

Radiation Polymerization

Grafting

Grafting

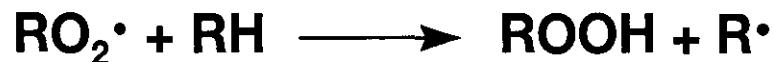
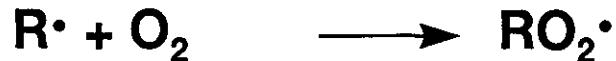
- **Chemical bonding of a monomer, to a polymer, by a polymerizing reaction**
- **Results in a polymer with short chains of another polymer on its surface**
- **A good method to change surface properties of a polymer**
- **Products include specialty textiles (wrinkle- or fire-resistant), battery separators, immobilized biomaterials, slow-release drugs**

Grafting Methods

- Pre-irradiation



- Peroxidation

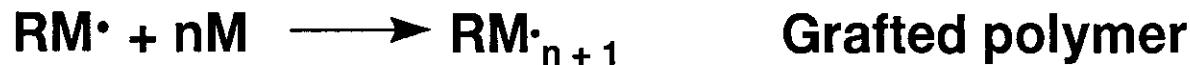
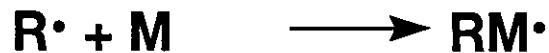


Extrusion
Injection
moulding

↓
Grafted Polymer

Grafting Methods (contd)

- Simultaneous irradiation



Variables Affecting Grafting Yields

- *Solvent*
 - Grafting yields may depend on the solvent, and on any additives present

Effect of Monomer Concentration, and Acid, on the Grafting Yield (%) of Styrene on Polypropylene, on Irradiation to 3 kGy

Solvent	Styrene (%)			
	20	20 ^a	40	40 ^a
Methanol	29	214	50	86
Ethanol	44	176	65	72
n-Butanol	123	214	34	83
n-Octanol	49	154	68	128
Dimethylformamide	24	32	43	56
Dimethylsulfoxide	11	17	66	93
Acetone	13	20	24	32
1,4-Dioxane	6	14	15	30

^a The solution contains 0.2 mol.dm⁻³ H₂SO₄, (Dworjanyn and Garnett , 1992)

Variables Affecting Grafting Yields (contd)

Comparison of Acid with Polyfunctional Monomers for Enhancing Grafting Yield (%) of Styrene to Polyethylene Film on Irradiation to 2.4 kGy

Additives ^a	Styrene (%) in Methanol			
	20	30	40	50
None	14	37	76	109
H ⁺	19	51	81	134
DVB	15	41	74	136
DVB + H ⁺	27	58	119	188
TMPTA	--	39	73	137
TMPTA + H ⁺	--	54	106	181

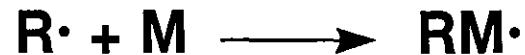
^a H⁺, 0.20 mol.dm³ H₂SO₄; divinylbenzene (DVB) and trimethylolpropane triacrylate (TMPTA) at 1 vol %
Dworjanyn and Garrett, 1992

Variables Affecting Grafting Yields (contd)

- **Dose Rate**



- At low dose rates



- At high dose rates



- At high dose rates crosslinking of the polymer and homopolymerization of the monomer are favoured over grafting

Effect of Dose Rate on Grafting Yield (%) of Styrene to Polyethylene from Methanol Solution

(Dworjanyn and Garnett, 1992)

Styrene (%)	100 Gy/h	410 Gy/h	1120 Gy/h
20	24	14	7
30	61	37	14
40	51	76	23
50	409	109	25

Grafting on Textiles

- Cotton/Polyester Material
 - N-Methylolacrylamide grafting reduces electrostatic charging, gives the material permanent-press and non-wrinkle properties (electron irradiation process introduced in USA in 1960)
- Cotton Fabrics
 - Grafting with fluorinated acrylates and silicones makes them water-repellant
 - Grafting with vinyl bromide triallyl phosphate and vinyl phosphonate oligomers makes them fire-retardant

Woods and Pikaev (1994)

Other Products

- **Oil Resistance**
 - **Radiation grafting of acrylic acid and acrylonitrile improves oil resistance of butadiene-styrene copolymer, and of ethylene-propylene-diene terpolymer**
- **Encapsulated Fertilizer**
 - **Successive radiation grafting of methyl methacrylate, followed by vinylidene chloride, on carbamide (carbamide/polymer, 95/5) to a dose of ~ 30 kGy, results in slow-acting (≥ 30 days) fertilizer**

Conclusions

- The use of radiation processing for grafting would continue to grow
- This is primarily an application for low energy electron accelerators (~0.3 MeV)