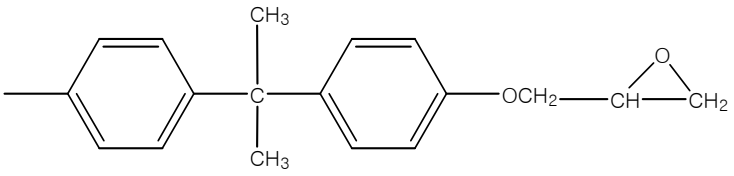
(반응2)



(BPA) (epichlorohydrin)

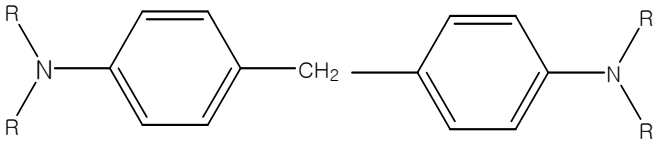


epoxy functional group

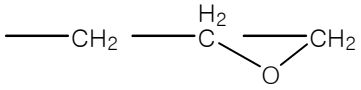


Diglycidyl ether of bisphenolA (DGEBA)

- 위의 DGEBA는 epoxy function group이 2개인 Bisphenol-A type epoxy 임
- 다음 아래의 epoxy 는 functional group이 4개인 Novolac type epoxy임

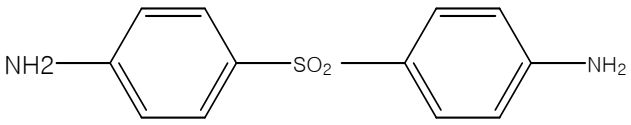


여기서..

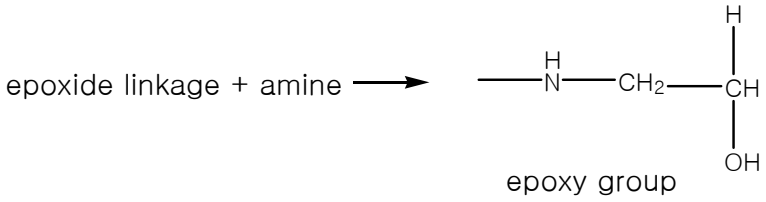
R = 

○ Tetra glycidyl diamino diphenyl methane(TGDDM)

- 위의 DGEBA 나 TGDDM 은 분자량이 수백 정도인 linear polymer로서 아직까지 경화되지 않은 상태임. 경화된 epoxy polymer를 얻기 위해서는 hydroxyl group 이나 epoxide linkage와 경화제로 사용되는 amine과 반응.
- 예로서 경화제(curing agent)로 이용되는 것.



Diaminodiphenyl sulfone (DDS)



○ 성질 및 용도

(a) metal 표면에 접착력이 좋음.

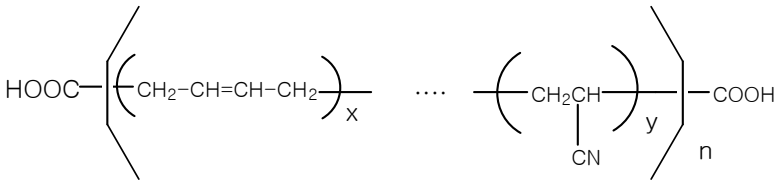
(b) 내 화학성이 좋음

(c) 최고 250~260℃ 까지 사용가능.

(d) Good dimensional stability (치수안정성이 좋음),

즉, low shrinkage property

○ Epoxy는 brittle하므로 carboxyl-terminated butadiene acrylonitrile(CTBN) liquid rubber를 사용하여 첨가함으로서 Epoxy의 toughness를 향상시킬 수 있다.



CTBN

(reference) Kim, Park and burns,

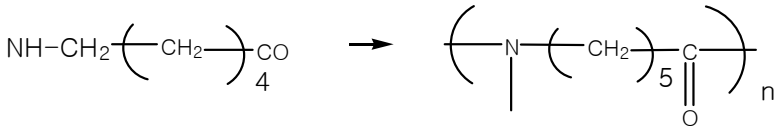
Journal of Applied Polymer Science, Vol. 50. page 1951~1957 (1993)

○ Engineering Polymers

(1)Nylon

(i) Nylon -6 (polycaprolactam)

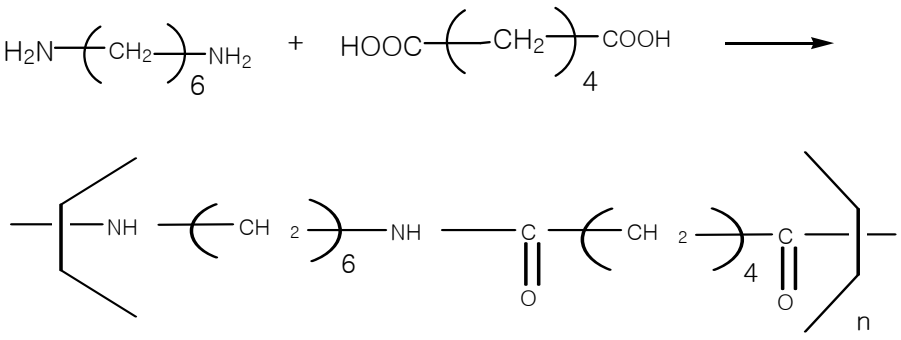
- produced by polymerization of caprolactam (condensation reaction).



(ii) Nylon -6,6 (polyhexamethylene adipamide)

- produced by polycondensation of hexamethylene diamine and adipic acid.

(반응)



(성질)

(i) High tensile and impact strength

(ii) toughness, good abrasion and wear resistance(내마모성)

(용도)

(a) Blow and injection molding

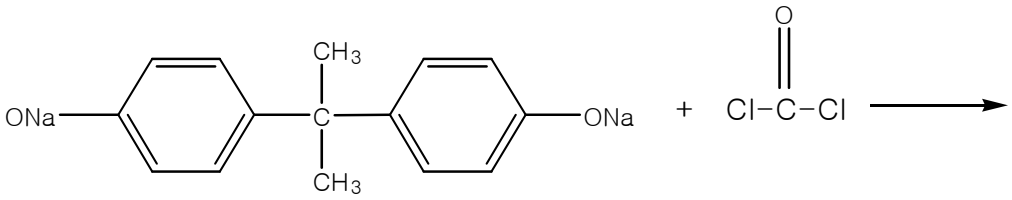
(b) Bearings, molded gears, molded automobile parts(부품), and

machinery parts

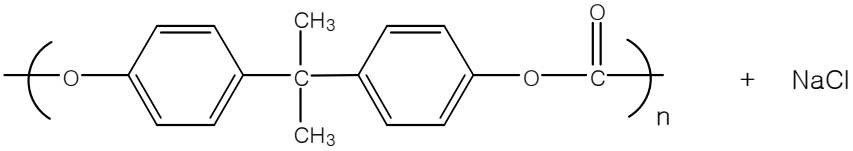
(c) Tubing, wire and cable insulation(전선절연재)

(d) 기타 thermoplastic engineering resin.

(2) Polycarbonate(PC)



sodium salt of Bisphenol-A phosgene



Bisphenol-A polycarbonate

(성질)

(a) 투명함(transparent), break and heat resistant

(b) very tough, self extinguishing (자체 소화성)

(c) good electrical property(전기절연체)

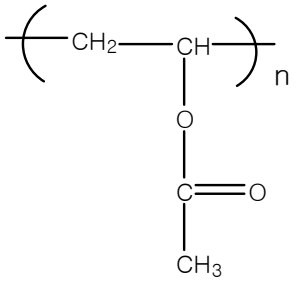
(용도)

(a) Injection, blow molding, extrusion

(b) Lab safety shields, street lighting globes

(c) Safety helmets, sun glasses, school windows

(3)Polyvinyl acetate :



- produced from ethylene and acrtic acid
- free radical 중합
- the polymer is highly branched, amorphous and atactic

(성질)

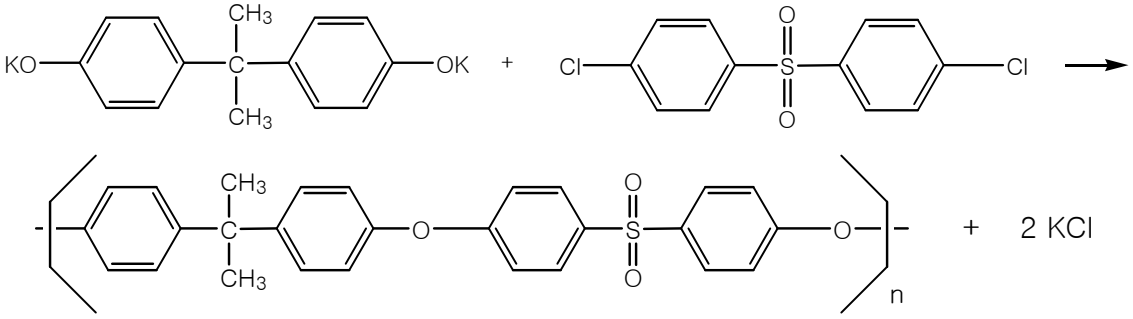
(a) colorless, odorless and nontoxic

(용도)

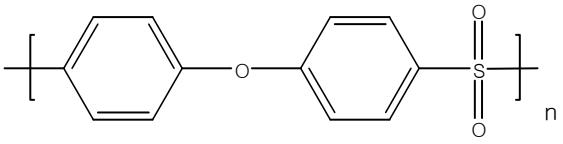
(a) polyvinyl alcohol 생산에 이용

(4)Aromatic polyethersulfone (PES)

– prepared by sodium or potassium salt of bisphenol -A and 4,4 -dichlorodiphenyl sulfone



(상품명 : Udel : Union carbide)

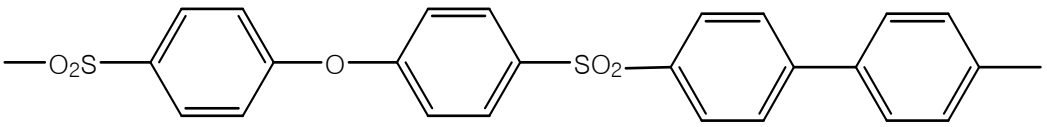


상품명 : PES 200P (by. ICI)

PES

.Fig. 13-10 shows the maximum use temperature for several engineering plastics

(5)Polyaryl sulfone



상품명 : Radel (Union Carbide)

(성질)

(a) Resistant to alkalies, acid and inorganic salts, but not resistant to highly polar chlorinated hydrocarbons

(b) Similar to those of PC

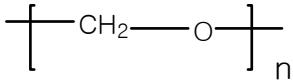
(c) Can be used at higher temp.

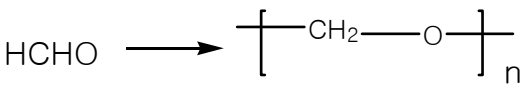
(용도)

(a) extruded into thin films and foils

(b) injection molded into various objects which need high temp stability.

(6) Polyacetal,





(form aldehyde) polyoxymethylene(polyacetal)

(성질)

(a) highly crystalline with good dimensional stability

(b) High impact resistance

(c) great strength

(d) resistant to chemical and hydrolysis

(용도)

(a) door handles 등 moding 용

(b) gears, electrinic equipment

(c) appliances, (가전제품) 의 parts

(7) Termoplastic. polyesters

(a) PET

(b) PBT : 1,4 -butandiol + Terephthalic acid

(용도)

electronics parts

sporting goods, automobile bumper

(ex) PBT + PC -> "Xenog Bumper"

Blends

Chapter 14. Synthetic Fibers

- Fiber로서 필요한 중요한 물성

(1) high melting point (100℃ 이상)

(ex) PET : Tm=253℃

Nylon-6 : Tm=230℃

(2) linear and symmetrical structure

(3) high molecular weigh

(ex) PET, Mw = 30,000 (g/mol)

Nylon-6, Mw=35,000 (g/mol)

○ 합성섬유(synthetic fiber) 의 생산비율

Polyester(PET등)	49%
Nylon	33%
Acrylic	9%
Olefin 등	9%
	100%

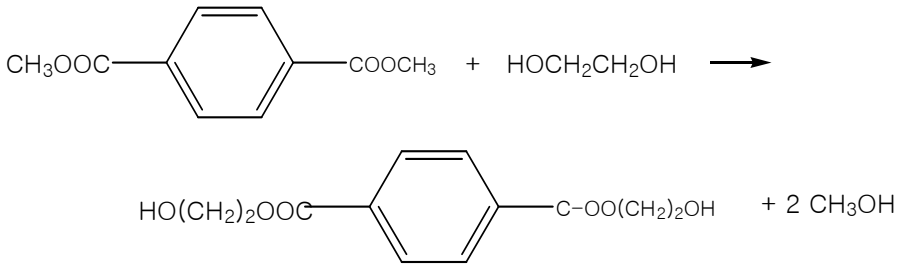
○ Polyester Fibers

-Pet(Polyethylene terephthalate) :

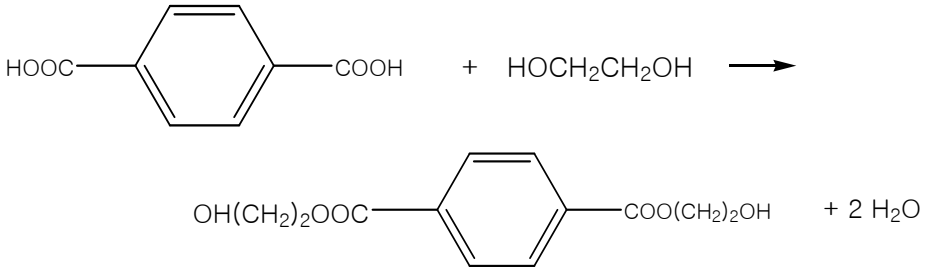
(생산)

(i) dimethyl terephthalate (DMT) + ethylene glycol (EG)

-> PET



(ii) terephthalic acid + ethylene glycol (EG) > PET



- PET 는 cotton 과 clending 가능
- PET staple fiber/cotton = 50: 50 or 65:35

○ Polyamides

- Nylon 의 종류 :

condensation polymers formed by the reaction between :

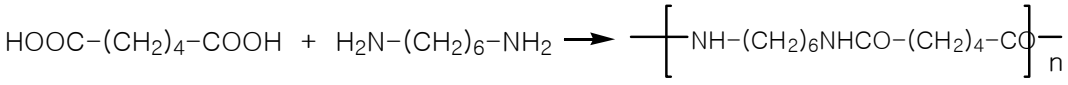
(a) dicarboxylic acid a diamine : Nylon -6,6, 610

(b) a ring opening of lactams : Nylon6,12

(c) polymerization of amino acids : Nylon -7,11

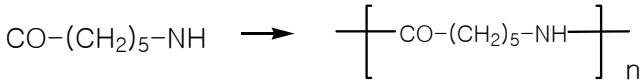
.Nylon -6,6(polyhexamethylene adipamide)

adipic acid + hexamethylene diamine - > Nylon -6,6



Nylon6,6

. Nylon-6 (polycaprolactam)



(성질)

(a) linear polymer and highly crystalline

(b) Nylon-6 의 Tm=230℃

Nylon-11 Tm=190℃

(c) Nylon-4 는 moisture absorption이 cotton 만큼 큼

(d) Nylon은 빛에 약하다.

(용도)

(a) 자동차용 타이어의 보강재로서 tire cord로 이용됨

(b) carpet로 이용됨. ropes, parachutes, selt belts, conveyor belts

○ Acrylic Fibers

- the acrylics are the third major class of synthetic fibers.
- polyester와 비슷한 시기에 개발됨
- polyacrylonitrile
- temperature sensitive 하므로 melt spinning 하지 않고 solution spinning 함.
- solvent 로서dimethylformaide(DMF) 사용.

○ modacrylic fiber

- the fiber-forming substance is any longchain synthetic polymer

composed of less than 85% but at least 35% by weight of acrylonitrile units, -(CH_2CHCN)- 다른 chemicals로서 vinyl chloride, are incorporiated as modifiers.

(성질 및 용도)

(a) 상업적 tradename으로서 Orlon, Acrilan 등

(b) 태양이나 화학약품에 highly resistant함

(c) 탄소 섬유의 원료로도 쓰임

○ Polypropylene Fibers

isotactic PP(I-PP) : Tm = 171℃

결정화도 = 60~85%

(성질)

(a) high abrasion resistance

(b) strenth, low static build up

(c) resistance to chemicals.

(d) low softening point

(e) low resilience and dyeing problems

(f) 주로 carpet에 이용

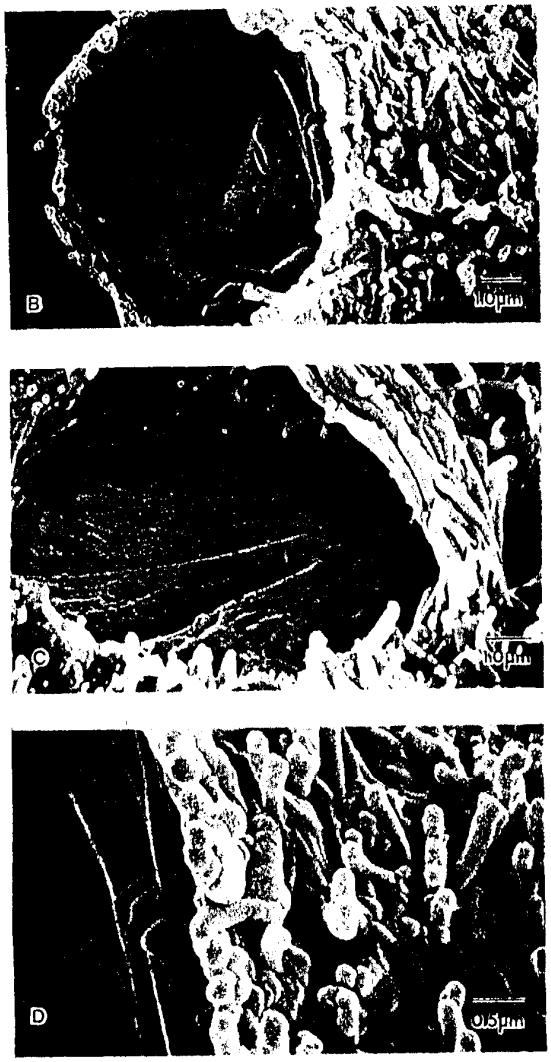


Fig. 5.96 A glass fiber reinforced LCP composite is shown to have interesting morphology. A polished thin section is shown in polarized light (A) (color section) to exhibit a fine domain texture with some orientation of the polymer on the glass surfaces. SEI fracture views (B–D) show the tenacious adhesion of the LCP to the fibers. Fibrillar structures are oriented paralled to the fiber surface and submicrometer sized domains are observed (D).

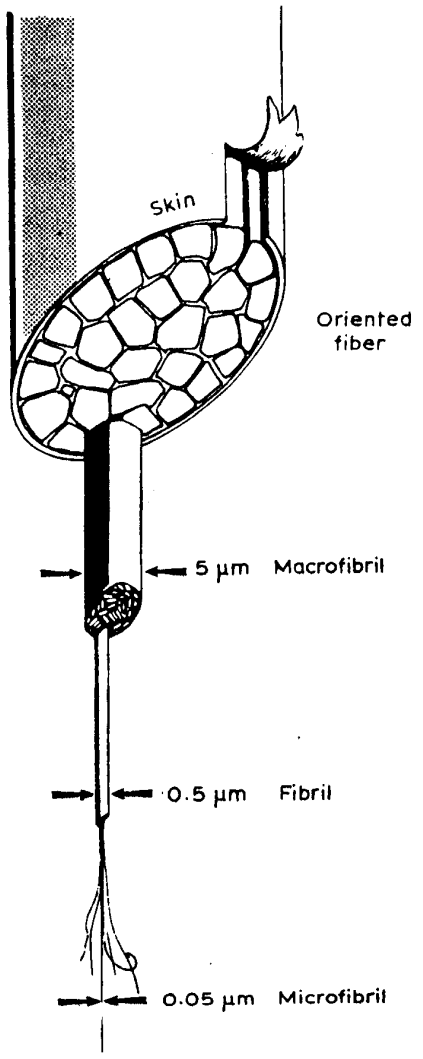


Fig. 5.97 The structures observed in uniaxially oriented LCP fibers, ribbons and films can be summarized by this structural model. The model defines the nature of the fibrillar textures into three categories based upon size: macrofibrils, fibrils and microfibrils. In each case the sizes of structures have been determined from complementary microscopy techniques. (From Sawyer and Jaffe [353]; reproduced with permission.)

(ref.) J. Mater. Sci., 21, 1897 (1986).

(reference) "polymer Microscopy", by Sawyer and Grubb, Chapman and Hall, 1987, page 254

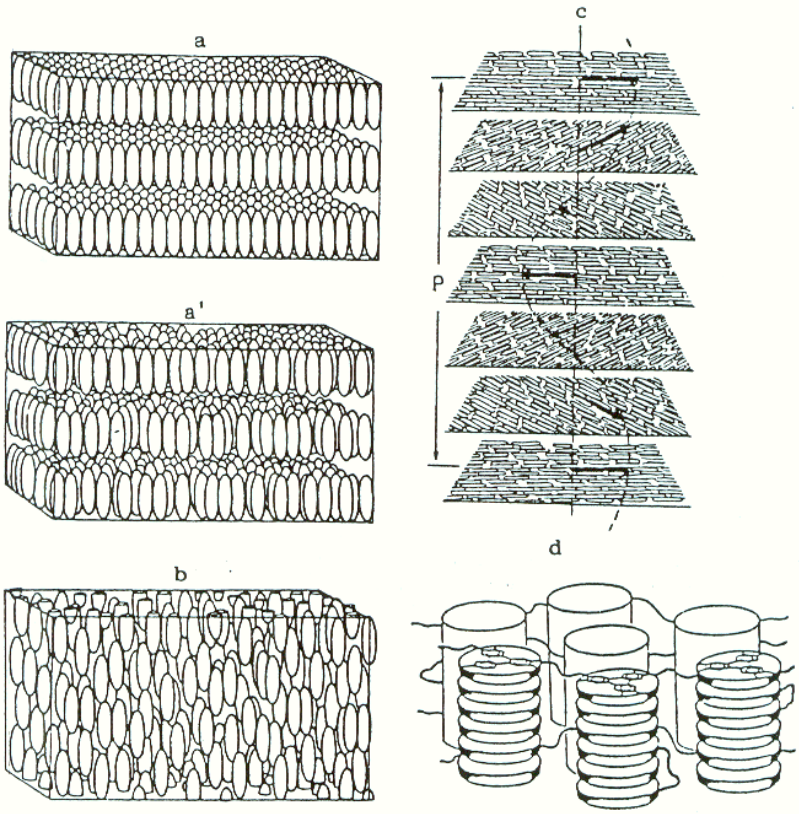


Fig. 2.17. Schematic representation of the different types of mesophases. Smectic with ordered (a) and unordered (a') arrangement of the molecules in layers; b) nematic; c) cholesteric; and d) discotic. (From Platé and Shibaev (1987); Courtesy Plenum Press).

order (from kheir, hand, and from kholè and stereos: bile and firm); sometimes a fourth category is distinguished: the *discotic* one (piles of disclike molecules). Fig. 2.17 gives a schematic representation.

If monomeric liquid crystals are polymerized, the polymers also show in most cases the liquid-crystalline effects. In addition, their viscosity during flow is unexpectedly low in the anisotropic phase state.

There is no consensus yet as far as the name of these materials is concerned. Some investigators use the name *Polymer(ic) Liquid Crystals* (*PLC's*), others call them *Liquid Crystalline Polymers* (LCP's) or *Mesogenic Macromolecules*.

PLC's which melt without decomposition are called *thermotropic*; those who decompose on heating before melting but can be dissolved in liquids, are called *lyotropic*.

(ref) "Properties of Polymers", by van Krevelen, Elserier, 2nd ed(1990), page, 35

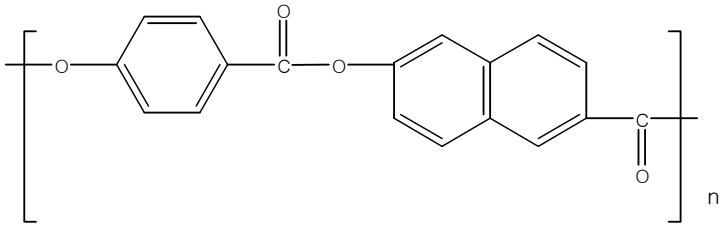
구조 - (a) ordered smectic (b) unordered smectic

(c) nematic (d) discotic

○ Liquid Crysatalline Polymer (LCP)

i) thermotropic LCP -열방성 고분자, 열을 가하여 crystal -to -nematic transition후에 액정 상태를 나타내는 고분자물성연구

ex) Hoechst -Celanese 의 Vectra A900



p -HBA HNA

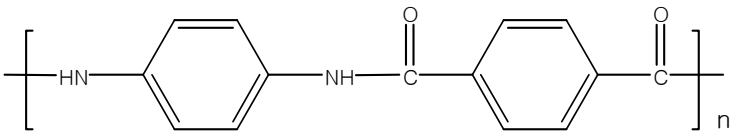
(hydroxy bezoic acid) 6hydroxy -2 -naphthoicacid

73mol% 27mol%

이외에도 Du pont, Eastman Kodak 및 Amoco에서 생산됨

ii) lyotropic LCP 액체 즉 용액 상태에서 액정 현상을 나타내는 고분자물성연구

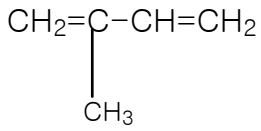
ex) DuPont 의 Kevlar

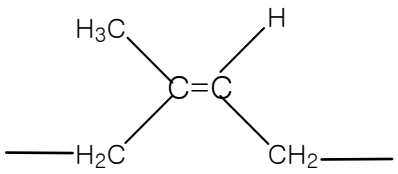


high modulus fiber (106 kg/cm^2)

○ Synthetix Rubber

.Natural Rubber - composed mainly of high molecular weight hydrocarbon made up of isoprene,





. The isoprene units are linked in a cis -1,4configuration

- high resilience, strength

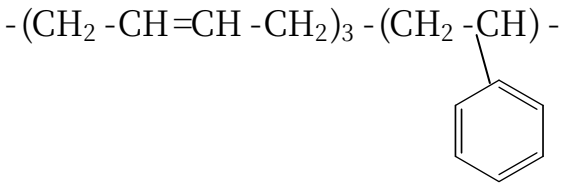
. Elastomers (탄성체), synthetic rubbers, are polymers with physical and mechanical properties similar to those of natural rubber.

. Elastomers are unsaturated and can be vulcanized.

○ Synthetic rubber의 종류

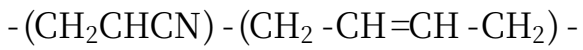
(a) Butadiene rubber, CH2=CHCH=CH2

(b) SBR(styrene -butadiene -rubber)



75mol% 25mol%

(c) ABR or NBR (acrylonitrile -butadiene rubber)



(d) Polyisoprene

(e) Transpolypentamer Rubber (TPR)

(f) Ethylene -Propylene Rubber (EPR)

(g) Polychloroprene Rubber (Neoprene)

(a) Polybutadiene Rubber(PBD)

- the most important synthetic rubber
- 다른 monomer와 공중합(copolymerization) 가능
- free radical initiator를 사용하여 1,4-PBD 생산, styrene과 공중합하여 SBR 생산
- acrylonitrile과 반응하여 ABR(or NBR) 생산
- natural rubber 나 ABR 과 blending 가능

(성질 및 용도)

- 생산량의 약 95% 는 tire industry에 이용
- high abrasion resistance(내마모성)
- high resilience
- cis 또는 trans에 따라 Tg가 변함

(ex)

- high cis(약 98%) 1,4-PBD (Tg=-108℃)
- medium cis (약 52%) 1,4-PBD (Tg=-80~-96℃)
- trans PBD (Tg=-14℃)

○ Thermoplastic Elastomer(열가소성 탄성체)

$$-(\text{PBD}-\cdots\cdots)_n-(\text{PS}\cdots\cdots\cdots\cdots)-$$

Poly(styrene-b-butadiene) block copolymer

- the poor mechanical strngth of cisPBD is improved by incorporating styrene block copolymer.

(b) Styrene -butadiene rubber(SBR)

- tire industry에 주로 이용
- good mechanical and physical properties
- favorable cost
- made by copolymerization Ca 75% butadiene and 25% styrene
- Styrene -butadiene -styrene(SBR) triblock copolymer 생산 - TPE

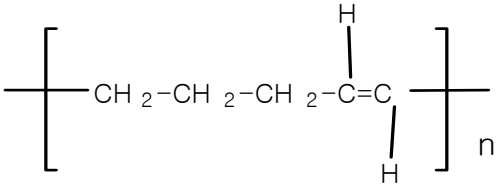
(c) ABR or NBR (acrylonitrile -butadiene styrene)

- produced by copolymerizing varying proportions of butadiene and acrylonitrile in an aqueos emulsion.
- NBR is resistant to hydrocarbon liquids
- fuel hoses 나 fuel cell liners, gaskets등에 사용

(d) Polyisoprene

- produced commercially by the polymerization of isoprene using either lithium and lithium compounds as catalysts
- butadiene 과 blending 하여 사용

(e) Trans poly pentamer(TPR) rubber;



- high abrasion resostance(내마모성)

- high mechanical properties - excellent processibility

(f) Ethylene-propylene rubber(EPR)

- ethylene-propylene copolymer 에는 crosslinking에 필요한 double bond가 없으므로, 1,4-hexadiene 등과 같은 제 3의 monomer 와 중합
- 이와 같은 elastomer를 ethylene-propylene terpolymer(EPT) or ethylene propylene diene monomer rubber(EPDM)
- good abrasion property
- good heat resistance
- slow cure rate
- SBR 보다 값이 비싸 SBR/EPR blending 하여 사용함

(용도)

tire, cable coatings, appliance parts

Table 21.1 Radial Passenger-Tire Tread Formulation

Ingredient	phr[a]	Function
SBR 1712[b]		
Polymer	45	Rubber polymer
Aromatic oil	37.5	Extending oil
cis-Polybutadiene 1252	55	Rubber polymer
Carbon black N-234	70	Reinforcing agent
Oil-soluble sulfonic acid	1	Processing aid
Sulfur	1.75	Vulcanizing agent
Stearic acid	2	Promotor
Zinc oxide	3	Promotor
N-Cyclohexyl-2-benzothiazole sulfenamid	1	Accelerator
Polymerized 1,2-dihydrotrimethylquinoline	2	Antioxidant
N-(1,3-dimethylbutyl)-*N'*-Phenyl-*p*-phenylene diamine	1	Antiozonant
Blended petroleum wax	3	Crack inhibitor and antiozonant
Total	222.25	

[a] Parts per hundred parts rubber, by weight.
[b] Oil-extended master batch. Cold emulsion polymer ≈75% butadiene, 25% styrene extended with highly aromatic oil.

Source. Stephens.[7]