Chapter 4

Industrial Polymers

addition polymers

condensation polymers

Overview

- history of development
  - cellulose nitrate ~ Hyatt, 1868
  - PF resin ~ Baekeland, 1909
  - concept of polymer ~ Staudinger, 1924
  - PVC, PMMA, PS ~ 1927-1930
  - nylon ~ Carothers, 1935
  - PE/PP ~ Ziegler/Natta, 1953
- classification of industrial polymers
  - addition polymers ~ C-C backbone
  - condensation polymers ~ heteroatoms
  - special ~ high-performance or high-functional

Addition polymers

- PE > PP > PVC > PS > PMMA ~ 5 GPPs
- mechanism
  - radical > coordination > anionic > cationic
- process
  - bulk ~ simple, heat, η, monomer ~ PS, PMMA, PVC
  - solution ~ solvent ~ PE, PP, PS
  - suspension (bead, pearl) ~ PS, PVC
  - emulsion ~ colloidal ~ only for radical

PE

- LDPE
  - free radical, high T and P
  - branched (LCB and SCB) ~ low X_c
    - chain transfer to polymer, not controlled
  - cheap, tough
  - sheet, packaging film
- HDPE
  - Ziegler-Natta or metal oxide
  - linear ~ high X_c
  - cheap, strong
  - bottles

- LLDPE
  - ZN copolym'n with α-olefin (4, 6, 8) ~ SCB
  - higher X_c, lower PDI than LDPE ~ better LDPE
  - films, molding
  - VLDPE ~ LLDPE w/ high comonomer content ~ rubbery
- high MW HDPE
  - MW > 2E5 ~ stiffer
  - pipes, larger BM
- UHMWPE
  - MW > 1E6 ~ high η ~ ram extrusion
  - high mechanical esp abrasion
  - machinery, fiber (Spectra®)

- modified PE
  - Cl- and SO_3Cl-PE
    - better (oil and weather) stability
    - low X_c ~ rubbery ~ fabric coating, cable sheathing
  - XLPE
    - radiation or peroxide Xlinking
    - foams, heat-shrinkable

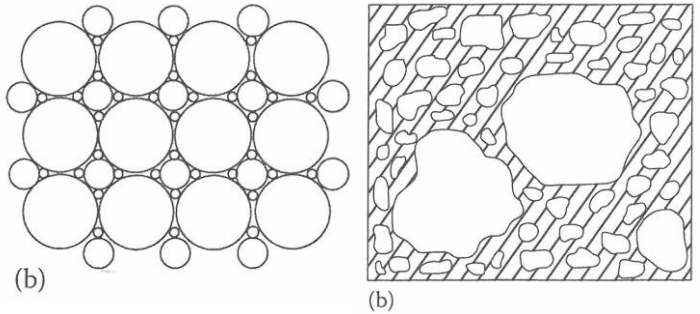
PP

- PP
  - ZN or metallocene catalyst
  - isotactic index (II)
  - compared to HDPE;
    - higher softening point (T_g)
    - lower stability (3° C)
    - less opaque (low $\Delta\rho$)
    - better hinge property
  - diverse applications
    - fiber > film (OPP, cast) > molding (growing ~ 'one material')

- random PP [random P-E copolymer]
  - compared to homopolymer;
    - higher clarity, lower T_m, lower strength ~ smaller parts
- block PP
  - higher impact ← phase separation
  - 'polyallomer' ~ block PP-PE ~ both crystallize

PVC

- polymerization
  - radical suspension popular
  - MW ~ ISO viscosity # Table 4.2
- UPVC
  - rigid (T_g = 80 °C)
  - pipe, wood substitute
- plasticized ~ paste
  - plastisol, organosol, plastisol w/ 'filler' polymer, hot melt (pouring), plastigel (putty) p455
  - η ← plasticizer content and particle size
  - many applications ~ film, sheet, molding



- CPVC
  - chlorination of PVC
  - higher T_g (> 100 °C), strength, stability
  - pipe for hot water, chemicals
- PVDC
  - high strength, good barrier (semicrystalline)
  - film, coating, fiber
    - Saran® (P(VC-co-VDC)) ~ food packaging

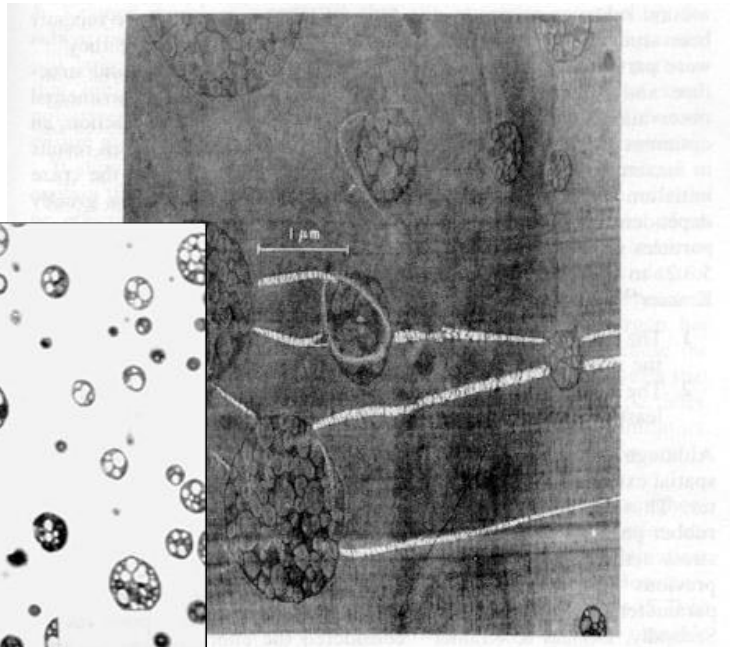
Fluoropolymers

- PTFE
  - suspension polym'n w/ or w/o pressure
    - granule or dispersion (lower MW, small part'l)
  - high X_c, stable C-F bond
    - thermal, chemical, electrical stability, non-stick
  - processing
    - granule ~ press-sintering, ram extrusion
    - dispersion ~ extrude with lubricant then sintering
    - coating ~ aqueous dispersion coating, baking, and sintering
  - coating, insulating, non-stick

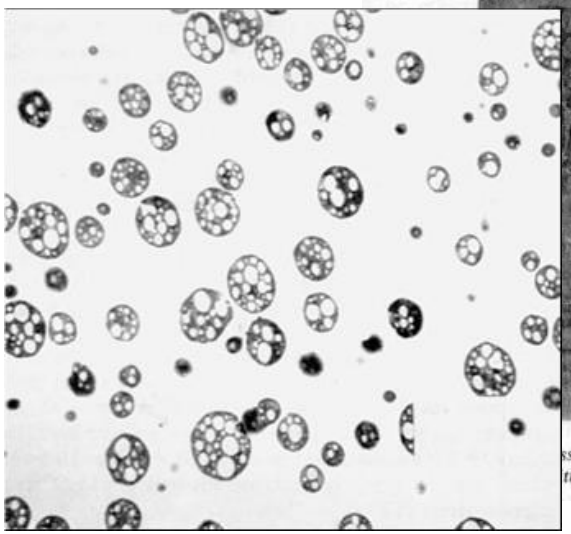
- variations of PTFE ~ melt-processable
  - copolymer (with HFP, E, PFA)
  - PCTFE, PECTFE
- PVF
  - better PVC ~ weatherability ~ outdoor film
- PVDF
  - good and cheap processable PTFE
  - piezoelectric, pyroelectric

PS

- easily polymerized and processed
- brilliant, brittle (fragile)
- HIPS
  - rubber (SBR or PBD) dissolved in ST and polym'n
  - 2-phase or 'salami' structure
- ABS
  - copolym'n of ST and AN with PBD
  - 'salami' structure
- EPS [XPS]



ssion electron micrograph of a microtomed section of HIPS, th osmium tetroxide (after Kambour & Russell[33]).

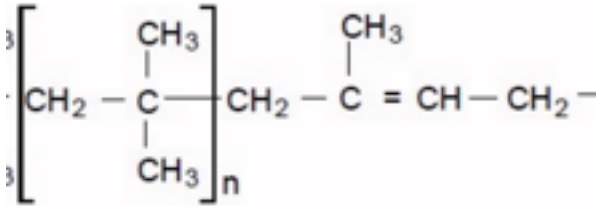


Rubbers

- PBD ~ BR
  - ZN polym'n ~ 1,2-, cis-1,4-, and trans-1,4
  - mixed with other materials for tire, HIPS, ABS
- PIP ~ IR
  - ZN polym'n ~ high cis, but lower cis than Hevea
  - tire, footwear, ---
- PCP ~ CR
  - radical emulsion polym'n
  - durable ~ belts
- SBR
  - emulsion polym'n
  - largest volume rubber ~ tire, ---

- NBR or nitrile rubber
  - emulsion polym'n
  - polar AN ~ oil-resistant
- EPR, EPDM rubber
  - ZN polym'n
  - EPR crosslinked with peroxide; EPDM with S
  - low or no = ~ better heat resistance ~ hose, seal
- butyl rubber ~ IIR
  - cationic polym'n ~ 98-99% PIB
  - good barrier ~ tire inner

<cf> 100% PIB ~ gum-base



p35 wrong

Thermoplastic elastomer (TPE)

- elastomer = rubber
  - rubber ~ (chemically) Xlinked ~ thermosetting
  - TPE ~ physically Xlinked ~ thermoplastic
- SBS, SIS
  - triblock copolymer by coupling SB or SI diblock
    - SB or SI by anionic polym'n
  - special type ~ T, X, star
  - glassy S domain
    - Xlinks and reinforces
  - blended for low creep
  - footwear, coatings, adhesives
  - Kraton®

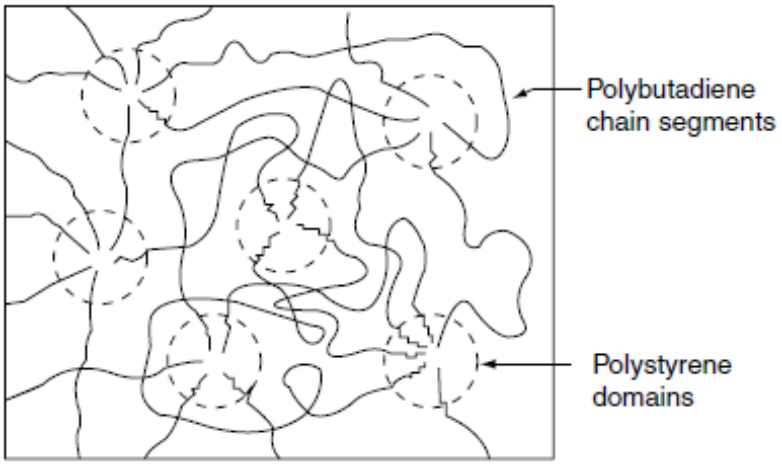
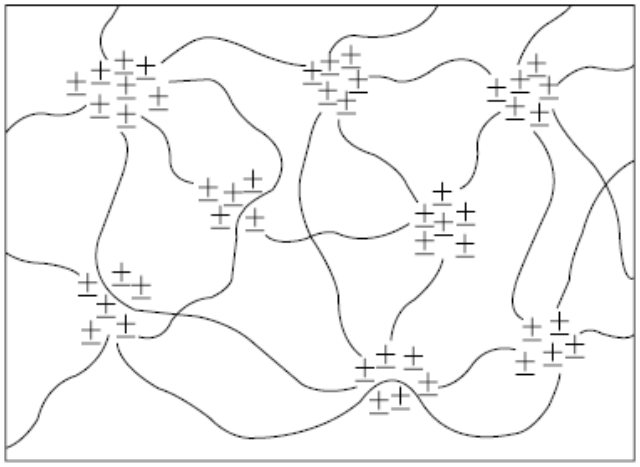


Fig 4.7

- polyester TPE
  - crystallizable polyester block + flexible polyether block
  - higher heat resistance (Hytrel®)
- TPU
  - hard and soft segments
  - elastomer or fiber (Spandex®, Lycra®)
- TPO
  - PP + EPDM ~ PP+P crystallize
  - auto parts
- ionic elastomers ~ an ionomer
  - EPDM-SO_3^- ~ Xlinked by M^+



Fluororubbers

- copolymers of VDF and other fluoro-olefins
  - Table 4.6 p470
  - Viton®
- high heat stability
- high chemical (oil) resistance

➢ summary of commercial rubbers Table 4.7 p471