

Crosslinked polyethylene

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Properties of polyolefins can be modified by crosslinking process. Different methods of crosslinking and effect of process parameters, selection of crosslinking agents and applications are briefly discussed.

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Polyethylenes are commodity plastics. They account for more than 70% of total plastics market. Polyethylene is easily available, at relatively low cost and easily processable. It finds applications in household items, packaging, insulation, net ropes, fishing rods or medical applications, etc. Polyethylene is processed at temperature in the range 150-250°C¹⁻³. Most polyethylene compounds contain reasonably good amount of fillers. Polyethylenes are thermoplastic in nature and therefore they can be reprocessed repeatedly. Polyethylene, however, will soften and flow, and lose critical physical properties at elevated temperature thereby limiting its applications^{4,5}. Therefore, crosslinking of polyethylene is carried out to retain desirable properties at high temperature. Crosslinking will change the nature of polymer from thermoplastic to thermoset to yield a non melting, more durable polymer matrix.

All types of important polyethylenes are crosslinked, like Linear low density polyethylene (LLDPE), Low density polyethylene (LDPE), High density polyethylene (HDPE) and Ethyl vinyl acetate copolymer (EVA) and Polyolefinic elastomer (POE). Branched structure is more suitable for crosslinking. Therefore, crosslinking of LLDPE and HDPE requires more attention.

Crosslinking leads to the formation of insoluble and infusible polymers in which polymer chains are joined together to form three-dimensional network structure⁶⁻⁸. In thermoset, crosslinking (curing) takes place through reaction between polymer chains with

several functional groups. These functional groups are capable of forming chemical bonds to convert thermoplastics into thermosets^{9,10}. McGrins¹¹ has described various commercially important crosslinked thermoset materials and their curing reactions. These are not of much relevance in the present study. For thermoplastics, crosslinking is a process in which high molecular weight thermoplastics are converted into thermosets.

Crosslinked polyethylenes are either extruded or injection moulded. When degree of crosslinking is deliberately maintained very low, the resulting compound is termed as crosslinkable polymer. Crosslinking can be combined with foaming also. Crosslinking of biopolymers and foaming is very common in food industry. Crosslinking for partially crosslinked extruded profile is commonly employed in furniture. Although crosslinking of thermoplastics such as nylon, polypropylene and styrenics has received attention in literature. Present review is directed to the crosslinking of polyethylenes only.

Crosslinked polyethylene forms a dense network of high molecular weight, which improves impact strength, environmental stress crack resistance (ESCR), creep and abrasion resistance without influencing tensile strength and density to any appreciable extent. Crosslinked polyethylene finds wide applications in packaging and electrical insulation applications and rotomoulding applications^{12,13}. The degree of crosslinking can change considerably from applications to applications. Some aspects of crosslinking are reviewed here.

Crosslinking process

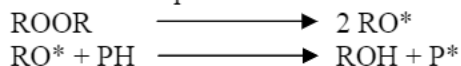
Crosslinking is a process in which carbon atoms of same or different polyethylene chains are joined together to form the three-dimensional network structure¹⁴⁻¹⁶. The crosslinking process essentially forms bonds between the polymer chains, which could be directly between carbon to carbon or a chemical bridge linking two or more carbon atoms¹⁸. The main difference between thermoplastic and crosslinked polymer is that, at temperature above the crystalline melting point crosslinked polymer behaves as a soft rubber while thermoplastic has no significant strength above melting temperature. The changes in the properties of polyethylene due to crosslinking have been compared and documented in literature^{16,17}. Thus, crosslinking reduces the melt index and elongation at break, while improves the impact strength, creep resistance, resistance to slow crack growth and also environmental stress crack resistance (ESCR). The density and tensile strength of polyethylene are not influenced by crosslinking.

The crosslinking of polyethylene takes place in four stages: initiation, propagation, branching and termination. The principal reaction involved in each step is discussed below.

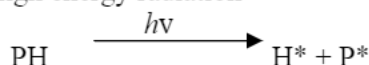
Initiation

The first step in crosslinking process is generation of free radicals, which can be through a chemical reaction or radiation energy. Decomposition of initiators which are normally peroxides, or high-energy radiations abstracts hydrogen atom from the backbone of polymer chain to produce free radicals.

a) Peroxide decomposition



b) High energy radiation



Propagation and branching

The free radicals react with atmospheric oxygen to generate peroxide radicals and through series of reaction crosslinking takes place, these are described by Peacock¹⁹. Crosslinking causes a dense network of different polymer chains through chemical bonding.

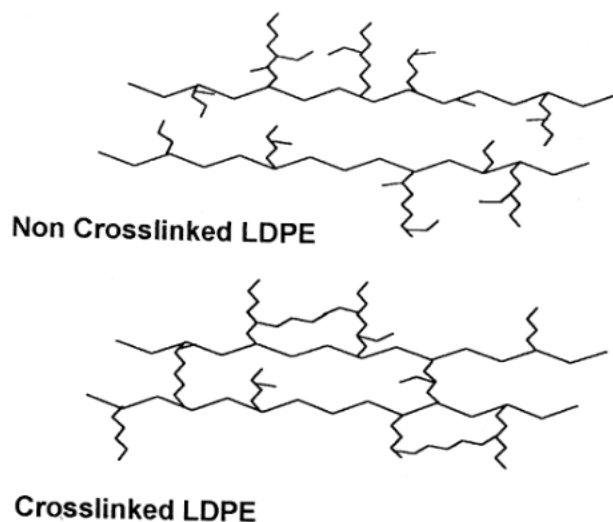
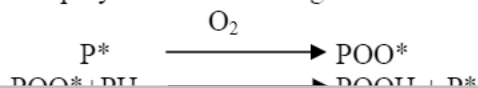
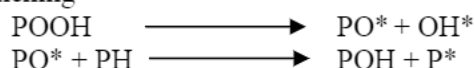


Fig.1—Schematic view of crosslinked and uncrosslinked polyethylene

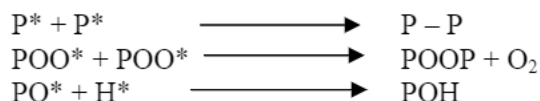
Branching



When P* on two sites join, it leads to branching or network formation.

Termination

Termination takes place by quenching of free radicals due to presence of additives, impurities etc.



Presence of side branches in a polyethylene chain is a reason for variation in number of important physical properties such as density, hardness, flexibility and melt viscosity. Presence of branches is the point in the molecular network where oxidation may take place. Crosslinking takes place between carbon atom in neighboring chains or chain branches joined together with other branches of chain or with the same chain of polymer. This is depicted schematically in Fig. 1.

The polyethylenes have different structures depending upon manufacturing process. Low density polyethylene is highly branched, while high density polyethylene and linear low density polyethylene are linear polymers. In general, branched polymers are easy to crosslink as compared to linear polymers, since formation of network is more probable for

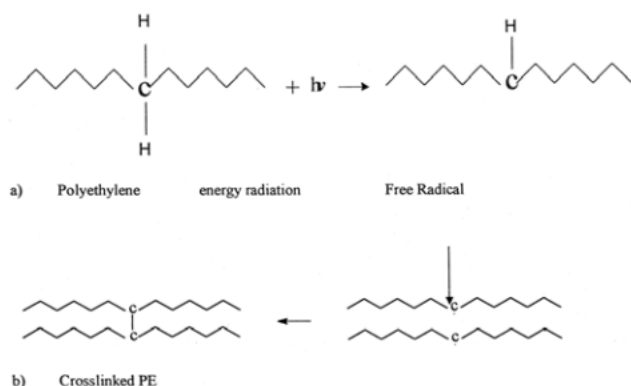


Fig. 2—Schematic representation of radiation crosslinking

Table 1— $G(X)$ and $G(S)$ values of some polymers

Polymers	$G(X)$	$G(S)$
LDPE	1.4	0.8
HDPE	2.1	1.3
Atactic PP	0.12 – 0.27	0.10 – 0.24
Isotactic PP	0.07 – 0.14	0.10 – 0.27
Polyvinyl chloride	2.15	-
Polypropylene oxide	0.15	0.22
Nylon (6 & 6,6)	0.5	0.6
Polyvinyl acetate	0.1 – 0.3	0.06 – 0.17
Polybutadiene	3.8	-
Polystyrene	0.045	< 0.018
Polymethyl acrylate	0.55	0.18
Polymethyl methacrylate	-	1.22 – 3.5

Crosslinking process is carried out by using (i) Physical or (ii) Chemical crosslinking methods.

Physical crosslinking

In this method, crosslinking is obtained by free radical mechanism. The free radical is generated in polymer chain by using high energy radiations²¹. This process is shown schematically in Fig. 2.

Thus, a free radical is generated by the high energy. Two or more chains, then, join together where the free radical is generated.

High energy radiation on polymeric material gives chain scission or crosslinking. The changes in physical and chemical properties depend upon the efficiency of crosslinking reaction and its relative ratio with degradation. Table 1 shows the number of crosslinking and chain scission per 100eV radiant energy absorption for different polymers.

Table 2—Types of radiation sources

Particulate	Non particulate
α - particles	Microwave
β - particles	Infrared
High energy electron	X-ray
Protons	γ -ray
Deuterons	Light energies (UV)
Neutron	

The relative scission to crosslinking ratio is given by²²

$$\frac{\beta}{\alpha} = \frac{1}{2} \frac{G(S)}{G(X)} \quad \dots (1)$$

Where,

α = probability of crosslinking of chains after one electron volt of energy absorbed.

β = probability of chain scission after one electron volt of energy absorbed.

$G(X)$ = number of crosslinking per 100eV radiant energy absorbed.

$G(S)$ = number of scission per 100eV of energy absorbed.

It is known that bond energy for cleavage of C-H bond is 364 kJ/mol. The electron beam having energy sufficient to break C-H bond is suitable for crosslinking²³.

Crosslinking of polymers by radiation and their technology involve four main variables.

- (i) Type of radiation and its sources.
- (ii) The nature of polymer structure to be irradiated.
- (iii) Mechanism and theories of reactions.
- (iv) Physical, chemical and mechanical properties of network formation.

Some of these radiation crosslinking are described briefly.

Radiation induced crosslinking of thermoplastics can be carried out using particulate or non-particulate radiations. These are listed in Table 2.

Particulate radiation sources are not commercially used. Only non-particulate radiation sources are used for commercial crosslinking of thermoplastics by radiation. Crosslinking by radiation mainly depends upon photon energy of radiation sources. The higher the photon energy, the more the penetration taking

Table 3—Wavelength and photon energy of some radiations

Type of radiation	Wavelength (nm)	Photon energy [MeV]
Infrared	1250	10^0
UV	125	10^1
Soft X - ray	12.5	$10^2 \cdot 10^3$
	1.25	
X - ray	0.125	$10^4 \cdot 10^5$
	0.0125	
γ - rays	0.001	1.2×10^6

energy of radiation is relatively dependent on wavelength. Table 3 depicts the relationship between radiation sources, wavelength and photon energies.

Selection of radiation sources mainly depends upon availability, the radiation penetration rate required, the dose rate and impact on manufacturing process (product handling, shielding, safety, equipment cost and maintenance).

The depth of high energy penetration is given by²¹,

$$r = k c^{1/2} e^{-1.151 \epsilon x} \quad \dots (2)$$

Where, r : rate of crosslinking reaction, c : concentration of photoinitiator, ϵ : extinction coefficient of photoinitiator, x : thickness of reactive polymer layer.

Thermoplastic crosslinking by UV radiation is a very slow process. Thermoplastic is mixed with photo-initiators, which makes it suitable to use UV light for crosslinking. UV radiation penetrates the polymer up to a depth of only a few millimeters^{24,25}. Therefore UV light is used for crosslinking of thin parts only²⁶. Ketones such as benzophenone, and benzil dimethyl ketal are suitable photo initiator for crosslinking of mainly polyethylene^{27,28}.

Electron beams will penetrate up to few centimeters of thermoplastic polymers. The crosslinking of moulded parts having thick wall results in variable crosslink density. Therefore, this process is mainly used for thin wall products such as films, shrinkable insulating parts and crosslinking of insulating cables and foams^{29,30}.

A microwave represents very high electromagnetic spectrum [10^9 to 10^{12} Hz]. Therefore, it is called as ultra high frequency (UHF) radiation source. Microwave crosslinking is independent on the part

energy gained by polymer in UHF field is given by the following equation³¹,

$$N = E^2 \cdot 2 f \epsilon_t \tan \zeta \quad \dots (3)$$

Where,

N = loss or gain of energy.

E = field intensity.

f = frequency (Hz) of the alternating field.

ϵ_t = dielectric coefficient.

$\tan \zeta$ = dielectric loss factor.

The drawback of microwave field is that, only components with polar group are excitable in this field. Thermoplastic such as polyethylene or polypropylene is non polar compound with very low $\tan \zeta$ value. Therefore, crosslinking of polyethylene in UHF field becomes very difficult. Crosslinking of polyethylene in microwave field is possible only by using intensely polar additives such as carbon black, peroxide, metallic powders and triallyl oxy-*s*-triazine^{32,33}.

Most of the applications of radiation crosslinked polymers are in electrical insulation and packaging films. These are briefly described in Table 4.

Advantages of radiation induced crosslinking

Advantages of radiation induced crosslinking are briefed below:

- (i) crosslinking reaction takes place at room temperature,
- (ii) reaction is completed in fraction of seconds, hence high output is obtained,
- (iii) reaction can take place without any additives,
- (iv) highly suitable for relatively thin insulating layers,
- (v) crosslinking takes place in only one step.

Disadvantages of radiation induced crosslinking

Some of the disadvantages of radiation induced crosslinking are given below:

- (i) high capital cost,
- (ii) difficult to cross-link article with irregular shapes,
- (iii) Safety precautions are needed to protect

Table 4—Commercial uses of radiation-processing techniques

Substrate	Radiation process	Commercial use
Polyolefins and PVC	Cross-linking with high-energy radiation sources in 0.4-3 Mev range.	Wire insulation for computers, and communication application
Polyolefins and PVC foams	Cross-linking with high energy electron	Improved thermal stability for insulating and packaging application
Polytetra fluoroethylene (Teflon)	Degradation by high energy electron or cobalt-60 in 0.2-0.4 May	Conversions of waste Teflon material into easily moldable powder or waxes of commercial value
Wood impregnated with acrylic or methacrylic monomers	Polymerization with cobalt-60 source	No-wear high performance wood floors for high traffic areas
Curing of coating and adhesives	Low energy electron processing equipment in 100-500 Kev range	Adhesive products for modification of wood, textiles, paper, film and metal substrates

Chemical crosslinking

Chemical crosslinking is a method, in which chemicals or initiators are used to generate free radicals, which in turns leads to crosslinking. In this method, crosslinking takes place through direct carbon-to-carbon bonds or through the chemical bridges which connect different polyethylene molecules³⁴⁻³⁶.

Degree of crosslinking in thermoplastic resin varies according to crosslinking process. Chemical crosslinking by using peroxide gives highest and uniform degree of crosslinking as compared to physical crosslinking method. Kim and White have reported the difference in degree of crosslinking between physical and chemical crosslinking processes³⁷. Accordingly, radiation crosslinking yields between 34-75% degree of crosslinking. In chemical crosslinking method, peroxide gives much high degree of crosslinking (up to 90%), while silane based crosslinking can be 45-70% degree of crosslinking.

Peroxide initiated crosslinking process depends on several variables, namely operating temperature, type and concentration of peroxide, and molecular characteristics of virgin resin such as, molecular weight, molecular weight distribution, branch distribution and concentration of terminal vinyl groups.

The two main chemical crosslinking methods are,

- (i) organic peroxide based and
- (ii) silane based (moisture cured).

Crosslinking of thermoplastic by peroxide

Peroxide crosslinking has been in use for more than 40 years and is the most common method for crosslinking of thermoplastics especially polyethylenes. In this method, organic peroxide is used as initiator. Usually, organic peroxide is used in

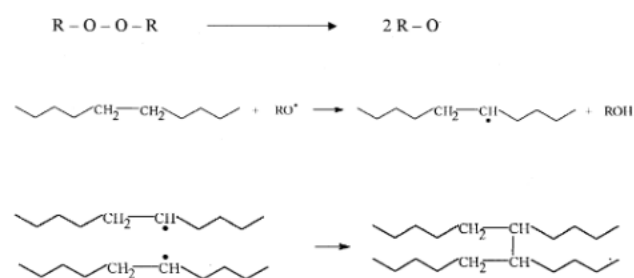


Fig. 3—Schematic representation of crosslinking of polyethylene

processing equipment operates at higher temperature. The compounding of polyethylene and peroxide must be carried out at low temperature, below the peroxide decomposition temperature. Crosslinking is carried out in the downstream equipment at significantly higher temperature and pressure. The higher temperature decomposes the initiator and liberates a free radical that will abstract a hydrogen atom from polymer chain. This abstraction site then becomes reactive radical, forming a crosslinked bond with another reactive radical of same or different chain. This reaction occurs until all peroxide is consumed or the temperature falls below the decomposition point^{38,39}. Schematic representation of this reaction is shown in Fig. 3.

Elimination of hydrogen atom converts tertiary hydrogen atoms of polypropylene and polyethylene to tertiary radical chain with low reactivity. Tertiary radical sites are not very reactive and are not converted easily into more reactive secondary radicals. The shifting of the radical site along branched chain is hindered, and dimerization of chain radical becomes more difficult. Number of peroxides, which are suitable for crosslinking of thermoplastic and their dissociation temperatures, are listed in Table 5.

Dicumyl peroxide (DCP) is widely used for

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