

Unusual cases of polymer crosslinking: additives and techniques

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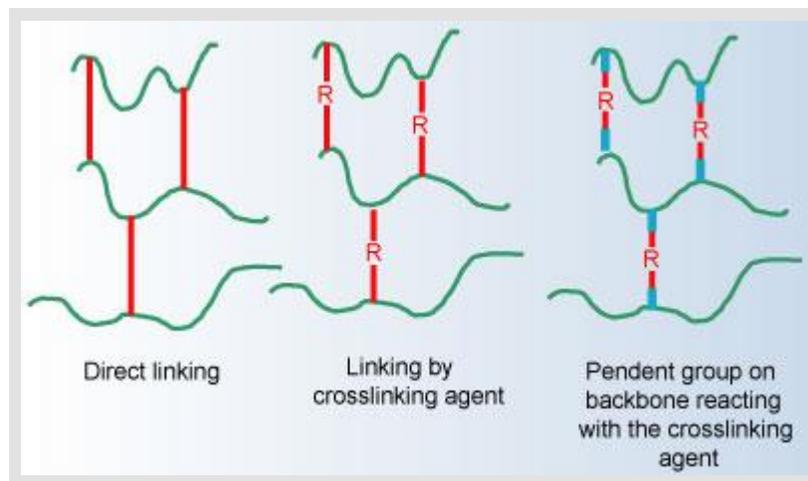
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Introduction

The crosslinking or curing consists in linking the independent macromolecules of a polymer to build a three-dimensional structure obtained by chemical or physical means. The following figure 'Polymer-Crosslinking-Examples' schematizes three examples of the molecular arrangements of the linked macromolecules forming a 3D network:

- Either by direct linking between two backbones
- Or by indirect ways consisting of intermediate species, crosslinking agents, branched to two backbones
- Or by indirect ways consisting of intermediate species, crosslinking agents, branched to pendent chemical groups (crosslinking sites).



Polymer-Crosslinking-Examples

Direct linking is often obtained by peroxides or electron beam irradiation. Crosslinking agents are a versatile and heterogeneous family including sulphur for the best known, isocyanates for polyurethanes, silane for polyethylene, resins or amines for special elastomers...

To make short, the processing methods can be classified into:

- Chemical reactions involving added crosslinking agents, possibly accelerated by heat brought by moulding, extrusion, oven, autoclave, salt bath, fluidized bed, microwaves...

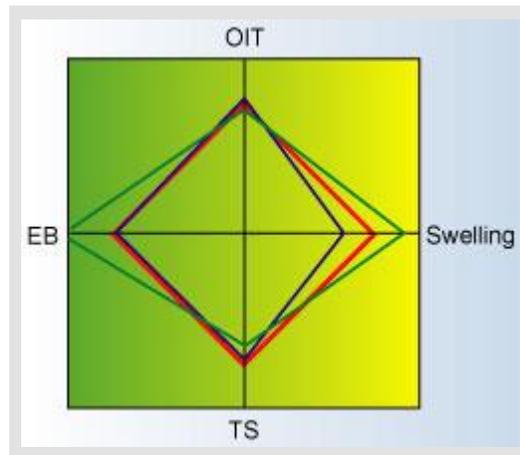


- Radiation processes: electron beam, UV, gamma rays, laser sintering...

Cursory glance at common and less common cases

- Epoxy resins can be crosslinked by cold & hot curing systems based on acid species, amines, amino resins, isocyanates, merkaptanes, phenolic resins...
- Amino resins can be crosslinked by cold & hot curing systems based on isocyanates, carboxylic acids or anhydrides, epoxy resins, phenolic resins...
- Phenolic resins can be crosslinked by cold & hot curing systems based on acid species, epoxy resins, isocyanates...
- Alkyd resins can be crosslinked by cold & hot curing systems based on acid species, amines, amino resins, isocyanates, phenolic resins, peroxides, photoinitiators...
- Acrylic resins can be crosslinked by cold & hot curing systems based on amines, amino resins, epoxy resins, isocyanates, phenolic resins, free radicals...
- Polyethylene can be crosslinked by systems based on peroxides, silanols, electron beam...
- Conventional elastomers can be crosslinked by cold & hot curing systems based on sulphur, peroxides, sulphur donors, isocyanates...
- Special elastomers can be crosslinked by cold & hot curing systems based on metal oxides, silanols, resins, amines...

This versatility expands the application field of polymers but leads to a large range of properties, each method bringing its advantages and drawbacks depending on the polymer and the used additives. The following figure 'PE-Properties-for-3-Curing-Processes' shows differences for Oxygen Induction Time (OIT), Swelling, Tensile Strength (TS) and Elongation @ Break (EB) according to the curing method: peroxide, silanol or radiation.



PE-Properties-for-3-Curing-Processes

One must keep in mind that heat and radiations can damage the polymer and that the end properties are a balance between crosslinking rate and degradation rate. Peroxides and radiation curing can lead to such a high degradation rate that the process becomes unworkable. For example, the polypropylene cannot be cured with peroxide and PTFE is powdered by electron beam exposition.



Brief reminders concerning some crosslinking processes

Microwave processes: the principle is well known but it can be useful to remember that commodity polymers made out of carbon and hydrogen cannot heat by microwaves. Let us quote polyethylene, polypropylene, polystyrene, natural rubber & polyisoprene, SBR, EPDM, butyl rubber, polybutadiene. To apply this technique it is necessary to add tiny amounts (10-50 % by weight) of materials heating under microwaves such as:

- carbon blacks
- metal powders (beware of fire risks)
- surface-treated silicas
- ferro- and ferri-magnetic powders
- barium and lead titanates and zirconates
- highly dipolar organic esters, phthalates, carboxylates
- polyoxyethylene glycols and related ethers and esters,
- Amines...

Another way consists in using low amounts (0.2 to 1%) of catalysts. Dr. F. PARODI (Smart Microwave Catalysts for UHF-Enhanced Polymerization Processes) describes the use of reaction catalysts promoting high rate increases (more than 4 times) in a great variety of chemical reactions including crosslinking. These catalysts generate microwave-sensitive intermediate species under microwaves but are thermally inactive in the absence of microwaves. Examples of applications are epoxy resin hardening by amino, anhydride and carboxylic acid curatives, crosslinking of epoxidized rubbers, silicone elastomers, sulphur-vulcanization of unsaturated rubbers, peroxide-vulcanization, curing of unsaturated polyester resins, allyl carbonate and allyl phthalate resins...

By contrast, some other polymers such as acetals, plasticized PVC, polychloroprene, nitrile rubbers, acrylic rubbers etc. are directly processible by microwaves.

UV curing

UV energy being at best equal to that of weak chemical bonds, is not energetic enough to directly activate most of chemical reactions. It is essential to add photoinitiators to start the initiation, propagation and termination steps of the polymer crosslinking. The photoinitiators can be classified as:

- **Type 1 Photoinitiators:** They create activated species by a unimolecular reaction - bond breakage within the photoinitiator itself:
 - Benzoin Ethers
 - Benzil Ketals
 - Alpha-Hydroxyketones
 - Alpha-Aminoketones
 - Acylphosphine oxides...
- **Type 2 Photoinitiators:** They create activated species by a bimolecular reaction - the excited photoinitiator acts as a photosensitizer to induce bond breakage within a second molecule.
 - Benzophenones
 - Amines
 - Thioxanthenes...

▲ **Type 2 photoinitiators are kinetically less efficient than Type 1**

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- **Cationic Photoinitiators**
 - Diaryliodonium salts
 - Sulphonium salts...
- **Anionic Photoinitiators**
- **Mixtures of Photoinitiators such as:**
 - hydroxycyclohexylphenylketone and benzophenone (Irgacure 500)
 - Alpha hydroxyketone and phosphine oxide...

Curable resin types: Only specific resins are curable by UV processing, such as, for example:

- epoxy-acrylate resins (the earliest UV curable resins)
- acrylate esters of polyfunctional alcohols or glycols
- polyester acrylates,
- polyether acrylates
- polyurethane acrylates
- epoxy-cationic

Processable parts: UVs are more or less rapidly absorbed by the polymer to be crosslinked and only thin parts are UV curable. Favourite applications are, for example:

- Inks, coatings for graphic arts.
- Adhesives.
- Decoration, printing, coating of wood, metals...
- Electrical, electronics and opto-electronics uses: Fibre-optics coating...
- Footwear, leather and textile industries...

In this framework, UV curing can offer:

- **Economical advantages:** High product output, cost effectiveness, energy savings...
- **Technical advantages:** low temperature processing, new product capabilities, high speed process...
- **Environmental advantages:** Energy savings...

Electron beam (EB) crosslinking

Ionizing radiations promote crosslinking of linear molecules but also degradation by scissions, cyclization etc. To be industrially used, it is essential for the ratio between crosslinking and degradation rates to be higher than 1. This ratio for a given polymer is radiation dose dependent. For example, ANDRADE E SILVA and ALL (Radiation Technology Center - IPEN, 'Polymer processing and modification by ionizing radiation') study the ionizing radiation effects on recycled polyamide-6. They show that for doses up to 500kGy in the presence of air, the crosslinking process is predominant while the degradation exceeds the crosslinking for doses above 600kGy. (Radiation doses are measured in Gray (Gy) or Rads (rd) or megarads (Mrd): 1 Gy = 1 J/kg = 100 rd = 0.0001Mrd)

The radiolysis resistance of polymers depends on general guidelines (and exceptions!) such as,

 among others:

- A simple structure of carbon and hydrogen atoms as, for example, $-(\text{CH}_2-\text{CH}_2)_n-$ for polyethylene, simultaneously leads to efficient crosslinking and low scissions and makes an EB crosslinkable polymer.
- Aromatic rings are radiation resistant but the other functions of the polymer can be radiation sensitive and jeopardize the resistance of the macromolecule. So, the replacement of one hydrogen of a polyethylene by an aromatic ring leading to polystyrene improves the radiolysis resistance.
- On the contrary, the replacement of two hydrogen atoms on the same carbon of a polyethylene by two methyl groups in polyisobutylene leads to a high sensitivity to radiolysis. Tetra substituted carbon atoms and branched chains are unfavourable.
- Halogen atoms, chlorine, fluorine, bromine make the polymer sensitive but there are exceptions such as PVDF, ETFE and so on.
- For backbones containing other atoms than carbon:
 - PDMSs $-(\text{SiR}_2-\text{O})_n-$ vulcanize by ionization.
 - Polyamides $-(\text{R}_1-\text{NH}-\text{CO}-\text{R}_2)_n$ vulcanize by ionization.
 - Cellulose based polymers are sensitive to radiolytic degradations.
 - Polyacetals $-(\text{CH}_2-\text{O})_n-$ are very sensitive to radiolytic degradations.

What doses with what accelerators?

Accelerators can be rated as follow:

- Low energy, up to ~ 0.5 MeV for surface treatment and crosslinking of thin films and coatings
- Medium energy, up to ~ 5 MeV for films, sheets, and composites
- High energy, up to ~ 10 MeV for pipes, thick sheets and plates, and composites.

The doses depend on thickness, type and recipe of polymers, for example:

- 30-160 kGy for coatings and foams
- 70-250 kGy for heat-shrinkable films and sheaths
- 80-400 kGy for rubbers and common plastic goods.

Supramolecular crosslinking by non-covalent interactions

K. CHINO (IRC 2005, Yokohama, papers 27-S4-08) and C. WU (IRC 2005, Yokohama, paper 28-G6-101) study the supramolecular crosslinking by hydrogen and coordination bonding using aminotriazole (ATA) and EPM or copper sulphate and NBR. Table 1 shows some properties compared to those of conventional vulcanizates:

- Thermoreversible hydrogen bond crosslinked EPM (THC-EPM is quite comparable to TPV but substantially different from a sulphur vulcanized EPDM (S-EPDM)
- Neat CuSO_4 -NBR is tougher than a neat sulphur vulcanized NBR (S-NBR) and less performing than a carbon black reinforced S-NBR.

Both have the economic and environmental advantages to be easily recycled.

		Property changes, %	
		THC-EPM	S-EPDM
Thermoreversible hydrogen bond crosslinked EPM			
Hardness, Shore A	73	48	72
Tensile strength	9		7
Compression set after 22 h @ 70°C, %	38	12	34
Thermoreversible coordination bond crosslinked NBR			
	CuSO4-NBR neat	S-NBR neat	S-NBR reinforced
Hardness, Shore A	60	54	72
Tensile strength	16	9	24
Elongation @ break, %	660	600	330

Table 1: Tensile Strength and Elongation of supramolecular crosslinked elastomers

Effect of electron beam irradiation on injection moulding Nylons

E-BEAM Services, Inc. ('Electron-Beam Processing of Plastics: An Alternative to Chemical Additives' presented at the 58th SPE Annual Technology Conference, ANTEC-2000) studies the crosslinking of an aromatic cycloaliphatic amorphous polyamide and its alloy with a linear nylon by electron beam irradiation to doses of 25 up to 75 kGy using a 4.5 MeV DC accelerator..

Table 2 displays the large differences of the behaviours:

- Aromatic cycloaliphatic amorphous PA is slightly affected
- The alloy tensile strength is highly improved while the elongation @ break dramatically decreases which probably is the sign of a significant crosslinking.

	Unexposed	EB irradiated		
		Property changes, %		
Irradiation doses, kGy	0	25	50	75
Aromatic cycloaliphatic amorphous PA				
Tensile strength	60 MPa	-13	-12	-11
Elongation @ break	121%	-11	-5	+8
Blend of the previous PA with a linear aliphatic PA				
Tensile strength	43 MPa	+66	+63	+57
Elongation @ break	132%	-96	-96	-97

Table 2: Tensile strength and elongation @ break of electron beam-processed Nylons

S. DADBIN and ALL (Polymer Degradation & Stability, 89, 2005, p.436) study the crosslinking of a polyamide 6 by electron beam irradiation to doses of 40 up to 150 kGy using a 5 MeV accelerator..

Table 3 displays significant differences with the previous results:

- The tensile strength and elongation @ break of pure PA6 are slightly affected
- The molecular weight of pure PA6 is slightly affected up to 100 kGy and then substantially increases
- Compounding with TAC slightly improves the tensile strength but the elongation @ break hardly drops. The HDT highly increases.

Irradiation doses, kGy	Unexposed	EB irradiated		
		Property changes, %		
	0	50	75	125
Pure PA				
Tensile strength	44 MPa	~0	~0	
Elongation @ break	260%	~0	~0	
Molecular weight	23000	+10	+20	+40
PA compounded with triallyl cyanurate (TAC)				
Tensile strength	44 MPa	+10	+10	
Elongation @ break	260%	-80	-85	
HDT	120°C	+33	+40	

Table 3: Property examples of a PA6 after EB-processing

A jumble of potential applications

Crosslinking is a versatile technique investigated as method to improve mechanical properties, solvent resistance, interfacial bonding, and to solidify liquid polymers or harden surface of polymers...

- T. SEMBA and ALL (ANTEC 2005 p. 2423) study the improvement of the brittle behaviour of PLA resin by alloying with PCL in the presence of peroxide. A low content of peroxide (0.1 to 0.2phr) imparts high elongations at break and a less brittle behaviour. The Authors consider that the co-crosslinked structure of the two polymers improves their interfacial adhesion.
- J.C. SANCHEZ-DIAZ and ALL (ANTEC) synthesises microstructured polyacrylamide-co-chitosan and polyacrylamide-co-chitosan/xanthan hydrogels with large swelling capacity and improved mechanical properties. Crosslinked polyacrylamide particles are dispersed in an aqueous solution of acrylamide and polymerized in the presence of a crosslinking agent and chitosan solution with or without the presence of xanthan polysaccharide solution. The swelling capacity of these hydrogels is superior to those of conventional acrylamide hydrogels.
- Australian scientists of the Swinburne University of Technology, M.STRAUB and ALL, make tiny models using a laser light fired into liquid polysiloxane resin, which starts a crosslinking reaction that locally solidifies the material. A computer programme controls the beam of light and the device allows the construction of complex microstructures as thin as about half the diameter of a human hair.
- United States Patent 5130161 describes the surface hardening of certain polymers by ion beam bombardment in presence of elements having a hardening effect and allowing crosslinking of the polymer surface. These elements are multivalent, such as, for example Fe, B, Cr, V, Ti, and S.
- United States Patent 4746725 describes the production of a crosslinked polycarbonate network by the reaction of cyclic polycarbonate oligomers with at least one polyepoxide compound, in the presence of a catalyst.
- United States Patent 4073577 describes contact lenses of hydrophilic polymer hydrogel made by photopolymerizing a hydroxyalkyl acrylate or methacrylate in the absence of a cross-linking agent.

Conclusion

The crosslinking of independent macromolecules of a polymer to build a tougher and more

 performing three-dimensional structure is often obtained through chemical reactions with sulphur and peroxides but other ways are also used such as isocyanates for polyurethanes, silanols for polyethylene, resins or amines for special elastomers...The reactions are often sped up by heating. Beside these technologies, there are more exotic routes, some of them being industrialized and the others being rarely used or being even at the lab step.

Microwaves, electron beam, UVs, gamma rays, laser sintering are industrialized for specific applications concerning, for example films, tubes, elastomers; coatings...

Certain supramolecular crosslinking are at the study step but can be considered promising. Many other applications are emerging to improve mechanical properties, solvent resistance, interfacial bonding, and also to solidify liquid polymers or to harden material surfaces...

References

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