



Polyethylene Cross-linking by Two-step Silane Method: A Review

Jalil Morshedian* and Pegah Mohammad Hoseinpour

Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115
Tehran, Iran

Received 18 August 2008; accepted 27 January 2009

ABSTRACT

Cross-linking of polyethylene is a subject of interest, having been emerged as a result of the need to meet application requirements which were not satisfied by the neat polyethylene itself. Although this review is aimed at silane method of cross-linking, the other cross-linking methods, namely: radiation, peroxide and azo methods have been presented briefly for a better understanding of the merits of perspectives of the more recent methods, especially the two-step silane method. Free-radical grafting of unsaturated hydrolyzable alkoxy-silanes onto polyethylene chains by a peroxide initiator followed by moisture cross-linking is the most versatile cross-linking method and may be successfully used for other thermoplastics as well. Different techniques of silane cross-linking, i.e., the "one step" Monosil[®] process and the "two-step" Sioplas[®] process have been discussed with more emphases on Sioplas[®] process, as it is less expensive and readily achievable. The grafting step which is performed by reactive processing is the major and key process in Sioplas[®] technique. The state-of-the-art of a two-step silane grafting and cross-linking has been presented. In this regard, the effects of various parameters, such as the type and quantity of silane, peroxide, stabilizing agent, catalyst, micro and macromolecular structures and physical form of polyethylene, additives, and reaction temperature and time have been described in relation to efficiency of grafting and cross-linking. These data were evaluated in turn by torque, MFI, FTIR, and gel content studies.

Key Words:

polyethylene;
grafting;
cross-linking;
Sioplas[®] process;
FTIR.

CONTENTS

Introduction	104
Methods of Cross-linking of Polyethylene	105
Radiation Method.....	105
Peroxide Method	106
Azo Method.....	106
Silane Method.....	107
Sioplas [®] Process.....	107
Monosil [®] Process	109
Alternative Variations for Sioplas [®] and Monosil [®] Processes	109
Ethylene-silane Copolymers.....	109
Dry-silane	110
Applications	110
Comparison of Different Cross-linking Methods	110
Study of Sioplas [®] Process.....	112
Principles of Manufacturing Process.....	112
Moisture Curing.....	112

(*) To whom correspondence to be addressed.

E-mail: J.Morshedian@ippi.ac.ir

Evaluation of the Grafting and Cross-linking Reactions	114
Important Parameters in Silane Grafting and Cross-linking.....	116
Peroxide.....	116
Silane	116
Antioxidants.....	116
Catalyst.....	117
Pre-mixing the Reactants and Polymer Physical Form	118
Polyethylene Molecular Weight, Molecular Weight Distribution, and Grade	118
Curing Time and Temperature.....	119
Incorporation of Typical Additives	120
ZnO.....	120
Carbon Black.....	120
EVA	120
EPDM.....	121
Typical Properties.....	122
Mechanical Properties.....	122
Thermal Properties.....	122
Conclusion and Future Outlook.....	123
Abbreviations.....	124
References.....	124

INTRODUCTION

Polyethylene is a volume leader in the global plastic industry with numerous applications. However, its low upper service temperature makes ordinary polyethylene unsuitable for the applications requiring con-

tinuous use under stresses at temperatures up to 100°C (for example in hot water pipes) or occasional increases in temperature above a certain limit during extrusion and temporary electrical overloads on cables. By cross-linking of polyethylene some important properties would be drastically improved (Table 1) [1-5]. Some applications include heat shrinkable products (in cable installation), heat-resistant foodstuff packaging (up to 200°C), foams for thermal insulation, and chemical-resistant seals [6-9]. Moreover, cross-linked polyethylene is more resistant to water treeing and tracking which are undesirable in cable jacketing industry. Besides the capability of cross-linked polyethylene in withstanding higher electric loading, its ability to tolerate thermal shocks, and the small thickness required for insulation, makes it a suitable candidate for cable jacketing industry. Polyethylene has the melting point of 100-130°C, however, after cross-linking no flow would be noticed even at 150°C [10] where elastic behaviour prevails. In addition to the advantages associated with cross-linked polyethylene, it is also capable of absorbing high loadings of fillers (e.g., carbon black) compared to uncross-linked polyethylene which becomes brittle on incorporation of fillers. The reason is that by formation of cross-links, the particles are bonded and trapped within the polymer matrix. As a result, levels of filler that are disadvantageous and make the polymer brittle would impart reinforcement in cross-

Table 1. Changes in properties of polyethylene after cross-linking.

Property of polyethylene	Change after cross-linking of polyethylene
Melt index	Decrease
Density	No changes/decrease
Molecular weight	Significantly increased
Tensile strength	No changes/slightly increase
Elongation-at-break	Decrease
Impact resistance	Significantly improved
Abrasion resistance	Greatly improved
Stress-crack resistance	Greatly improved
Elastic properties	Greatly improved
Environmental stress crack resistance	Increase
Resistance to slow crack growth	Increase
Temperature resistance	Greatly improved
Chemical resistance	Significantly increased

linked polyethylene [11]. Some advantages of using cross-linked polyethylene pipes instead of metal pipes include: lower installation costs, long service life, easy replacement of damaged parts, good chemical and abrasion resistance, etc. [12-14]. Table 1 briefly presents some properties of polyethylene which are subjected to change by cross-linking.

There are different methods of cross-linking of polyethylene. However, despite being the most important cross-linking technology in production of cables and pipes, there is not yet a comprehensive review study on silane method, particularly on the “two-step” Sioplas® process which is the subject of this study.

METHODS OF CROSS-LINKING OF POLYETHYLENE

XLPE and PEX are the terms used in this review for cross-linkable and cross-linked polyethylene, respectively. Cross-links may comprise either direct carbon-carbon bonds or bridging species such as siloxanes [15]. Cross-links occur at random intervals along the chains; in which the concentration can vary widely, from an average of only one cross-link per several thousand carbon atoms to one per few dozens [16]. Several methods have been developed to cross-link polyethylene including: azo, peroxide, and silane as chemical methods and the radiation as a physical method (Figure 1). Amongst these methods,

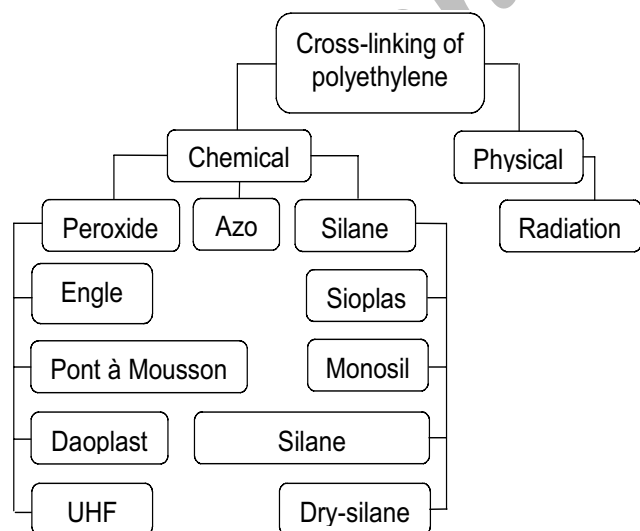


Figure 1. Polyethylene cross-linking methods.

cross-linking via silane grafting is a common and efficient approach to cross-link polyethylene which per se has no functional group or curing site for cross-linking in a way similar to thermoset resins [17,18].

It is possible to quantify the degree of cross-linking (i.e., a measurement of quality control) in any of the aforementioned cross-linking methods by the xylene extraction process set forth in ASTM D2765 or DIN 16892 [19-22]. The measurement of gel content is a direct way to assess the degree of cross-linking [23].

Radiation Method

In 1948, Dole treated low density polyethylene with high energy radiation [24]. Electron beam, gamma rays, or ultraviolet radiation were used for radiation cross-linking of polyethylene [25]. In radiation method, the excited electrons are used to strike the molecules at or near a carbon-hydrogen bond, and thus, creating a free hydrogen atom to leave the parent molecule in an excited state (free radical). Two adjacent aforementioned sites can form a chemical bond. Meanwhile, the two corresponding hydrogen atoms also form a hydrogen molecule which diffuses out of the structure. Radiation is carried out on the already formed articles, i.e., in solid state and typically in an inert atmosphere to prevent oxidative degradation. The cross-linking density at a given irradiation dose depends on the amorphous portions of the polymers, as it occurs in the amorphous phase of the polymer [11]. No temperature restriction in extrusion processing and no residual peroxide or unwanted byproducts, high cross-linking rates, and space savings for the equipments are the advantages of radiation cross-linking method [13]. However, there is an uneven cross-linking which may occur as well as having a limitation in cross-linking maximum thicknesses. Meanwhile, the high initial investment and running costs, high voltages needed for cross-linking thick sections, and the necessity of protecting technicians from radiation and the required governmental permission are some of the other important drawbacks of this method.

In industry, accelerated electrons are more common as the radiation source, since they are capable of reaching high doses of energy per unit time compared with other sources and also the equipments are easier

to control; γ -rays (if used as irradiation source) are produced through a nuclear process and thus are difficult to be controlled or to cut the emission whenever it is needed [26]. The most important advantage of radiation method is that there is no limit in the extrusion rate, as there is no risk of premature cross-linking.

Peroxide Method

Peroxide cross-linking of polyethylene (at high temperatures) was the very first commercial method, similar to rubber vulcanization [27-29]. In this method, peroxide based chemicals (dicumyl peroxide as the most common initiator) are used and thus create carbon-carbon links to form the network in polyethylene by the elimination of hydrogen atoms. Polyethylene, containing a peroxide compound, is melted quickly under controlled temperature to prevent premature cross-linking, in a chamber equipped with a reciprocating piston and then it is shaped into a pipe with conventional dies, or is wire coated via cross-head extrusion. Further heating under pressure allows the peroxide to decompose and cross-link the product.

Methane gas is released as a by-product during the cross-linking reactions [30]. Therefore it is required to use high pressures (typically 12 to 20 bar) on the reaction mixture, unless pin holes or pores would be formed in the final product as a result of methane release. The extruder used in this process should have a short L:D ratio with a specially designed screw. Since peroxide is incorporated within the polyethylene compound, the processing temperature (for example in extruder) should be under the precise control, or it may lead to premature cross-linking.

The common variations of peroxide cross-linking are Engel method (the first commercially available cross-linking method), Pont à Mousson method (PAM) and Daoplast method [31]. In the Engel process, a mixture of polyethylene (HDPE) and peroxide is fed into a reciprocating plunger extruder; this is done under high pressure, therefore the polyethylene powder is sintered together, and then passed through a long, heated die, allowing the cross-linking to take place. Low- and medium-density polyethylene or HDPE with a fairly low molecular weight can be cross-linked via Pont à Mousson process, in which a mixture of polyethylene and peroxide is extruded, fol-

lowed by cross-linking in a salt bath at temperatures ranging from 250°C to 280°C. In the Daoplast process, polyethylene (without peroxide) is extruded into a pipe and profile; peroxide would diffuse into the extruded product by putting the product in a surrounding media containing peroxide. Peroxide decomposes under applying high temperature and pressure. Ultra high frequency (UHF) initiation can be used to cross-link HDPE pipes and the peroxides used in this method are decomposed by microwave radiation. A kinetic study of the peroxide cross-linking of polyethylene has been reported in literature [32].

High capital investment for the equipments, energy-intensive nature of the process, high scrap rates and low outputs are some limitations of the peroxide cross-linking method.

Azo Method

In this two-stage method, azo compounds (molecules containing -N=N- groups) e.g., aliphatic azoesters such as 2,2'-azobis(2-ethoxypropane) are used as initiators to form the cross-linked network in polyethylene [13,33]. As in the radiation method, the products can be processed via common thermoplastic processing methods. To avoid the premature cross-linking during the product formation, the processing temperature should be kept below the critical temperature of azo compounds reactivity. Thereafter, cross-linking is carried out in a vulcanization tube or a salt bath at high temperatures (240-270°C). It should be noted that the decomposition temperature of azo initiators is higher than that of the most thermally stable peroxides. These azo compounds are particularly suitable for cross-linking of products of high molecular weight polyethylene which requires higher processing temperatures. The resulting products of azo compounds decomposition include nitrogen, methane, carbon monoxide, ketone, alkyl acetate, and radicals that abstract hydrogen from polyethylene and leads to the formation of carbon-carbon cross-linking. Azo compounds are more stable than peroxides and in the case of 2,2'-azobis(2-ethoxypropane) the decomposition products include ethoxy propane radicals that may react with a hydrogen atom of polyethylene chain and form two alkyl macromolecules [33]. Some 2-ethoxy propane radicals also decompose and form acetone, carbon monoxide, acetyl and methyl radicals. Methyl

radicals may react with hydrocarbon chain to produce methane and alkyl macro-radicals. It is important to note that in this method there is a limitation in incorporating antioxidants, as they may interfere with the reaction. Besides, considering the formation of aforementioned gaseous low molecular mass compounds, azo initiators can be used for the production of expanded cross-linked polyethylene products.

A disadvantage of a typical azo compound would be the low activity of the primary radicals formed during the transfer reactions which lead to low cross-linking efficiency.

Silane Method

Silane coupling agents are silicon-based organic chemicals that contain two types of substituent (inorganic and organic) in the same molecule [34,35]. Their typical general formula is $(X)_3Si-Y$, where X represents a hydrolyzable group such as ethoxy or methoxy, Y is a functional organic group (amino, methoxy, acetoxy, epoxy, etc.) that reacts with water to form silanol (Si-OH). They include more than 90 percent of the plastic coupling agents market and are also used in cross-linking of polyolefins and some other polymers [36-38].

Since the silane groups are polar they provide compatibility in polyethylene based blends, where the polyethylene is non-polar in nature [15]. Vinyl alkoxy silanes (e.g., vinylmethyldimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane) are suitable compounds for these kinds of reactions due to their double bonds and ability to rapid cross-linking. Vinyltrimethoxysilane is the most common silane used in the manufacturing of silane cross-linkable polyethylene [39].

The silane-grafting by water-cross-linking method consists of at least two stages that would also proceed consecutively [40]. In the first stage, a proper silane (vinylalkoxysilane) is grafted via its vinyl groups on polyethylene through a peroxide initiated free radical reaction; it should be noted that during the grafting reactions, new polyethylene radicals are formed (Figure 2) and the required amount of peroxide is relatively low. In the second stage, the resultant copolymer is cross-linked via the exposure to hot water or steam with the aid of a catalyst. Moisture leads to hydrolysis of alkoxy groups of silane and thereafter,

these hydroxyl groups condense to form stable siloxane linkages (the cross-links). Figure 2 illustrates the reaction mechanism during peroxide induced melt grafting of vinyl silane onto polyethylene, followed by the hydrolysis and condensation step during the silane cross-linking reaction.

The grafting step may be performed while the polymer is in molten state and the cross-linking step is normally carried out after the grafted polymer has been shaped into the final product and is below its melting temperature. Easy processing, low capital investments, and favourable properties of processed materials are the advantages of silane method. Besides cross-linking of polyethylene, silane method is also used for some other polymers such as poly(vinyl chloride) [41], polypropylene [42], polyamide [37], poly(vinylidene fluoride) [43], ethylene-propylene rubber [68], etc.

Cross-linking polyethylene through silane grafting has some disadvantages: an increase in the material costs due to the expensive organosilane compounds; long, geometry dependent reaction times due to the diffusion controlled mechanism of cross-linking; significant differences in the gel content and consequently in the product properties in case of minute changes in the formulation [44].

The term "silane cross-linkable polymer" refers to a silane grafted polymer which is intended for curing but has not yet been cured, and the term "silane cross-linked (cured) polymer" refers to a product which has already been subjected to a moisture curing step and is the finally cured product which is intended for end use [20]. Based upon the possibility of performing the two stages in silane cross-linking either together or separately, two processes have been introduced, namely Sioplas[®] and Monosil[®].

Sioplas[®] Process

Sioplas[®] process was developed in 1968 by Midland Silicones Co. (Dow Corning Co.) [45]. In this method, a mixture of silane and peroxide is added to molten polyethylene, leading to silane grafting reaction, which is a classical free radical chain reaction involving a catalyst. The silane grafting reaction is usually performed in molten polyethylene by means of reactive extrusion, where an extruder is used as a reactor of continuous action. Grafting reaction in the

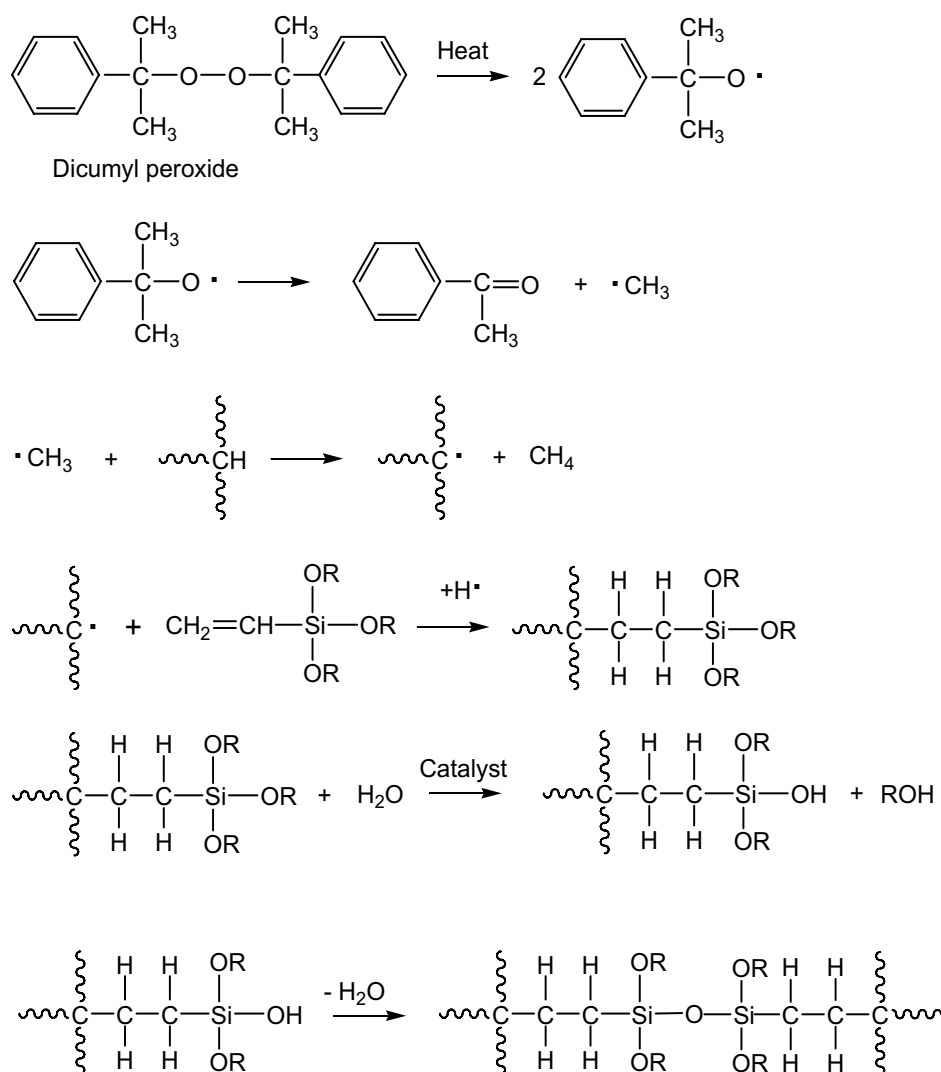


Figure 2. Principal reactions involved in silane cross-linking of polyethylene.

extruder (140-240°C) is very fast which allows the choice of industrial processing extruder. Usually high-shear compounding extruder such as co-rotating twin-screw extruders with L:D ratio range of 30 to 36, or ko-kneaders such as Buss-kneaders are used. Feeding may be done by discontinuous or continuous metering and mixing of ingredients into the extruder hopper or direct injection of the silane and peroxide solution into the melted polymer. Thereafter, the grafted polymer is pelletized and is capable of being stored in a dry place, usually in sealed vacuum bags (although not more than 6 to 9 months, or premature cross-linking would occur). When it is intended to produce the final product, a catalyst masterbatch (con-

sists of polyethylene, a catalyst, an antioxidant, a proper stabilizer, and an internal lubricant) is mixed with the above mentioned pellets in a typical weight ratio of 5:95 [46], and the resultant mixture is melted, followed by extruding into the product (Figure 3). Cross-links are created through exposing the product to water or steam (at temperatures of 70 to 90°C). High output rates, low scrap and the possibility of using conventional extrusion equipments are advantages of this method.

The grafting rate can be described by a kinetic equation of first order with respect to vinyl silane. Feeding, temperature profile, screw configuration and design, shearing actions and residence time are

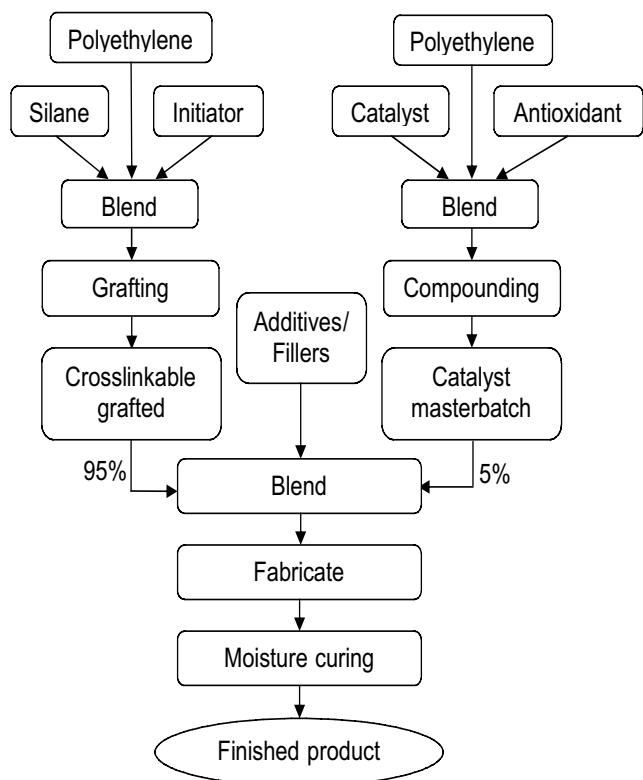


Figure 3. Procedures of Sioplas® process.

important processing parameters.

Monosil® Process

Monosil® process, announced by BICC Limited and Establishments Maillefer SA in 1974 [47], is a one-step process by using a specially designed extruder with a high L:D ratio, silane is grafted onto polyethylene and the product is cross-linked in presence of moisture [48]. Initially all the equipment for this type of process bore the name Monosil, but now it is also known as the Nokia-Maillefer process [49]. In this process, all the ingredients are fed directly into the extruder and there is a risk of premature and excessive cross-linking (Figure 4). Some disadvantages of this process are high initial investment, extensive operation training, and high degree of specialization to manage and reduce the scraps. Besides, as some chemicals would interfere with grafting reaction, the formulation in this process is critical and usually a know-how technology which is provided by material supplier company. Maillefer has developed a special screw geometry with an L:D ratio of from 24 to 30, whereas Nokia-Maillefer uses single-screw extruders

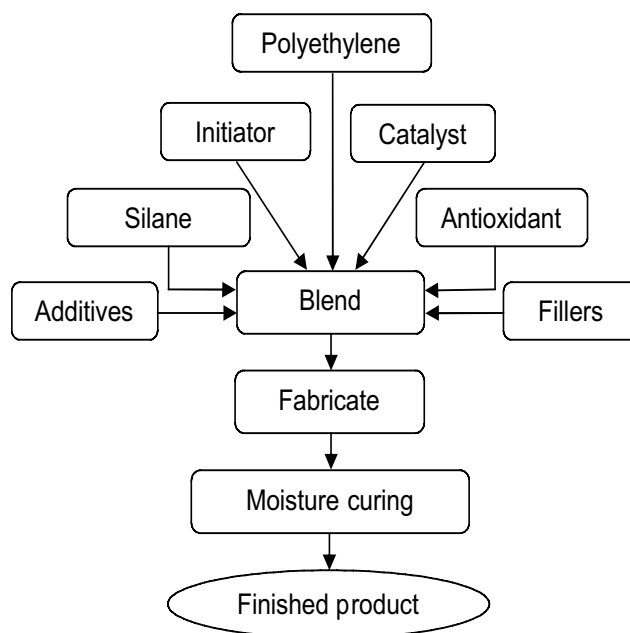


Figure 4. Procedures of Monosil® process.

with specially adapted screws. However, one step silane cross-linking is now also carried out via twin screw extruders [9]. Low density polyethylene grades which are suitable for the Monosil® process have densities of between 0.918 and 0.930 g/cm³ and melt flow indices of around 0.3 g/10 min.

Alternative Variations for Sioplas® and Monosil® Processes

Ethylene-Silane Copolymers

A one-pack method in creating silane cross-linkable polyethylene involving the use of ethylene-silane-copolymers has been introduced in 1986. Some companies, e.g., Union Carbide (USA), Borealis (Sweden), and Mitsubishi (Japan) have taken the lead by offering these copolymers [49]. The copolymer is produced by adding silane during the production of polyethylene in reactors. The copolymer products are more stable during storage and are cured using a catalyst and water, precisely as in the case of a Sioplas® graft copolymer [49]. Ethylene-silane copolymer is used as insulation in low and medium voltage cables and its main application is for underground, overhead, industrial, and floor heating cables. A detailed study of cross-linking reactions in ethylene-silane copolymers is available in literature [50].

Compounds which are based upon these ethylene-

silane copolymers would be capable of absorbing high loadings of filler. Meanwhile, as the silane monomers have enough time in the polymerization reactor, they would have a regular distribution in final polymer, which makes it possible to have a more uniform network after cross-linking. Cross-linking process in these compounds is carried out like the two other previously mentioned methods (Monosil[®] and Sioplas[®]). Considering that this one-pack method involves no free radical formation, there is less limitation in selection of antioxidants and additives. Furthermore, due to the presence of no volatile by-products, no void or pin-hole would form in the final product. This feature makes ethylene-silane copolymer a proper material for cable manufacturing. Another advantage is the longer storage life prior to introducing the catalyst (even up to one year storage is possible).

In this one-pack method, standard polyethylene extruders as well as PVC extruders could be used [26] and there is no need to handle flammable liquids (i.e., silane). However, as the silane copolymers are prepared under high pressure, it would be only possible to manufacture LDPE type copolymers, while the Monosil[®] and Sioplas[®] can involve LDPE, LLDPE, MDPE or HDPE or even copolymers such as EVA, EPDM, or EPR.

Dry-silane

A relatively new variation in silane method is Dry-silane technology. It is very similar to Monosil[®] except that instead of using liquid additives, the silane, initiator, and catalyst are absorbed into a porous resin (typically polypropylene, ethylene vinyl acetate (EVA), high- or low density polyethylene), called masterbatch [48]. Swellable carriers and encapsulated masterbatches are also reported [51]. The Dry-silane masterbatches (in pellet, powder or granular form) are available with different silane loadings in the range 40 to 70 wt% [52]. Dry-silane technology can be used for a wide range of LDPE and LLDPE grades. The sensitivity of Dry-silane masterbatches to humidity makes it necessary to use carriers substantially free from water.

Applications

In polymer blends the polar silane groups provide

compatibility. In applications with surface adhesion, bonding to inorganic surfaces of glass, metals, or other materials is achieved via the silanol groups of the silane. In the case of filler, the degree of filling is considerably increased. Flame-retarding materials become much more effective through the formation of a stable ash. Silane products are used for example in the following applications: shrink articles (gaiters for cable/pipe joints), films (including multilayer) for elevated temperature applications, foams (foamed profiles, closed-cell foams of high flexibility and good resilience), roto-moulded articles of high impact strength and good chemicals resistance such as automotive fuel tank, wire and cable coatings, hot-water pipes and tubing, floor coatings, steam-resistant films and multilayer packaging can be used as adhesion promoter due to the adhesion properties, heat-resistant foodstuff packaging (up to 200°C), chemical-resistant seals, blow-moulded products of high impact strength and chemical resistance.

Comparison of Different Cross-linking Methods

Several polyethylene cross-linking methods are briefly compared in Table 2, while a comparison of different silane methods is presented in Table 3.

A priority of silane grafting method in cross-linking polyethylene over the conventional high cost peroxide method is that cross-linking is carried out in solid shaped polymer in former rather than in melt state as in latter. In manufacturing of low voltage cables (i.e., <10 kV, although this value differs in different countries), silane cross-linkable polyethylenes are used, whereas for manufacturing high voltage cables (i.e., 30 kV), peroxide cross-linked polyethylene is preferred as this applications need very clean polyethylene.

Compared to peroxide- or radiation-cross-linked materials, silane-cross-linked products offer advantage in ageing behaviour. The important achievable mechanical properties are almost the same in these three methods, however, the three-dimensional cross-linking structure of the silane-cross-linked products means that they meet requirements even at lower degrees of cross-linking. It has been also reported that the degree of shrinkage decreases upon increasing the gel content and molecular orientation becomes permanent and mostly irrecoverable in silane grafted

Table 2. Comparison of several major cross-linking methods.

Method \ Aspect	Silane	Peroxide	Radiation
Process flexibility	Very good	Small	Very good
Operation	Easy	Difficult	Difficult
Extruder	Standard	Special	Standard
Production rate	High as for PE	Low	High as for PE
Cost of post treatment	Low	-	High
Capital investment	Low	High	High
Diameter	No limit, thickness limited by speed of cross-linking	Difficult to achieve big diameters because of output	Limited by penetration depth of electron
Scrap rates	Low	High scrap	
Raw material costs	Slightly high	Low	Low
Levels of attainable cross-link density		High	Probability of variation
Other	Wider scope for formulation through broad processing window, recyclability	Energy intensive	Clean (pipe) because of fewer additives

Table 3. Comparison of the moisture cure technologies.

	Process	Advantages	Disadvantages
Main Processes	Sioplas	<ul style="list-style-type: none"> ✓ Fast curing ✓ Versatility of base resins (i.e. LDPE, EVA, EPR, DPE ,etc) ✓ Low capital investment ✓ No need to special equipments 	<ul style="list-style-type: none"> × Two step technology × Limited shelf life × Higher raw material costs × Risk of pre-crosslinking on the surface of pellets during storage
	Monosil	<ul style="list-style-type: none"> ✓ Low material cost ✓ Versatility of base resins ✓ Fast curing ✓ Shelf life not an issue 	<ul style="list-style-type: none"> × Limited use of some additives × Handling of hazardous liquid chemicals × High scrap rates × High capital investment × Specific equipments required
Alternatives for main processes	Reactor copolymer	<ul style="list-style-type: none"> ✓ Long shelf life ✓ Low capital investment 	<ul style="list-style-type: none"> × Slow curing × Low density product only × Higher raw material costs
	Dry-silane	<ul style="list-style-type: none"> ✓ Potential low material costs ✓ Ease of storage ✓ Improved safety and handling ✓ Versatility of base resins ✓ Fast curing ✓ Good homogeneity ✓ Less gels and fish eyes 	<ul style="list-style-type: none"> × Use of additives limited or impossible × Moderate capital investment × Limited shelf life

moisture cross-linked polyethylene even at 150°C [10].

In the irradiation process, it is not necessary to add cross-linking additives but the promoters to the compound. Consequently, the materials can be extruded at reasonable temperatures. This imparts a great advantage considering that high melting temperature and high viscosity in the melt state of some polymers (such as HDPE containing flame retardant materials) makes it difficult to fulfil chemical cross-linking methods [35]; ignoring proper selection of cross-linking method would lead to the occurrence of premature cross-linking in the extruder.

Amongst the different silane methods, the copolymerization process is the most advanced and complex technology [49].

STUDY OF SIOPLAS® PROCESS

Principles of Manufacturing Process

The peroxide-activated grafting of the vinyl silane onto the polymer chains is the most critical stage of the whole process and is carried out in compounding equipments such as ko-kneader or co-rotating twin-screw extruder. The compounding equipment is being used as a chemical reactor in addition to its normal function of mixing, dispersing and pumping. The twin-screw compounder used for grafting process has L:D ratio of at least 30 and features a modular design for a choice of several barrel configurations and various conveying, kneading and mixing elements which can be combined to produce the optimal configuration for the process. Base polymer, processing aid and fillers are conveyed via gravimetric feeders into the extruder feed zone heated to about 150°C. The feeding rate and rpm are optimized at not very high values. After going through shearing and mixing elements polymer becomes molten and liquid silane/peroxide mixture is fed via a high precision diaphragm pump into the polymer melt between second and third process zones of extruder. Downstream feeding of other compounds such as carbon black, stabilizer, scorch retardant, etc. into the polymer melt is carried out via a side-feeder. Cable grades which are exposed to the decomposing effect of metal ions (in particular copper ions) are additionally stabilized by metal deac-

tivators. A limitation of the method is the propensity for the premature cross-linking (scorching) of material which can lead to product defects. This problem of scorching can be solved by including scorch retardant additives which react with water faster than the polymer itself and hence the extrusion process time can be significantly extended.

Followed by free and forced degassing and homogenization, the melt is extruded through a strand die at about 200°C. The strands are cooled down in a water bath and are dried by compressed air before pelletizing. The manufactured grafted polyethylene granules are packed inside vacuum-sealed aluminium-laminated sacks. Hence, the product is protected against moisture ingress which could trigger premature cross-linking of the granules.

A well equipped conventional compounding machine is necessary for dispersing small quantities of catalyst, antioxidants, and other chemicals into the matrix of polyethylene and its copolymers for manufacturing of catalyst masterbatch.

In the second step, a blend of ~95 parts of graft copolymer and ~5 parts of catalyst masterbatch is prepared by either tumble blending or metering which is then converted into cables, pipes or other finished parts in conventional forming extruders, or by injection or extrusion blow moulding. The product is cross-linked in a steam bath under action of temperature and humidity. Figure 5 shows the plant settings for the development of Sioplas® product.

LDPE and LLDPE are used in the low-voltage sector while MDPE is mainly used in pipe production. The-state-of-the-art of moisture cross-linkable polyolefins for different applications has been disclosed in several patents [45, 53-56].

Moisture Curing

The cross-linking procedure would be fulfilled through the exposure of grafted polyethylene to hot water, steam, or humid air. The functional end groups saponize to silanols in a hydrolysis reaction with water molecules, which are provided by diffusion [44]. The generated OH groups then condense with adjacent Si-O-H groups and form Si-O-Si bonds; the polymer is thus cross-linked. The rate of cross-linking depends on the extent of silane grafting, the temperature, and accessible water, which makes the required

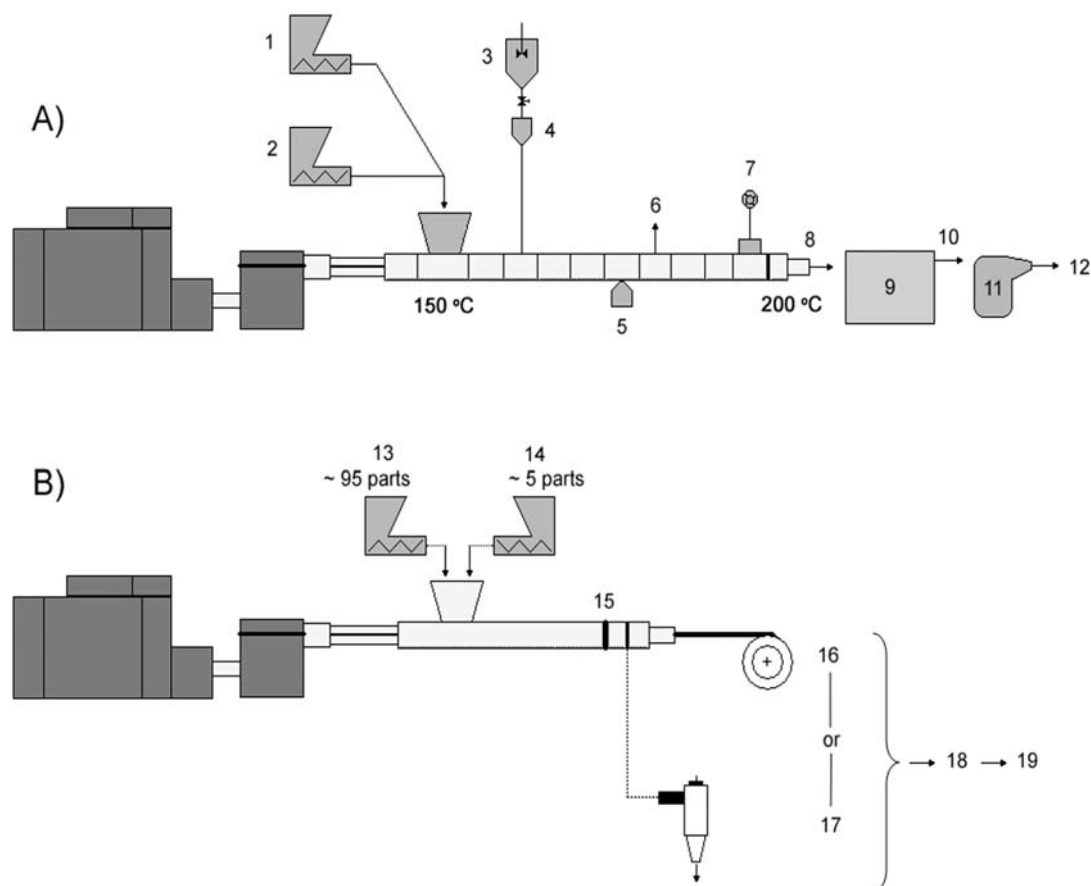


Figure 5. Typical plant for manufacturing Sioplas®-based products.

- 1: Loss-in-weight feeder, polyethylene
- 2: Loss-in-weight feeder, additives (EVA, processing aid, filler)
- 3: Storage tank (silane-peroxide)
- 4: Liquid feeder
- 5: Side feeder (carbon black, stabilizer, scorch retardant)
- 6: Atmospheric vent
- 7: Vacuum pump
- 8: Strand die head
- 9: Cooling bath (60-70°C)
- 10: Air knife

- 11: Pelletizer
- 12: Grafted polyethylene granules
- 13: Loss-in-weight feeder, grafted polyethylene granules
- 14: Loss-in-weight feeder, catalyst masterbatch
- 15: Screen changer
- 16: Cross-linkable pipe
- 17: Cable coating
- 18: Exposure to moisture
- 19: Finished cross-linked product

time for cross-linking vary from a few hours to a few weeks. The cross-linking reaction is catalyzed in the presence of catalyst (incorporated via catalyst masterbatch) such as dibutyltin dilaurate which is mixed with pellets before fabrication and shaping [10]. The product can be shaped by various techniques: extrusion, injection and blow mouldings, or other conventional thermoplastic shaping methods.

In both Sioplas® and Monosil® processes, there is a difficulty of uniform distribution of silane and thus there exists the probability of localized grafting and

consequent formation of small gels. As the homogeneity of graft dispersion amongst the polyethylene chains are also the direct result of the good dispersion of the peroxide, it is required to choose a peroxide compound having a good solubility parameter in polyethylene melt besides having optimum oxygen content in the reaction condition [17].

During processing, even in the absence of silane, peroxide is apt to make carbon-carbon cross-links between polymer chains [57]. Besides, as reported elsewhere [58] different peroxides do not act similar-

ly in grafting silane onto polyethylene which means some peroxides would tend more for initiating self-cross-linking in polyethylene during the silane grafting reactions and thus reducing the ultimate efficiency of grafting.

However, in the absence of peroxide, no functionalization (silane grafted groups) is observed and silane merely acts as a plasticizer. When both silane and peroxide exist and the temperature is high enough for the grafting reactions to occur, peroxide-initiated cross-linking (carbon-carbon linkages) competes with peroxide-initiated silane grafting, and thus an optimum composition of these components should control and favour the grafting reactions rather than the self cross-linking (HDPE and LLDPE are apt to such cross-linking during grafting reactions as reported [59]).

The higher degrees of grafted silane and higher final torques are obtained with increase in the silane concentration at low peroxide levels and increase in peroxide level at low silane concentrations. Besides, based upon the processing conditions, there is always an optimum ratio of silane and peroxide which yields the best efficiency of grafting [60]. This is also reported elsewhere [61] through studying the cross-linking reaction of low density polyethylene in detail with applying a wide range of reactant concentrations and determining the resultant properties (mechanical, hot set testing, gel content, burning). In this report it is concluded that at or beyond a certain threshold concentration of silane, samples are not only qualified for hot-set testing, but show other properties at optimum levels.

After the completion of cross-linking, the by-products of the cross-linking reaction should be extracted (by the same water molecules) from the wall of the tube or moulding [9]. The main component to be extracted is methanol. This would be of greater importance if the ultimate usage of the moulding article is for drinking (portable) water applications [12]. There are three main methods for moisture cross-linking as follows:

- Immersion in hot water: The articles are immersed in steel tanks containing hot water (minimum temperature of 80°C), by placing them in stainless steel cages or baskets [9]. After fulfillment of cross-linking, the mouldings are removed

from tanks and allowed to drain in a well-ventilated area.

- Circulation of water and steam through the interior of pipes: In this method, hot water or steam is pumped through the moulding (herein, pipes) at a high temperature [9]. It is also possible to allow venting of the steam into a chamber surrounding the articles to increase the rate of cross-linking. Circulating water is more efficient than static water in extracting the reaction by-products.

- Steam bath (the action of low pressure steam): The mouldings are placed in a chamber filled with low pressure steam at about 100°C. As steam is a freshly distilled vapour it excludes surface contamination of the mouldings.

Finally, it is also possible for cross-links to form in ambient conditions at reasonably short times with the aid of a new catalyst technology.

Evaluation of the Grafting and Cross-linking Reactions

It is possible to detect the onset of grafting reactions via monitoring the torque during the processing in an internal mixer [62,63] (a dump criterion) the first increase in torque observed in Figure 6 is due to adding material(s). The torque decreases as the polymer starts plasticating and melting. The followed increase is an indication of starting grafting reaction and is occurred because of the associated increase in melt viscosity; then it continues as a plateau.

FTIR characterization is commonly used to follow the grafting. In FTIR spectrum of silane grafted

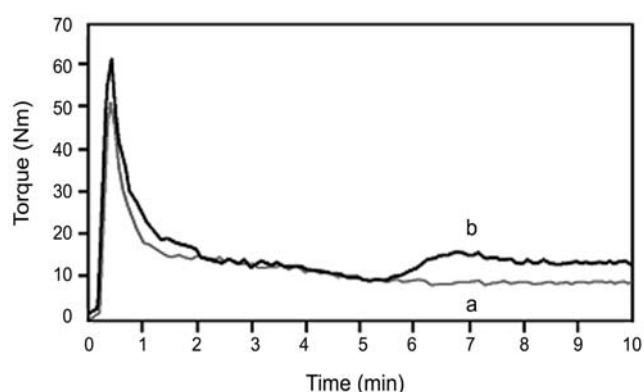


Figure 6. Typical plot of torque vs. time observed for (a) virgin and (b) silane grafted LDPE [84].

polyethylene, peaks at 799, 1092 (or sometimes 1090), and 1192 cm^{-1} are the characteristic absorptions for Si-alkoxy groups (e.g., $-\text{Si}-\text{OCH}_3$) [18, 64]. The 1092 cm^{-1} peak typically has the strongest absorbance/transmittance [70] and is frequently used as an indication of the silane grafting extension. The peak at 1378 cm^{-1} relates to $-\text{CH}_3$ symmetric deformation [67]. In silane grafting reactions, the secondary and tertiary carbons are more frequent and also more apt to participate in reaction compared with primary carbons which are located at the end of the chains and chain branches. Thus, it is rational to choose the peak at 1378 cm^{-1} as the internal standard within a polyethylene compound as it changes little in content, if any, during the silane grafting reaction. By choosing such an internal standard, the efficiency of silane grafting can be investigated by calculating the ratio of the absorption peak of the Si-O- CH_3 groups at 1092 cm^{-1} to the absorption peak of the $-\text{CH}_3$ groups at 1378 cm^{-1} (A_{1092}/A_{1378}). However, as the content of tertiary carbon is not the same for different types and grades of polyethylenes, using such internal standard would not be rational in comparing the silane grafting efficiencies of different grades of polyethylene. In such cases the preferred method would be the measuring of the corresponding peak height divided by the film thickness and comparing the resultant normalized height (per unit thickness) [63,67].

The peak at 1080 cm^{-1} is assigned to the Si-O-Si bonds (cross-links) [65] and would be formed to some extent even during grafting process. In such cases, the Si-O CH_3 is apt to be masked by strong Si-O-Si absorption and a subtraction of the peaks should be done, or complementary methods are to be used to reach a correct data.

Quantitative characterization of the FTIR data, especially a decrease in absorption intensity of methoxysilane groups, may not provide a direct cross-linking value; however, the technique is non-destructive and presents meaningful information on the progress of silane-water cross-linking reaction. It is also less time consuming and needs no solvent therefore it is more environmentally friendly compared to the gel content determination and solvent uptake factor methods [23]. Thus, FTIR is the common method for following the silane cross-linking reaction (however, measuring the extent of cross-linking by FTIR is

impossible in peroxide and irradiation cured polyethylene) [13]. FTIR can be used to study the kinetics of cross-linking reaction along with measuring the gel content [18]. By these simultaneous methods, it has been shown that although the cross-links are formed continually till a definite time (e.g., 100 h at 90°C), there is no simultaneous increase in gel content after reaching its maximum value. This indicates that the cross-links formed after reaching the maximum value of gel content should be within the already existing gel. Besides, cross-linking reactions follow first order kinetics with respect to both catalyst and moisture concentration [68]. A good relationship has been found between the FTIR absorption data and the gel content in silane cross-linked polyethylene [69].

However, care must be taken in this method when analyzing gel content in samples with low gel content, as there is the possibility of observing some gel outside the cage. This has been reported to be due to the presence of heterogeneous cross-link network in such samples, which is probable in the silane-cross-linked products. The reason for this heterogeneity is that in silane method, cross-linking process is carried out when the polymer is in the solid state (and thus with limited mobility), unlike the peroxide cross-link where the polymer cross-linking process generally takes place in almost molten state, leading to a more homogeneous cross-linked network. In addition, there is the possibility of separation of grafted compound into silane-rich phase (preferably the amorphous phase) and silane depleted fractions (crystalline phase) during the crystallization [70].

This is also obvious with regard to the fact that relatively high gel contents are achievable in peroxide cross-linking method, whereas in the case of silane method these values are generally much lower. The multiple reactivity of the tri-functional silane-alkoxy structure (three end groups at the end of each silane side chain) will also support a heterogeneous network formation during the silane condensation reaction. As it is shown in Figure 7 a considerable number of silanol groups can easily condense in close proximity.

As the occurrence of grafting leads to the reduction of melt flow index, reaching a specified value of melt flow index would be an approximate way of assessing the extent of grafting and is commonly used in industry. Additionally, hot set tests (duration of

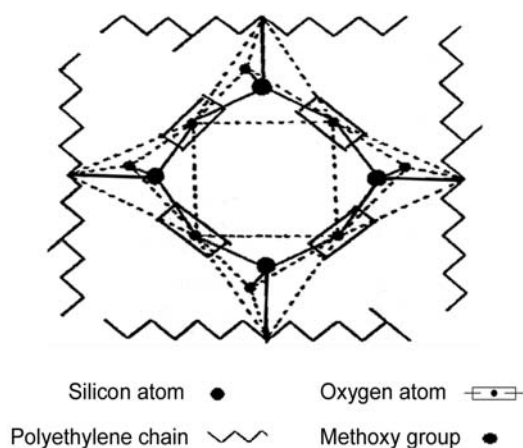


Figure 7. Three-dimensional network formed by silane cross-linking method [46].

15 min, at temperature of 200°C, and under definite static load) are carried out on cross-linked samples to evaluate and quantify the cross-link density [71-73].

Important Parameters in Silane Grafting and Cross-linking

Peroxide

Free radicals are needed to initiate silane grafting by abstracting hydrogen atoms from the macromolecules (referring as alkylradicals). These free radicals are generated from thermally degradable organic peroxides, such as dialkyl peroxides. To avoid the premature cross-linking during the processing, only peroxides with a half-life of more than 2 h at 130°C can be considered for silane grafting [74]. In this regard, commercially available peroxides include dicumyl peroxide (DCP), tert-butylcumyl-peroxide, bis(tert-butylperoxyisopropyl)benzene, 2,5-bis(tert-butylperoxy)-2,5-trimethyl-cyclohexane, and 2,5-bis(tert-butylperoxy)-2,5-trimethylcyclohexane-3, among which the most preferred peroxide is DCP. It is also possible for unsaturation on silane to be attacked by peroxide followed by reaction with the polyethylene chain [61].

Silane

Using differential scanning calorimetry, it has been reported [68] that the kinetics of grafting vinyltrimethoxysilane on polyethylene is the same as that of vinyltriethoxysilane, although vinyltrimethoxysilane has a lower activation energy and thus

is superior in grafting polyethylene compared with vinyltriethoxysilane [64,69]. Moreover, typical increase in the amount of silane, the reaction time or the temperature would result in an increase in the silane grafting extent.

Antioxidant

The alkyl radical formation in polyethylene molecules (during the grafting reactions) is suppressed by some antioxidants, where the decomposition products of peroxide react with the antioxidant in a non-useful reaction, which means that this portion of consumed peroxide has to be compensated for by additional peroxide and if not, the silane grafting efficiency would be dropped. The grafting process limits the choice of antioxidants, since many of them are effective radical scavengers and can inhibit the grafting reaction. Frequently used antioxidants for cross-linked polyethylene are mentioned in plastics additives handbooks [75] among which the influence of some common types of antioxidant within the grafting reactions has been reported in literature [63, 76-78].

The effect of some specific antioxidants (Irganox 1010, Irganox 1076 and Irgastab® Cable KV10) on silane grafting reactions of LDPE is studied in a recent work [62] and the resultant spectra are shown in Figure 8. The thermo-oxidative products has the characteristic peaks between 1650 and 1800 cm^{-1} ; here the transmittance peak at 1720 cm^{-1} is considered as the indication of thermo-degradation of polyethylene (designation of C=O groups) which is absent in virgin polyethylene and strongly present in processed virgin one (containing no other reactant). Thus the standardized height of this peak is a designation of the extent of degradation in a specified type of polyethylene. Shorter the peak height at 1720 cm^{-1} and higher the peak height at 1092 cm^{-1} would be the indications of the antioxidant efficiency.

As incorporation of antioxidant would be inevitable to prevent the product from degradation [63], a possible practical method to reach a desirable grafting extent as well as the least thermal degradation, is to incorporate a part of a predetermined amount within the process and the remainder to be mixed in the catalyst masterbatch (to be used during cross-linking process). This has been done before in case of other additives (such as carbon

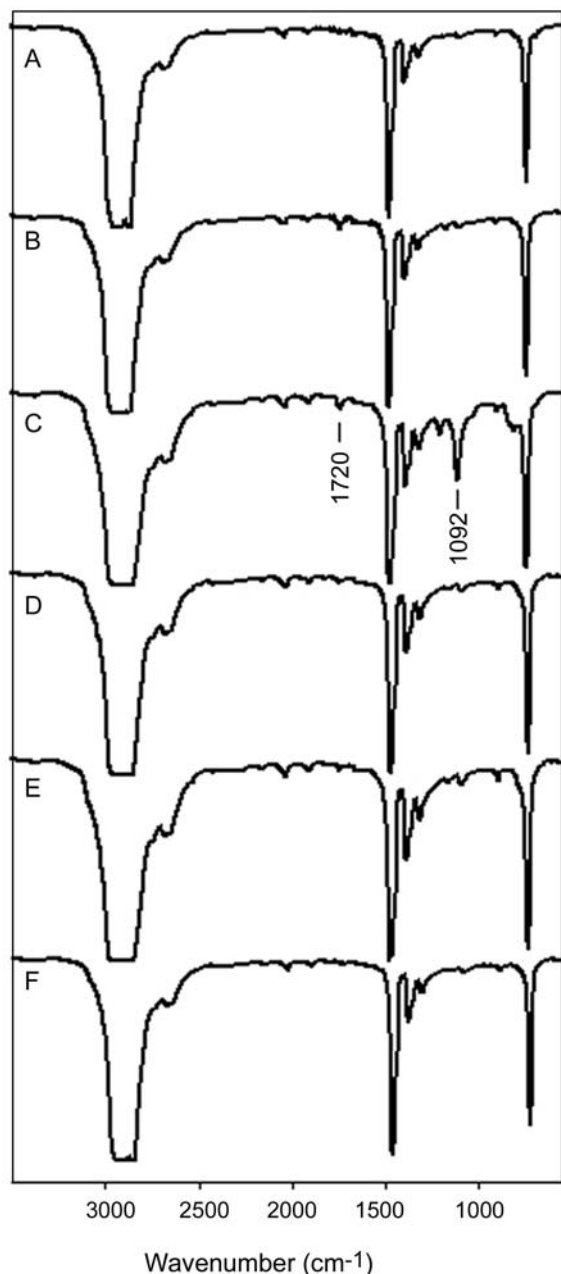


Figure 8. FTIR spectra for (A) virgin LDPE; (B) processed LDPE, solely mixed in internal mixer for 15 min at 190°C; (C) silane grafted LDPE, processed as B; D, E, and F are the samples processed as C but containing Irganox 1010 (D), Irganox 1076 (E) and Irgastab® Cable KV10 (F) [62].

black) which otherwise would interfere with the silane grafting reactions. An alternative is to take advantage of higher amounts of peroxide which associates with some scorch occurring during the grafting stage and consequent gelled spots and a rough product surface.

Catalyst

Hydrolysis or condensation catalysts catalyze the cross-linking of the extrudate or moulded article through facilitating the curing reaction with water. The catalysts may accelerate either the hydrolysis reaction of the grafted silyl groups with water to form silanols, or the reaction condensation of silanols to form Si-O-Si bond, or both. These catalysts would be of acidic form, basic form, or neutral (salt). Depending on the kind of catalyst, the mechanism of formation of siloxane bridges can involve three possible reaction pathways as shown in Figure 9 [79].

The most effective catalyst for silane cross-linking is dibutyltin carboxylates such as dibutyltin dilaurate (DBTDL). Other common types of catalysts would include: stannous acetate, stannous octoate, dibutyltin dioctoate or di-octyl-tin-bis (isooctylthioglycolate).

The cross-linking catalyst is of great importance in determining the achievable degree of cross-linking in a specified time period, and reaching a rapid bimolecular condensation between silanol groups which are at low concentration in polymer [80, 81].

Prior to formation of cross-links it is necessary for water molecules to diffuse into the wall of the article and reach the cross-linking sites. This procedure takes time and is mostly responsible for the long time required to achieve full cross-linking. Increasing the water (or steam) temperature leads to increase in polyethylene (article) temperature and consequently due to the resultant thermal expansion, there would be an increase in water diffusion rate. Furthermore, this increased temperature would also enhance the rate of hydrolysis and cross-linking reactions, as all chemical reactions speed up under higher temperatures. Consequently, the time required for cross-linking reactions to occur would be shortened. It takes about 90 days for an article of 1.5 mm wall thickness at 20°C in ambient air to reach 60% cross-linking (this set of data is just typical), for an specified commercial product). In practical terms, the rate of diffusion is inversely proportional to the square of the wall thickness. Cross-linking from both inner and outer surfaces of the article is faster than performing it from one surface only.

Recently, it is also possible to cross-link the silane-polyethylene copolymer in ambient conditions with no need to high moisture content. This would be

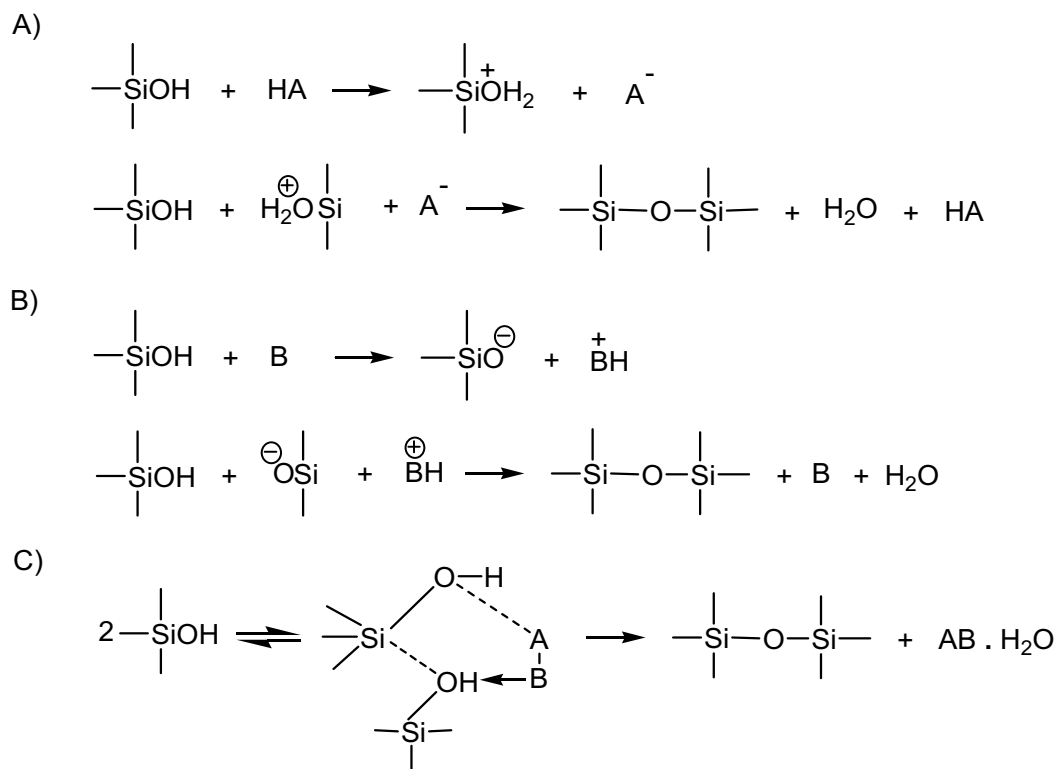


Figure 9. Different mechanisms for catalyst performance in silane cross-linking method: (A) acid (HA)-catalyzed; (B) base catalyzed; (C) catalysis by neutral salts (AB) [79].

possible through choosing some special tin free catalysts, as a sulphonic acid based catalyst with a long alkyl chain attached [53,82].

Pre-mixing the Reactants and Polymer Physical Form

Pre-mixing the solution of silane and peroxide with polyethylene, prior to processing in internal mixer, plays an important role in final results since silane is hard to be absorbed by the polymer [62]. In case of no pre-mixing, as it consumes more time to fulfill the whole process with incorporating silane and peroxide separately into internal mixer, the mixture would pass a longer time under processing before reaching the increase in torque. At such a high temperature (typically 190°C) and in presence of ambient water vapour, undesirable cross-linking reactions would occur.

Figure 10 illustrates the fact that for silane grafting of LDPE in two forms of granules and powder, different extent of grafting would be observed: higher extensions of silane grafting would result when the polyethylene is in powder form (with regard to polymer in granule form) [62].

Polyethylene Molecular Weight, Molecular Weight Distribution, and Grade

Polyethylenes with different MFI values have different extents of silane grafting. Within each grade of polyethylene (LDPE, LLDPE, and HDPE), the polymer with lower MFI value (and thus a higher molecular weight) has the least silane grafting extension, due to being less apt to radical formation, and vice versa. On other words, for a polymer with higher molecular weight there is less tendency and probability for radical formation, as there would be less accessibility of polymer backbone for silane and the peroxide decomposition species [63]. However, this cannot be generalized into all the existing types of polyethylenes within a grade, as different topological and intrinsic properties would affect the grafting (as well as the cross-linking) reactions in a different manner. Such studies have been carried out for other types of polyethylene cross-linking [83]. For example, higher branching number and its broader distribution mode versus molecular weight, higher unsaturation content in polymer backbone, lower polydispersity index, and

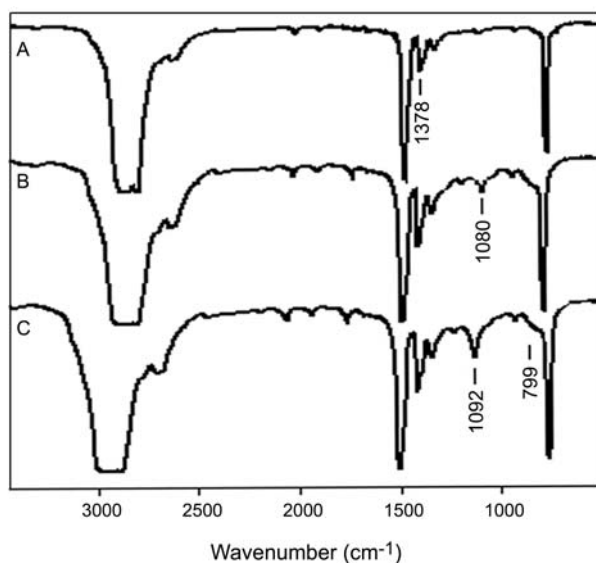


Figure 10. FTIR spectra for (A) virgin LDPE; (B) granular LDPE grafted with silane; (C) powder LDPE grafted silane [62].

lower weight average molecular weight would all positively affect silane grafting efficiency [63]. Furthermore, the higher MFR value (the ratio of MFI at 10 kg load to that value under 2.16 kg load) can contribute to lower tendency for grafting reactions [62].

Under the same conditions, LLDPE is more apt to silane grafting reactions compared to LDPE. This is also true for LDPE compared to HDPE [2,64,69]. In initiating the silane grafting reaction by decomposition of peroxide, the resultant decomposition species would participate in different reactions; they would combine with each other to form unsaturated species; induce β -scissioning in polymer chain and thus leading to chain extension; and finally they would react with the vinyl unsaturation of the vinyltrimethoxy silane for grafting the molecule onto the polyethylene. Among all the aforementioned reactions, only the last one is desired and the other two would result in molecular structure changes and consequently lead to differences in cross-linking performances [67].

Different grades of polyethylene show different tendencies and probabilities for these side reactions and thus different degrees of silane grafting would be obtained in fixed amounts of reactants for each grade of polyethylene. However, the more efficient grafting in LLDPE rather than LDPE and HDPE would be due

to the existence of its tertiary carbons which are more apt to react with free radicals initiating grafting reactions, since the associated hydrogens are relatively easy to be abstracted during silane grafting reactions. Despite the tertiary carbons in LDPE, there also exists stereochemical hindrance due to clustered short chain branches. Weaker tendency of HDPE to silane grafting can be related to the shortage of tertiary carbons.

The structural polymer parameters, also affect the cross-linking behaviour [44,63]. Under similar conditions, LLDPE cures more rapidly with regard to LDPE and HDPE due to the faster diffusion of moisture in the former. In the case of HDPE, the relatively low level of silane grafting and free radical induced chain extension together with the tightly packed lamellar structure of HDPE render the resin difficult to cross-link rapidly.

Curing Time and Temperature

At low temperatures, the rate-determining step of the cross-linking reactions is water diffusion, rather than the hydrolysis and the subsequent condensation reactions of the silyl trimethoxy groups. However, at high temperatures and high degrees of silane grafting in the samples, the chemical reactions dominate in the cross-linking process [69]. The effect of curing time and water temperature is shown in Figure 11 [84]. In general, the period required to obtain full cure depends on wall thickness, percentage and type of catalyst masterbatch, temperature, and moisture content.

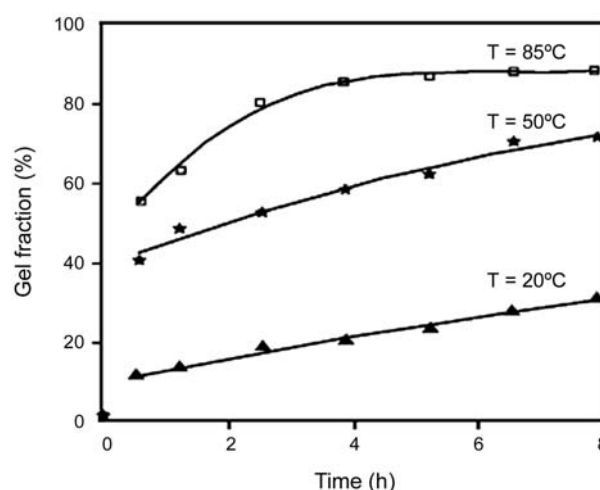


Figure 11. Effect of curing time and water temperature on silane cross-linking of LDPE [84].

Incorporation of Typical Additives

ZnO

Incorporation of zinc oxide powder within silane grafted polyethylene would result in the prolonged shelf life of the non-cross-linked product [85,86]. This is due to the role of ZnO in absorbing the excess of water and acid which exist in the surrounding environment. In practice, a minimum of six months storage is needed [49] and the use of ZnO satisfies this requirement with elimination or significant reduction of the risk of premature cross-linking. Along with increasing the shelf life period, the extent of grafting also increases through inhibitory effect of ZnO on the occurrence of undesired reactions between water (or other impurities) and silane [86]. Furthermore, no negative effect is observed on the curing rate of the shaped samples, using catalyst-rich ZnO-added compounds.

Carbon Black

The incorporation of carbon black reduces the silane grafting efficiency [17]. The numerous functional and chemical active groups on the surface of carbon black are responsible for bond formation between carbon black and polyethylene chain. Meanwhile, it seems that carbon black consumes the available radical sites and also by introducing spatial obstacles, reduces the possibility of silane attack to polyethylene radicals in a specified period of time, and consequently reduces the extent of silane grafting. Additionally, carbon black reduces the achievable gel content and a straight

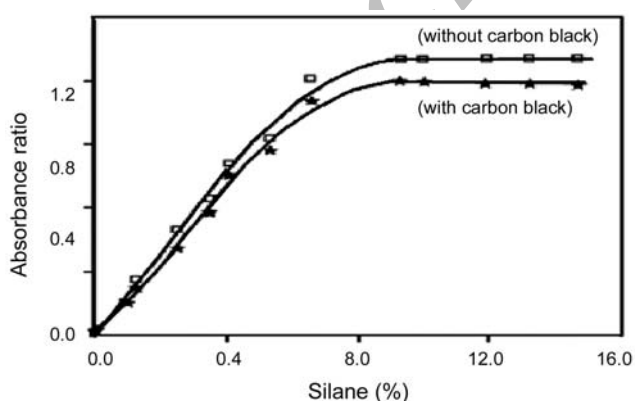


Figure 12. Effect of silane content on grafting extent in presence of carbon black and without carbon black (absorbance ratio: FTIR peak height at 1090 cm^{-1} /FTIR peak height at 729 cm^{-1})[84].

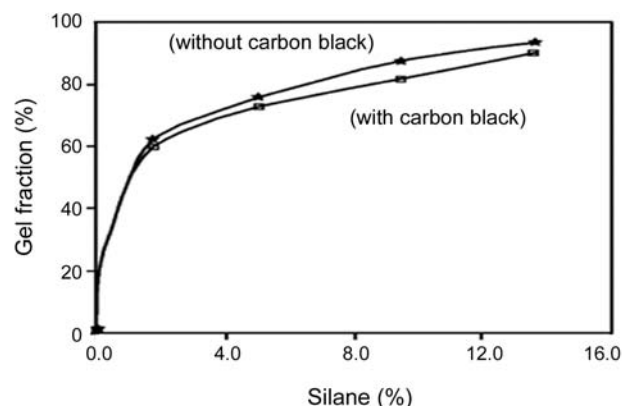


Figure 13. Effect of silane content on cross-linking extent in presence of carbon black and without carbon black [84].

relationship exists between reduction of silane grafting (Figure 12) and decreasing of gel content in the presence of carbon black (Figure 13).

Increase in gel content increases volume resistivity, thus the cross-linked polyethylene has a lower electrical conductivity compared to virgin one [87]. This is possibly due to the presence of the fewer charge carriers and the more efficient charge trapping in cross-linked polyethylene compared to non-cross-linked polyethylene. Carbon black reduces the volume resistivity, due to its semi-conductive nature; this makes carbon black a profitable additive in semiconductor cable jacketing.

EVA

Polyethylene is blended with EVA in many cases to reach desired properties. In special applications which require surface adhesion to metals, EVA enhances adhering between different layers and adheres to metals easily. In cable jacketing especially for low voltage applications ($<10\text{ kV}$) it is common to blend EVA with low density polyethylene for improved flexibility, ageing behaviour, low temperature flexibility, and increased impact strength [88]. Moreover, it makes possible to apply more amounts of filler (e.g., CaCO_3 , talc, carbon black, etc.) into the polyethylene compound [89]. Due to the polarity of acetate groups in EVA, dielectric constant and dissipation factor also increases.

Incorporating EVA in LDPE or increasing the vinyl acetate content in LDPE/EVA blends increases the extent of silane grafting [62] (Figure 14). By

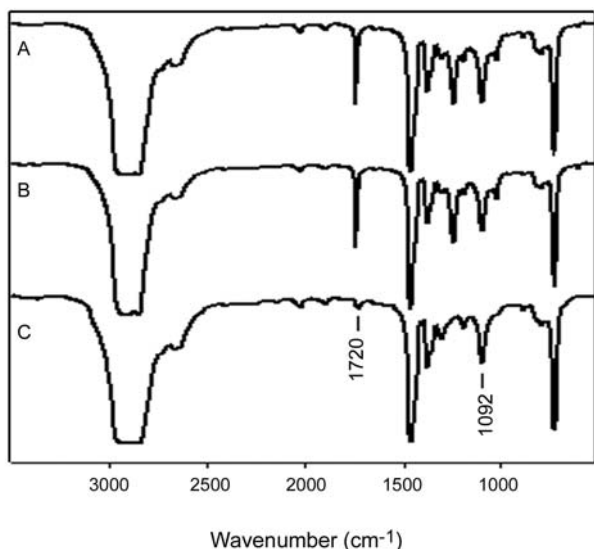


Figure 14. FTIR spectra for LDPE blended with 4 phr of: (A) EVA 28%, (B) EVA 40%, and (C) No EVA; grafted with silane in the presence of peroxide [62].

increasing EVA content, the amount of side chains increases thus, the amount of tertiary carbons which is apt to grafting reactions increases as well. Moreover, the polarity of vinyl acetate (compared to non-polar nature of LDPE) facilitates the permeation of silane component into molecular structure of LDPE and thus providing better condition for grafting to occur. The presence of unsaturated structures in the polyethylene, especially vinyl groups, increases the grafting efficiency [13].

Increase in EVA content leads to a decrease in crystallinity and increase in the amount of side chains which per se accelerates the diffusion of water into the polyethylene and thus increases the gel content as an indication of cross-linking (Figure 15) [90]. The polarity induced by incorporation of EVA would make a tendency for the water to permeate in LDPE during the cross-linking process. Considering the less required time to reach specified gel content in presence of EVA, as shown in Figure 16, EVA increases the rate of cross-linking in LDPE/EVA blends.

Increasing the amount EVA in the blend results to increase in tensile strength [88,91]. EVA causes the strain hardening phenomena which become more dominant in regards to crystallization. The higher elongation-at-break values of EVA compared with that of polyethylene is also a reason for higher

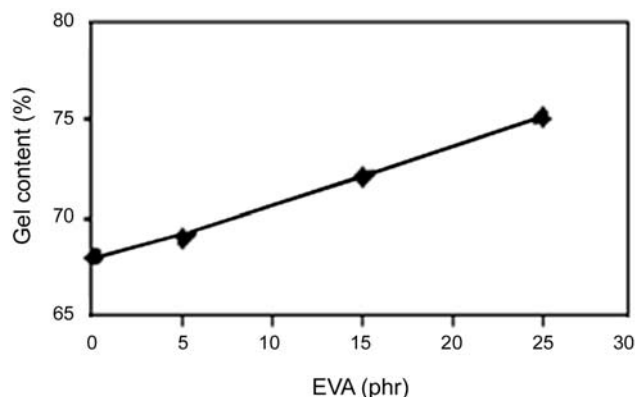


Figure 15. The effect of EVA concentration on gel content in silane cross-linked LDPE [88].

elongations-at-break in their blend in regards to virgin cross-linked polyethylene.

EPDM

EPDM has an outstanding resistance to heat, light, oxygen, and ozone and used to improve polyethylene properties [50,92-94]. Blends of LDPE with EPDM are useful in heat-shrinkable objects. For these applications, cross-linkable polyethylene is cross-linked after extrusion to the desired finished size, and then mechanically expanded above its melting point followed by rapid quenching. At this stage, heating the product above the crystalline melting point leads to shrinkage and rapid return to the original shape.

When blended with LDPE, EPDM has the same effect as EVA on grafting extent of LDPE. However, EPDM is more effective in increasing the grafting efficiency. This could be due to the unsaturation in diene monomers existed in EPDM which create some additional reactive sites for silane grafting to occur

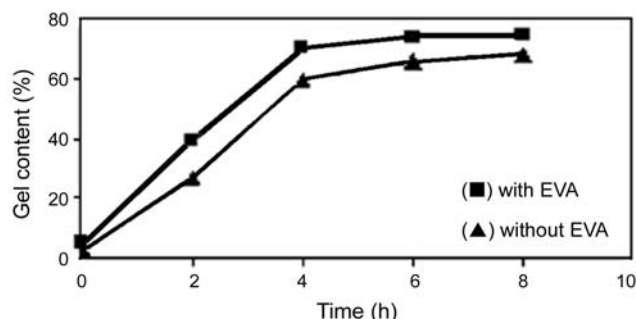


Figure 16. The influence of cross-linking time on gel content with and without EVA [88].

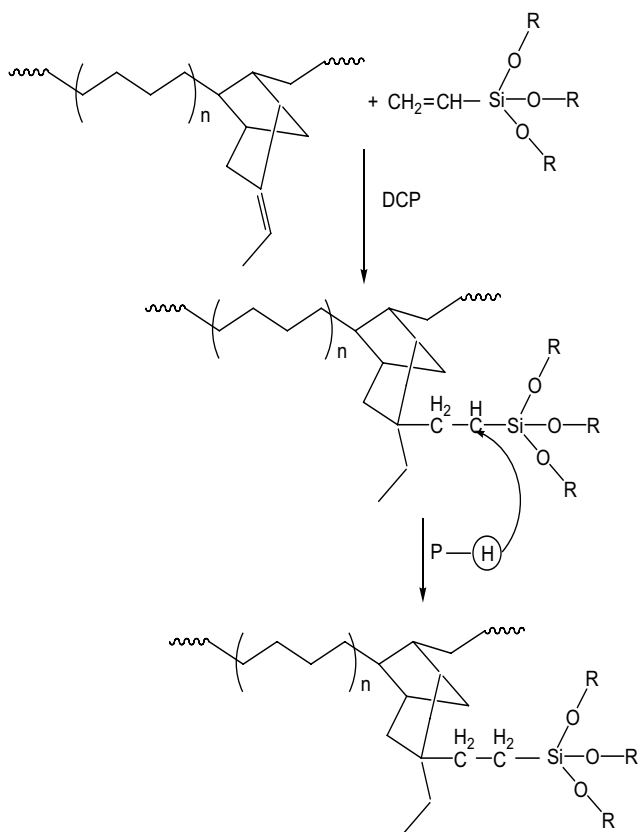


Figure 17. Schematic of silane grafting on EPDM [93].

(grafting may also occur by the abstraction of secondary hydrogen from a polyethylene sequence of EPDM). Since no similar unsaturation is present in EVA, less efficient grafting would result in case of LDPE/EVA blends compared to LDPE/EPDM [62]. A schematic of silane grafting on EPDM is illustrated in Figure 17.

Typical Properties

Mechanical Properties

Increase in the extent of grafting, results in increased tensile strength and elongation-at-break [87]. This would be due to the more effective strain-hardening during the elongation of the silane grafted polyethylene. Also, increase of the gel content enhances the tensile strength. However, a different behaviour is observed for elongation-at-break, as generally, cross-linked polyethylene has a lower elongation-at-break compared to non-cross-linked polyethylene. The reason is that cross-linked polyethylene is less flexible and its strain hardening is more limited. The little increase in elongation-at-break value at intermediate

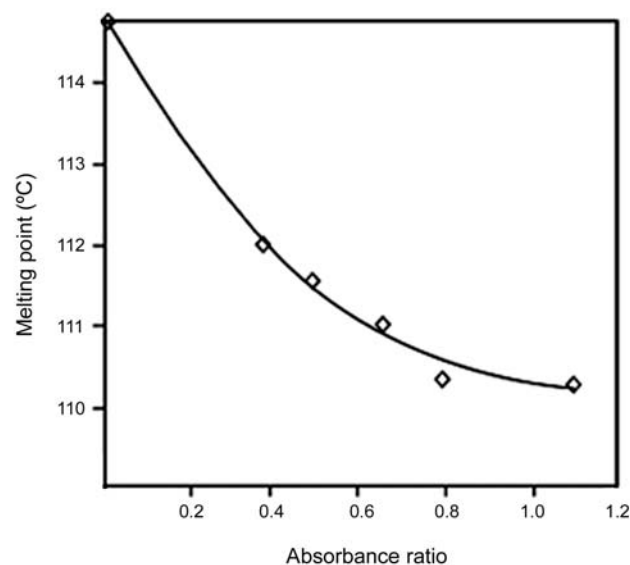


Figure 18. The changes of melting point with silane grafting on LDPE (absorbance ratio: FTIR peak height at 1090 cm^{-1} / FTIR peak height at 729 cm^{-1})[87].

gel content would be the result of reduction in crystallinity and possibility of chain mobility, however, at higher gel contents the chain mobility and thus the elongation-at-break decrease.

Thermal Properties

Melting point and crystalline percentage decrease with increased grafting level and gel content [95,96] (Figure 18). DSC data show that silane grafts on the LDPE molecules are thermally stable in the absence of moisture under a typical temperature of 130°C under which the silane grafted LDPE can be processed or recycled.

In differential scanning calorimetry analysis, a broad endothermic peak appears for silane cross-linked polyethylene due to phase separation during moisture cross-linking of LDPE, which implies an existence of heterogeneity in molecular structure [87]. A multiple melting behaviour of silane cross-linked LDPE has been reported elsewhere [96] and claimed to be due to phase separation during cross-linking of LDPE with water.

Thermogravimetric analysis determines that the thermal stability of LDPE (also reported for LLDPE [97]) increases by increasing the amount of silane grafting, as demonstrated in Figure 19 [84]. It should be noted that in cross-linked polyethylenes, the

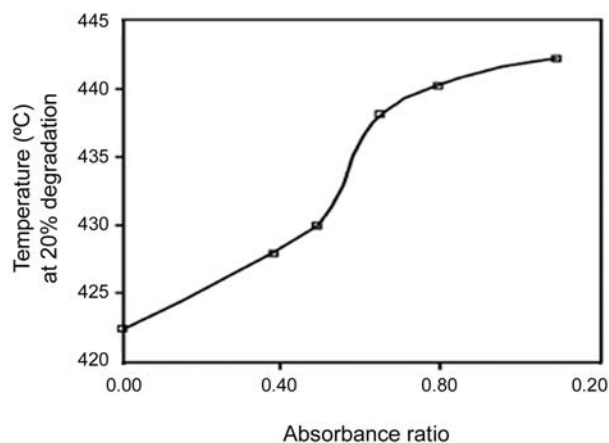


Figure 19. Effect of silane grafting on thermal degradation of LDPE [84].

required dissociation energy of Si-O and Si-C bonds is 191.1 and 107.9 kcal/mol, respectively [95]. Besides, the possible occurrence of peroxide-induced cross-linking reactions during the silane grafting reactions would be also responsible for the increase in the decomposition temperature.

CONCLUSION AND FUTURE OUTLOOK

In this review study, besides focusing on details of silane method in cross-linking polyethylene, it was also aimed to introduce and investigate other different methods of preparing cross-linked polyethylene. Herein, by comparing the available methods of cross-linking polyethylene i.e., azo compounds, peroxide, silane and radiation methods, it shows that cross-linking via silane grafting is a common and efficient approach to cross-link polyethylene. In silane method, there is not a high capital investment and higher production rates are possible; less waste is produced on starting up and switching off the equipments. The advantage of two-step silane cross-linking is particularly pronounced in the production of relatively short cable lengths or sector cables.

FTIR and MFI are good quality control tests for judging the extent of silane grafting reaction. FTIR can also be used to study the kinetics of cross-linking reaction along with measuring the gel content. Type and content of peroxide, silane, antioxidants, catalyst,

temperature, and moisture content are considered as some of the important parameters in silane grafting and cross-linking; for instance, the higher the temperature and amount of catalyst, the shorter the cure time. Also, increase in the amount of antioxidant would impair the grafting reactions (as radical scavengers) and thus the amount and type of antioxidant as well as the optimum balancing of the components of this system is of considerable importance. Moreover, proper selection of screw geometry, arrangement of screw elements, process conditions (temperature profile, rpm, etc.) also would improve melt homogeneity, grafting distribution, and efficiency.

The degree of grafting increases with increase of tertiary carbon and narrowing of molecular weight distribution of the polymer. In general, LLDPE is easily silane grafted and it is faster than LDPE and HDPE. Molecular weight might have different effects on grafting and cross-linking reactions. Along with the molecular weight, vinyl group content (unsaturation) and short and long chain branches would also take part in determination of ultimate degree of grafting and cross-linking. No strict rule has been concluded yet which would imply the direct effect of molecular weight on grafting and cross-linking. The introduction of polar groups such as vinyl acetate or ethyl acrylate into the polymer significantly increases the reactivity and allows further acceleration of the cross-linking. Blending polyethylene with an optimum amount of EVA or EPDM increases the extent of silane grafting, EPDM being more efficient in comparison with EVA. They also reduce moisture cure time and contribute positive effects on mechanical properties and product appearance. On the other hand, incorporating carbon black or flame retardants reduces the silane grafting efficiency and the target gel content.

The problem of scorching with grafting extruder can be solved by including scorch retardant additives reacting with water very fast. Incorporating zinc oxide powder within silane grafted polyethylene would result in the prolonged shelf life of the non-cross-linked product as well as increase in the extent of grafting.

The patent for the basic Sioplas® two-stage process was disclosed in 1989; this matter enabled

many producers to market graft polymers. The lower capital investment, higher productivity processes associated with silane-type XLPE are likely to ensure a continued growth in demand for extruded cables and tubing, expanded products, rotational and injection moulded parts and other related industries. Research developments are currently under way for increasing the cross-linking rate by developing new catalyst systems, faster cross-linking blends, and incorporation of the micro- and nano-organic and inorganic particles. Thus, in near future this technology will be applied for medium-to-high voltage cable insulation. By using special polymerization catalysts, silane copolymers would be also based on LLDPE, MDPE, HDPE and polyolefin copolymers in addition to current high-pressure process producing LDPE copolymer. The future of the productions of wiring, cabling, and tubing in world markets lie in silane cross-linking. It should be noted that there are yet vacancies in the field of studying and evaluating the effects of topological and intrinsic characterization of polyethylene in silane grafting and cross-linking and thus, more detailed works on this subject are expected in near future.

ABBREVIATIONS

DBTDL	Dibutyltin dilaurate
DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
EPDM	Ethylene propylene diene monomer
EPR	Ethylene propylene rubber
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infra red
HDPE	High density polyethylene
LDPE	Low density polyethylene
L:D ratio	Length/diameter ratio
LLDPE	Linear low density polyethylene
LOI	Limiting oxygen index
MDPE	Medium density polyethylene
MFI	Melt flow index
MFR	Melt flow ratio
PAM	Pont à Mousson
PEX	Cross-linked polyethylene
PVC	Poly (vinyl chloride)
TGA	Thermogravimetric analysis

UHF	Ultra high frequency
XLPE	Cross-linkable polyethylene

REFERENCES

1. Ghasemi I, Morshedian J, The effect of co-agent on peroxide crosslinking of polyethylene, *Iran Polym J*, **12**, 715-720, 2005.
2. Shieh YT, Chen JS, Lin CC, Thermal fractionation and crystallization enhancement of silane-grafted water-crosslinked low-density polyethylene, *J Appl Polym Sci*, **81**, 591-599.
3. Abbassi F, Morshedian J, Peroxide crosslinking of low density polyethylene, 4th *Int Sem Polym Sci Tech (ISPST)*, Tehran, 3rd -5th Nov, 1997.
4. Roberts B, Verne S, Industrial applications of different methods of crosslinking, *Plast Rubber Process Appl*, **4**, 135-139, 1984.
5. Sultan BÅ, Oderkerk J, Johansson K, Jungkvist J, Crosslinkable high pressure polyethylene composition, a process for the preparation thereof, a pipe and a cable prepared thereof, *US Patent 2007/0161758 A*, (Jul 12, 2007).
6. Khonakdar HA, Morshedian J, Mehrabzadeh M, Wagenknecht U, Jafari SH, Thermal and shrinkage behaviour of stretched peroxide-crosslinked high-density polyethylene, *Eur polym J*, **39**, 1729-1734, 2003.
7. Khonakdar HA, Morshedian J, Eslami H, Shokrollahi F, Study of heat shrinkability of crosslinked low-density polyethylene/poly(ethylene vinyl acetate) blends, *J Appl Polym Sci*, **91**, 1389-1395, 2004.
8. Zhu Y, Yoon HG, Suh KS, Electrical properties of silane crosslinked polyethylene in comparison with DCP crosslinked polyethylene, *IEEE Trans Dielec Electrical Insul*, **6**, 164-168, 1999.
9. SILON International GmbH, Silane crosslinkable polyethylene compounds for pipe manufacture, http://www.silon.eu/download/br_TA11XXHD.pdf, available in 21 December 2008.
10. Narkis M, Tzur A, Vaxman A, Some properties of silane-grafted moisture-crosslinked polyethylene, *Polym Eng Sci*, **25**, 857-862, 1985.
11. Morshedian J, Pourrashid A, Investigation of the effect of electron beam on polyethylene alloys,

- Iran J Polym Sci Technol (in Persian)*, **16**, 95-101, 2003.
12. Gedde UW, Ifwarson M, Molecular structure and morphology of crosslinked polyethylene in an aged hot-water pipe, *Polym Eng Sci*, **30**, 202-210, 1990.
 13. Sultan BÅ, Crosslinking of Polyolefins. In: *Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, 1552-1565, 1996.
 14. Mahabir CM, Backman AL, Dalal GT, Carbon black-containing crosslinked polyethylene pipe having resistance to chlorine and hypochlorous acid, *US Patent 7,255,134 B2* (Aug 14, 2007).
 15. Gale GM, Silane compounds in hot-water pipe and cable technology, *Appl Organomet Chem*, **2**, 17-31, 1988.
 16. Peacock AJ, *Handbook of Polyethylene, structures, Properties, and Applications*, Marcel & Dekker, New York, 6, 2000.
 17. Mehrabzade M, Morshedian J, Barzin J, Preparation of silane grafting and crosslinking of polyethylene: studies of the factors affecting the grafting and crosslinking, *Iran J Polym Sci Technol (in Persian)*, **1**, 3-10, 1998.
 18. Hjertberg T, Palmlof M, Sultan BÅ, Chemical reactions in crosslinking of copolymers of ethylene and vinyltrimethoxy silane, *J Appl Polym Sci*, **42**, 1185-1192, 1991.
 19. Peacock AJ, *Handbook of Polyethylene, Structures, Properties, and Applications*, Marcel Dekker, New York, 306-309, 2000.
 20. Giacobbi E, Miglioli C, Improved Process for Producing Silane Crosslinked Polyethylene, *WIPO, WO/2005/056620* (June 23, 2005).
 21. ASTM D2765-01, Standard test methods for determination of gel content and swell ratio of crosslinked ethylene plastics, *Annual Book of ASTM Standards*, 8.01, 2006.
 22. DIN 16892, Crosslinked high-density polyethylene (PE-X) pipes-General quality requirements and testing, 2001.
 23. Yamazaki T, Seguchi T, ESR study on chemical crosslinking reaction mechanisms of polyethylene using a chemical agent. III: effect of amine type antioxidants, *J Polym Sci A Polym Chem*, **37**, 349-356, 1999.
 24. Peacock AJ, *Handbook of Polyethylene, structures, Properties, and Applications*, Marcel & Dekker, New York, 26, 2000.
 25. Dadbin S, Frounchi M, Sabet M, Studies on the properties and structure of electron-beam crosslinked low-density polyethylene/poly[ethylene-co-(vinyl acetate)] blends, *Polym Int*, **54**, 686-691, 2005.
 26. Morshedian J, Pourrashidi A, Nouranian S, The effect of electron beam irradiation on PE and EVA compounds: changes in properties and applications, *5th Int Sem Polym Sci Tech (ISPST)*, Tehran, 12th-14th September 2000.
 27. Graff G, Colvin R, Silanes produce PE cable insulation process steps, *Mod Plast Int*, **26**, 38-40, 1996.
 28. Kang TK, Ha CS, Effect of processing variables on the crosslinking of HDPE by peroxide, *Polym Test*, **19**, 773-783, 2000.
 29. Pérez CJ, Cassano GA, Vallés EM, Failla MD, Quinzani LM, Rheological study of linear high density polyethylene modified with organic peroxide, *Polymer*, **43**, 2711-2720, 2002.
 30. Abbasi Sourki F, Morshedian J, On the improvement of physical and mechanical properties of PE by crosslinking, *Iran J Polym Sci Technol (in Persian)*, **14**, 95- 100, 2001.
 31. Meola C, Carlomagno GM, Giorleo G, Cross-linked polyethylene. In: *Encyclopedia of Chemical Processing*, Lee S, Lee L (Eds), CRC, USA, **1**, 577-588, 2005.
 32. Ghasemi I, Morshedian J, Kinetic study of crosslinking reaction by peroxide method in LDPE using DSC, a rheometer and an internal mixer, *Iran J Polym Sci Technol (in Persian)*, **15**, 95-101, 2002.
 33. Lázár M, Rado R, Rychly J, Cross-linking of Polyolefins. In: *Advances in Polymer Science Series, Polymer Physics*, Springer-Verlag, Berlin, **95**, 177, 1990.
 34. Harper CA, Petrie EM, *Plastics Materials and Processes: A Concise Encyclopedia*, John Wiley, New York, 2003.
 35. Akutsu S, Isaka T, Ishioka M, Process for producing electric conductors coated with crosslinked polyethylene resin, *US Patent 4,297,310* (Oct 27, 1981).
 36. Rodriguez-Fernandez OS, Gilbert M, Amino-

- silane grafting of plasticized poly (vinyl chloride). I: extent and rate of crosslinking, *J Appl Polym Sci*, **66**, 2111-2119, 1997.
37. Schmid E, Method for the manufacture of crosslinked polyamide articles, *US Patent 5,055,249* (Oct 8, 1991).
 38. Cartasegna S, Silane-grafted/moisture-curable ethylene-propylene elastomers for the cable industry, *Rubber Chem Technol*, **59**, 722-739, 1986.
 39. Smedberg A, Hjertberg T, Gustafsson B, Crosslinking reactions in an unsaturated low density polyethylene, *Polymer*, **38**, 4127-4138, 1997.
 40. Yussuf A, Kosior E, Alban L, Silane grafting and crosslinking of metallocene-catalysed LLDPE and LDPE, *Malaysian Polym J*, **2**, 58-71, 2007.
 41. Rodriguez-Fernandez OS, Gilbert M, Aminosilane grafting of plasticized poly (vinyl chloride). II: grafting and crosslinking reaction, *J Appl Polym Sci*, **66**, 2121-2128, 1997.
 42. Hu M, Wang Z, Qu B, Hu K, Vapour phase grafting of vinyltrimethoxysilane and water crosslinking of polypropylene, *React Funct Polym*, **66**, 287-296, 2006.
 43. Sekiguchi I, Sunazuka H, Kobayashi H, Sekiguchi Y, Silane-crosslinkable halogenated polymer composition and process of crosslinking the same, *US Patent 4,758,624* (Jul 19, 1988).
 44. Ultsch S, Fritz HG, Crosslinking of LLDPE and VLDPE via graft-polymerized vinyltrimethoxysilane, *Plast Rubber Process Appl*, **13**, 81-91, 1990.
 45. Scott HG, Crosslinking of a polyolefin with a silane, *US Patent 3,646,155* (Feb 29, 1972).
 46. Micropol Limited, ISOPLAS crosslinkable polyethylene, <http://www.isoplas.co.uk/download/Isoplas-Crosslinkable-Polyethylene.pdf>, available in 21 December 2008.
 47. Swabrick P, Green W, Maillefer C, Manufacture of extruded products, *US Patent 4,117,195* (Sep 26, 1978)
 48. Padanaplast USA Inc, PEXIDAN Technical Bulletin, www.padanaplastusa.com/pages/TECHBULL_011901.pdf, available in December 2008.
 49. Panzer LM, Bisang W, Silane crosslinking of polyethylene for improving product quality and simplifying the production process, *Int Polym Sci Technol*, **25**, 51-56, 1998.
 50. Bullen DJ, Capaccio G, Frye CJ, Crosslinking reactions during processing of silane modified polyethylenes, *Bri Polym J*, **21**, 117-123, 1989.
 51. Weller KJ, Process for the production of crosslinked polymer employing low VOC-producing silane crosslinker and resulting crosslinked polymer, *US Patent 2008/0090971 A1* (Apr 17, 2008)
 52. Rosendahl Maschinen GmbH, The dry-silane process for crosslinking low-voltage cable, <http://www.read-eurowire.com/rosendahl2.htm>, available in 21 December 2008.
 53. Dammert R, Gustafsson B, Sultan BÅ, Polyethylene compatible sulphonic acids as silane crosslinking catalysts, *US Patent 6,005,055* (Jul 30, 1999).
 54. Mori T, Process for producing silane crosslinked polyolefin, *US Patent 5,756,582* (May 26, 1998).
 55. Mori T, Process for producing flame retardant silane crosslinked polyolefin, *US Patent 6,107,413* (Aug 22, 2000).
 56. Azizi H, Morshedian J, Khonakdar HA, Continuous Preparation of XLPE compounds used for low to Medium Voltage Cable Insulation, *Iranian Patent 31722* (2005).
 57. Fabris FW, Stedile FC, Mauler RS, Nachtigall SM, Free radical modification of LDPE with vinyltrimethoxysilane, *Eur Polym J*, **40**, 1119-1126, 2004.
 58. Kuan HC, Kuan JF, Ma CC, Huang JM, Thermal and mechanical properties of silane-grafted water crosslinked polyethylene, *J Appl Polym Sci*, **96**, 2383-2391, 2005.
 59. Muñoz M, Vargas M, Welang M, Yoshida V, Mauler R, High-density polyethylene modified by polydimethylsiloxane, *J Appl Polym Sci*, **82**, 3460-3467, 2001.
 60. Isac S, George E, Optimisation of silane grafting in single grafting in single screw extruder, *Plast Rubber Compos*, **30**, 34-38, 2001.
 61. Shah GB, Fuzail M, Anwar J, Aspects of the crosslinking of polyethylene with vinyl silane, *J Appl Polym Sci*, **92**, 3796-3803, 2004.
 62. Morshedian J, Mohammad Hoseinpour P, Silane grafting of polyethylene: Effect of molecular structure, physical form, blending, and antioxi-

- dants, *e-polymers* (in press).
63. Morshedian J, Mohammad Hoseinpour P, Azizi H, Parvizzad R, Effect of polymer structure and additives on silane grafting of polyethylene, *eXPRESS Polym Lett*, **3**, 105-115, 2009.
 64. Shieh YT, Tsai TH, Silane grafting reactions of low-density polyethylene, *J Appl Polym Sci*, **69**, 255-261, 1998.
 65. Launer PJ, Infrared analysis of organosilicon compounds: Spectra-structure correlations, <http://www.gelest.com/Library/11Infra.pdf>, available in 21 December 2008.
 66. Gulmine jV, Janissek PR, Heise HM, Akcelrud L, Polyethylene characterization by FTIR, *Polym Test*, **2**, 557-563, 2002.
 67. Wong WK, Varrall DC, Role of molecular structure on the silane crosslinking of polyethylene: the importance of resin molecular structure change during silane grafting, *Polymer*, **35**, 5447-5452, 1994.
 68. Sen AK, Mukherjee B, Bhattacharyya AS, De PP, Bhowmick AK, Kinetics of silane grafting and moisture crosslinking of polyethylene and ethylene propylene rubber, *J Appl Polym Sci*, **44**, 1153-1164, 1992.
 69. Sirisinha k, Chimdist S, Comparison of techniques for determining crosslinking in silane-water crosslinked materials, *Polym Test*, **25**, 518-526, 2006.
 70. Celina M, George GA, Characterization and degradation studies of peroxide and silane crosslinked polyethylene, *Polym Degrad Stabil*, **48**, 297-312, 1995.
 71. Khonakdar HA, Morshedian J, Wagenknecht U, Jafari SH, An investigation of chemical crosslinking effect on properties of high-density polyethylene, *Polymer*, **44**, 4301-4309, 2003.
 72. Khonakdar HA, Jafari SH, Wagenknecht U, Jehnichenc D, Effect of electron-irradiation on cross-linked density and crystalline structure of low- and high-density polyethylene, *Radiat Phys Chem*, **75**, 78-86, 2006.
 73. Lazar M, Rado R, Rychly J, Crosslinking of polyolefins. In: *Advances in Polymer Science Series, Polymer Physics*, Springer-Verlag, Berlin, **95**, 159, 1990.
 74. Jiao C, Wang Z, Gui Z, Hu Y, Silane grafting and crosslinking of ethylene-octene copolymer, *Eur Polym J*, **41**, 1204-1211, 2005.
 75. Edenbaum J, *Plastics Additives and Modifiers Handbook*, Van Nostrand Reinhold, New York, 195-198, 1992.
 76. Yamazaki T, Seguchi T, ESR study on chemical crosslinking reaction mechanisms of polyethylene using a chemical agent. II: the effect of phenolic antioxidants, *J Polym Sci Part A*, **35**, 2431-2439, 1997.
 77. Yamazaki T, Seguchi T, ESR study on chemical crosslinking reaction mechanisms of polyethylene using a chemical agent, *J Appl Polym Sci Polym Chem*, **39**, 2151-2156, 2001.
 78. Yamazaki T, Seguchi T, ESR study on chemical crosslinking reaction mechanisms of polyethylene using a chemical agent, *J Appl Polym Sci Polym Chem*, **35**, 279-284, 1997.
 79. Lazar M, Rado R, Rychly J, Cross-linking of Polyolefins. In: *Advances in Polymer Science Series, Polymer Physics*, Springer-Verlag, Berlin, **95**, 180-181, 1990.
 80. Toynbee J, Silane crosslinking of polyolefins: observations on the tin catalyst employed, *Polymer*, **35**, 438-440, 1994.
 81. Jarrin J, Serpe G, Dawans F, Cross-linked compositions based on polyethylene and cross-linked materials derived from them, *US Patent 5,324,779* (Jun 28, 1994).
 82. Blank WJ, Hessel ET, Abramshe R, Alkylated aryl disulfonic acid catalyst for crosslinking polyethylene, *US Patent 2002/0035215* (Mar 21, 2002).
 83. Anderson LHU, Hjertberg T, The effect of different parameters on the crosslinking behavior and network performance of LDPE, *Polymer*, **47**, 200-210, 2006.
 84. Barzin J, Azizi H, Morshedian J, Preparation of silane-grafted and moisture cross-linked low density polyethylene. Part I: factors affecting performance of grafting and cross-linking, *Polym Plast Technol*, **45**, 979-983, 2006.
 85. Morshedian J, Sioplas cross-linking of PE the effect of ZnO, EVA, Sb₂O₃ and Al(OH)₃ and shelf life and properties of the products, *PPS-2001 Region Conf*, Antalya, Turkey, 22nd-24th October 2001.

86. Morshedian J, Mehrabzadeh M, Aghdam MH, Nouranian S, Sioplas crosslinking of PE: The effect of ZnO on shelf life of silane-grafted polyethylene granules, 5th *Int Sem Polym Sci Tech (ISPST)*, Tehran, Iran, 12th-14th September 2000.
87. Barzin J, Azizi H, Morshedian J, Preparation of silane-grafted and moisture crosslinked low density polyethylene. Part II: Electrical, thermal and mechanical properties, *Polym-Plast Technol*, **46**, 305-310, 2007.
88. Azizi H, Barzin J, Morshedian J, Silane crosslinking of polyethylene: the effects of EVA, ATH and Sb₂O₃ on properties of the production in continuous grafting of LDPE, *eXPRESS Polym Lett*, **1**, 378-384, 2007.
89. Levesque G, Hibert F, Pimbert S, Evidence for chemical grafting during extrusion of copoly(ethylene/vinyl acetate)-aminopropyl tris(alkoxy)silane mixtures, *Plast Rubber Compos Process Appl*, **26**, 38-42, 1997.
90. Morshedian J, Azizi H, Salehi Mobarake H, Sioplas crosslinking of PE: Effect of EVA on properties of XLPE, *Iran J Polym Sci Technol (in Persian)*, **5**, 281-285, 2001.
91. Azizi H, Morshedian J, Salehi Mobarakeh H, The effect of EVA on properties of silane-crosslinked polyethylene, 6th *Int Sem Polym Sci Tech (ISPST)*, Tehran, Iran, 12th-15th May 2003.
92. Kumar MSC, Alagar M, Prabu A, Studies on dynamic mechanical and mechanical properties of vinyloxyaminosilane grafted ethylene propylene diene terpolymer/linear low density polyethylene (EPDM-g-VOS/LLDPE) blends, *Eur Polym J*, **39**, 805-816, 2003.
93. Alagar M, Abdul Majeed SM, Nagendiran S, Preparation and characterization of vinyltriethoxysilane grafted ethylene propylene diene terpolymer/linear low density polyethylene (EPDM-g-VTES/LLDPE) blends, *Polym Advan Technol*, **16**, 582-591, 2005.
94. Alagar M, Abdul Majeed SM, Selvaganapathi A, Gnanasundaram P, Studies on thermal: thermal ageing and morphological characteristics of EPDM-g-VTES/LLDPE, *Eur Polym J*, **42**, 336-347, 2006.
95. Barzin J, Morshedian J, Mehrabzadeh M, Preparation of silane crosslinked PE: study the effective parameters on grafting and crosslinking processes and the resultant physical and mechanical properties, 4th National Chemical Engineering Congress, Tehran, Iran, 9th-11th March 1999.
96. Shieh YT, Hsiao KI, Thermal properties of silane-grafted water-crosslinked polyethylene, *J Appl Polym Sci*, **70**, 1075-1082, 1998.
97. Zong R, Zhengzhou W, Liu N, Hu Y, Guanxuan L, Thermal degradation kinetics of polyethylene and silane-crosslinked polyethylene, *J Appl Polym Sci*, **98**, 1172-1179, 2005.