Effects of cross-linking methods for polyethylene-based carbon fibers: review

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Abstract

In recent decades, there has been an increasing interest in the use of carbon fiber reinforced plastic (CFRP) in aerospace, renewable energy and other industries, due to its low weight and relatively good mechanical properties compared with traditional metals. However, due to the high cost of petroleum-based precursors and their associated processing costs, CF remains a specialty product and as such has been limited to use in high-end aerospace, sporting goods, automotive, and specialist industrial applications. The high cost of CF is a problem in various applications and the use of CFRP has been impeded by the high cost of CF in various applications. This paper presents an overview of research related to the fabrication of low cost CF using polyethylene (PE) control technology, and identifies areas requiring additional research and development. It critically reviews the results of cross-linked PE control technology studies, and the development of promising control technologies, including acid, peroxide, radiation and silane cross-linking methods.

Key words: polyethylene, cross-linked, low cost carbon fiber

1. Introduction

The carbon fiber (CF) industry has been growing continuously, with a focus on aerospace, military, and construction industries, as well as on medical, automobile, and sporting goods applications [1-4]. As a consequence of the increasing use of CFs in wind power systems and in the specialist industrial applications sector, the demand in the coming five years is expected to establish CF in the mass market. However, due to the high cost of their petroleum-based precursors and associated processing costs, CF remains fairly expensive [5-20].

The price of CFs is primarily driven by its manufacturing costs [20]. The total price of CF consists of 43% precursor costs, 46% processing costs, and 11% other costs. Consequently, in efforts to lower the price of CF, research has mainly focused on the development of affordable precursors and processes [21,22]. Among all manufacturing processes, the manufacture of CFs is mainly based on polyacrylonitrile (PAN) [23], pitch [24], and rayon [25] based precursors.

Rayon-base precursors have proved to be inefficient, as the resulting fibers contain only about 20% carbon and have low strength and stiffness properties [26]. Although pitch-based CFs can be melt spun, the flow characteristics of mesophase pitch makes it extremely difficult to process. In addition, CFs derived from isotropic pitches have low tensile strengths, which do not meet the engineering requirements of the CF industry.
Among the precursors for the production of CFs, PAN is the predominant material, due to the excellent mechanical properties of PAN-based CFs [7]. However, the high cost of PAN precursors, which make up 46% of the CF manufacturing cost, limits its utilization in general performance grade applications in automotive parts [16].

To establish CFs in the mass market, the price of CF precursors has to be significantly reduced [10,20,23-25,30-40]. The lowest priced CF precursors primarily consist of polyethylene (PE) [41], lignin [33], and cellulose [42].

Cellulosic precursor fiber was first used by Thomas Edison in the 1880s as the basis for his revolutionary electric lamp filament [43]. Much later, in 1959, the National Carbon Company introduced a carbon cloth from a rayon precursor and 2 years later carbon yarn became available [26,44]. In 1965, the Thornel range of CFs was announced, whose properties were improved by a post-carbonization treatment involving stretching at 2500°C. This fiber had a tensile strength of 1.25 GPa and a Young’s modulus of 170 GPa [45]. However, due to the cost of the hot stretching process and disadvantages in the yield and mechanical properties of the cellulose precursor [46] the production of these fibers lasted little more than 10 years [8]. Much of the focus of current work is on designing microstructure through control of precursor morphology and processing conditions [42]. Lignin is one of the most abundant substances in nature and is present in all fibrous plants, and as a byproduct of the pulp and paper industry.

Because lignin is a readily available and comparatively inexpensive polyaromatic macromolecule, it may fulfill many of the requirements needed as a precursor to CFs. Using lignin as a renewable feedstock for fine chemicals and materials has the potential to generate significant environmental and economic benefits necessary for the viability of the main processes. In spite of these large advantages, lignin has not yet been effectively utilized, and this presents environmental problems. Unfortunately, today’s standard method for recovering lignin from paper mill streams is not suitable for producing a high volume of lignin with properties suitable for fast and economically viable wet-spinning and eventual conversion to CFs with the quality requirements that industry demands [47]. In contrast, PE can easily be used to produce fibers at low cost, and has been applied as an industrial fiber. Also, PE has a high carbonization ratio in the carbonization process, and it can be melt spun. Because of these advantages, PE is promising for the manufacture of a low-cost CF [41,48].

Among these materials, as a precursor for CF, PE has the ability to reduce the cost of manufacturing by more than 50% compared to PAN [49]. Textile-grade PEs have been considered good candidates for affordable precursors because of their low cost [50]. PEs (high density PE [HDPE], low density PE [LDPE], linear low density PE [LLDPE]) can usually be cross-linked by four different methods, that is, by energy radiation [51], peroxide [52], silane coupling agents [53], and sulfonation [54] cross-linking.

In this paper, we review the various cross-linking methods used for manufacturing low priced CF from PE-based fibers.

Fig. 1. (a) Chain scission in polyethylene (PE); (b) the cross-linking reaction, or formation of C-C covalent bonds between adjacent molecular chains in PE [55].

2. Processing Methods

2.1. Radiation

When exposed to ionizing radiation, two structural changes occur in a polymer such as PE (Fig. 1). The first is chain scission (C-C breakage) of the ‘taut’ tie molecules (Fig. 1a). The second is a reaction of free radicals (produced by the breakage of the C-H bonds) with each other to form crosslinks between adjacent molecule chains (Fig. 1b) [55].

2.1.1. Gamma irradiation

Alvarez and Perez [56] researched the crystallization behavior of PE cross-linked by radiation in different atmospheres, under non-isothermal conditions, using differential scanning calorimetry (DSC). The crystallization rate, the crystallization temperature and the crystallinity degree decreased with the radiation dose in nitrogen atmosphere, and with decreasing oxygen content at the same dose. On the other hand, the activation energy increased with the radiation dose and decreased with the oxygen content. These results are related to the increase in the degree of cross-linking, which restricts the crystallization process.

The full model was also used to build continuous cooling transformation (CCT) diagrams. The curves representing the relative degree of crystallinity at 0.3 were plotted as a function of time. Each point on these curves was obtained by the integration of the full model (nucleation and growth) at a given cooling rate. So, when the degree of crystallization curve is intercepted by a constant cooling rate curve, the obtained point represents the time necessary to reach a specific relative degree of crystallization under specific thermal conditions. From Fig. 2 it can be observed that the time necessary to reach the relative crystallinity degree of 30% increased with the radiation dose, indicating the dose increase had a retarding effect. On the other hand, the diagrams of samples irradi-
be determined for different processing conditions, which can be very useful for the design and optimization of processing steps, and clearly show a retarding effect with increasing irradiation dose and with decreasing oxygen content (Fig. 2).

Fig. 2. Non-isothermal crystallization of gamma irradiated low density polyethylene (LDPE) in the presence of oxygen. Reprinted with permission from [56]: (a) non-isothermal crystallization curves obtained at a cooling rate of 10°C/min of samples prepared with different oxygen concentrations (%v/v), irradiated with 33 kGy, 83 kGy, 153 kGy, and 222 kGy; (b) activation energies of studied materials as a function of the relative degree of crystallinity; (c) CCT plots for A original and irradiated LDPE (nitrogen atmosphere) and B irradiated with 222 kGy in different atmospheres.

Fig. 3. Characteristics and properties of gamma irradiated cross-linked low density polyethylene foams. Reprinted with permission from [57]: (a) presents thermal behavior results obtained by each individual foam sample; (b) melt strength, extrudate swell and expansion index for 0–30 kGy foams samples; (c) gel fraction and melt flow index results in 0–30 kGy foams samples; (d) ATR spectra for 0–30 kGy foams samples (identification of carbonyl range: 1699, 1716 and 1743 cm⁻¹).

ated in different atmospheres at 222 kGy (Fig. 2) indicate that the retarding effect increased when the oxygen content decreased.

These diagrams allow the evolution of crystallinity degree to be determined for different processing conditions, which can be very useful for the design and optimization of processing steps, and clearly show a retarding effect with increasing irradiation dose and with decreasing oxygen content (Fig. 2).
destruction of large crystals while the \(T_c\) was also reduced due to cross-linking, which prevented the macromolecular chains from crystallizing. Results from the Fourier transform infrared spectroscopy (FTIR) experimental technique strongly suggested that trans-vinylene double bond groups were formed, due to an increase in the intensity of the peak at 965 \(\text{cm}^{-1}\), which may be due to the presence of cross-linking. There was also strong evidence for the formation of oxidative products on the surface of the samples, which could be related to the reactions of the allyl radicals with oxygen molecules present in the air when the samples were exposed to air during and after the irradiation process. Therefore, it may be concluded that there are significant modifications in the thermal and structural properties of LDPE after irradiation (Fig. 4).

Using comparable irradiation doses, Khonakdar et al. [59] found that cross-linked LDPE samples which were more amorphous in nature, and which had highly active sites due to its branched structure, were more prone to cross-linking and hence had higher gel content as compared to cross-linked HDPE samples. The cross-link density and creep modulus calculated by rubber elasticity theory and hot set creep data, increased with increasing irradiation dose. As compared to HDPE, the LDPE had a higher cross-link density and consequently a lower \(M_n\) value for any comparable irradiation dose, implying a higher network formation in the LDPE. The hot set measurements showed that the high concentration of cross-links (cross-link density) in the PE samples led to a longer resistance time and a lower elongation and a higher...
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in DSC, the samples showed various levels of crystallinity, whose effect was clearly evidenced in the second heating cycle by a decrease in melting temperature. The confined crystallization behavior of XLPE in the molten state was related to the decrease in the $M_c$. The length of chain segment motion needed for usual crystallization by the chain folding process was decreased, and hence the crystallization process was hindered (Fig. 5).

2.1.3. Ion beam irradiation

Turos et al. [60] reported that the deposition of high-energy density during ion beam bombardment caused irreversible...

Fig. 5. Cross-link density and crystalline structure of electron-irradiation on low density polyethylene (LDPE) and high density PE (HDPE). Reprinted with permission from [59]: (a) gel content, cross-link density and hot set data for cross-linked LDPE and HDPE with different irradiation doses; (b) melting temperature $T_m$, heat of fusion $\Delta H_m$, degree of crystallinity $X_c$ of first heating of samples and crystallization temperature $T_c$ of irradiated LDPE and HDPE with different irradiation dose; (c) WAXS curves (shifted 3D-plot) for HDPE irradiated with different dose rates (dose in kGy: — 0; - + - 50; - × - 100; - ● - 150; - ○ - 200; - • - 250).
ments. Upon continued irradiation, cross-linking proceeds and leads to the formation of a dense three dimensional network in the surface region. These structural transformations lead to high-molecular weight, and increased backbone structure rigidity. The improved mechanical integrity of such highly cross-linked surface regions is the reason for the increase in the friction coefficient and hardness of irradiated polymers. With an increasing ion dose, the exhaustion of cross-linkable sites occurs leading to the subsequent predominance of scission. These arguments explain the dose dependence of the HDPE tribological parameters shown in Fig. 6.

2.2. Peroxide

The cross-linking of PE with peroxide is based on a free radical mechanism. The free radicals generated by the thermal degradation in polymers [61]. Both cross-linking and scission occur simultaneously, but one of these two processes may prevail for a given polymer. Polymers having quaternary carbon atoms with large pendant groups were considered to be of the degrading type. In contrast, polymers with at least one hydrogen atom bound to each structural backbone carbon atom, such as PE, were of cross-linking type. Although structure plays an important role, it has been shown recently that the density of deposited energy may be a decisive factor as to whether scission or cross-linking occurs [62].

Cross-linking can occur only when two dangling bonds are located in neighboring chains. Diminishing the distance between such chains will facilitate their interaction. Hence, the probability of cross-linking will be much higher in HDPE than in LDPE. At low ion doses, the resulting microstructure consists of a poorly cross-linked network with some scissioned fragments. Upon continued irradiation, cross-linking proceeds and leads to the formation of a dense three dimensional network in the surface region. These structural transformations lead to higher molecular weight, and increased backbone structure rigidity. The improved mechanical integrity of such highly cross-linked surface regions is the reason for the increase in the friction coefficient and hardness of irradiated polymers. With an increasing ion dose, the exhaustion of cross-linkable sites occurs leading to the subsequent predominance of scission. These arguments explain the dose dependence of the HDPE tribological parameters shown in Fig. 6.

**Fig. 6.** Surface properties of ion beam modification of polyethylene. Reprinted with permission from [60]: (a) AFM micrographs of the HDPE surface of pristine sample A and after the Ar-ion bombardment with a dose of $1 \times 10^{16}$ at/cm$^2$; (b) hardness and friction coefficient for HDPE as a function of the He-ion dose; (c) hardness and friction coefficient for HDPE as a function of the Ar-ion dose; (d) maximal values of hardness for different types of polyethylene prior and after ion bombardment; (e) maximal values of friction coefficient for different types of polyethylene prior and after ion bombardment.
Composition of peroxides can attack the molten PE free chains, and cross-linking of the polymer chains may occur. A general scheme for the cross-linking reaction of PE initiated by free radicals is quite simple, consisting of the formation of macro radicals and their subsequent recombination [63].

PE can be cross-linked by chemical initiators or by the use of a b, g or electron-beam irradiation sources. Within the literature on chemical methods, it is possible to find works where peroxides or silanes have been used for these purposes [64-70].

Cross-linking of PE can be initiated by a peroxide which decomposes as an effect of the temperature, as shown in the scheme in Fig. 7 [71]. The use of peroxides seems to present several advantages in comparison with other methods. For example, radiation cross-linking only modifies the properties on the polymer surface and the use of silane requires a two-step process, the grafting of the silane to the PE molecule and the condensation of silane groups, where the presence of
well developed spherulites to nonbanded axialites occurred at approximately the same crosslink density for both materials A and B. Hence, the morphological structure was similar irrespective of the different crosslink mechanisms, at a certain crosslink density. This indicates that the type of crosslink does not influence the results at the crosslink densities studied. However, the size and perfection of the supramolecular structures differed between the two materials, with material B having smaller and less perfect structures than material A (Fig. 8).

Research results obtained Marcilla et al. [71] revealed that the utilization of a catalyst enhances differences among samples with different degrees of cross-linking, in contrast to the case of samples decomposed in the absence of catalyst, where very slight differences could be observed. The changes undergone by cross-linking, even at very low gel content, were markedly reflected in the thermogravimetric behaviour. In this study, catalytic pyrolysis was proved to be an alternative technique to monitor cross-linking, which allows the comparison of samples with different degrees of cross-linking.

water (which has to diffuse through the polymer) is necessary [64,69].

Nilsson et al. [63] investigated a reference LDPE (material A) and a LDPE with increased vinyl content (material B). The two LDPE materials were cross-linked mainly using combination cross-linking (A) or via a combination of reacted vinyl groups and combination cross-linking (B), with a resulting difference in the cross-linked network. A comparison of the materials at a low crosslink density, i.e. ≥ca 4500 g/mol, where the difference in crosslink methods was most evident, there was no obvious distinction between the materials. Both materials showed a decrease in $T_m$, $T_c$, and $X_c$ after cross-linking with an increasing amount of peroxide, due to the restraining effect of the incorporated crosslinks. Some smaller disparities in $T_m$ and $X_c$ could be noticed between the materials, possibly due to the difference in crosslink structure. Mechanical testing, stepwise increasing strain test (SIST) and scanning electron microscopy (SEM) measurements supported the results obtained from the DSC studies. A change from fairly

Fig. 9. Thermal and catalytic pyrolysis properties of cross-linked polyethylene. Reprinted with permission from [71]: (a) calorimetric curves of samples with different peroxide concentration; (b) temperature corresponding to 10% of weight loss for different samples with and without catalyst; (c) gel content measurements; (d) TGA A and DTG B curves for samples without catalyst: (—) 0% peroxide, (♦) 0.5% peroxide, (*) 1% peroxide, (–) 2% peroxide, (●) 3% peroxide, and (▲) 4% peroxide; (e) melting enthalpy A and melting temperature B of crosslinked polyethylene samples with different peroxide concentration.
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Cal milling using a pan-mill equipment is a good method to re-cycle XLPE by partial de-cross-linking. In order to investigate the effect of the milling process on the crystallization kinetics of XLPE, three different kinetic models, the Avrami, the Ozawa and the Mo, were applied to systematically study the non-isothermal crystallization kinetics of XLPE, de-XLPE and LDPE based on the DSC technique. All three models were found to describe the experimental data very well.

The parameters \( Z_c \) and \( t_{1/2} \) derived from the modified Avrami method suggested that de-XLPE had a faster crystallization rate than XLPE due to higher chain mobility, which resulted from partial de-cross-linking. \( K(T) \) from the Ozawa method revealed a tendency that fit well with the results of the Avrami method. In addition, the Ozawa method was found to be a satisfactory description of the non-isothermal crystallization process of LDPE, while its secondary crystallization was not obvious and could be neglected. From the Mo method, the value of \( F(T) \) of de-

by a quicker procedure than solvent extraction. Furthermore, this method is able to reflect molecular changes associated to cross-linking not observable by other techniques, as determined by gel content. This procedure could be of particular applicability in amorphous polymers, where changes associated with cross-linking cannot be monitored by calorimetric curves (Fig. 9).

Yu et al. [72] studied the effect of chemical cross-linking on the thermal conductivity of HDPE in order to investigate the influence of chemical cross-linking on the thermal conductivity. The gel content, density, spherulite size, crystallite size and crystallinity were strongly affected by the content of the dicumyl peroxide (DCP) cross-linking agent. As the DCP content increased, the gel content increased while the density, spherulite size, crystallite size and crystallinity rapidly decreased. The thermal conductivity synchronously decreased with a decrease in the crystallinity (Fig. 10).

Wu et al. [73] demonstrated that solid state mechanochemical milling using a pan-mill equipment is a good method to re-cycle XLPE by partial de-cross-linking. In order to investigate the effect of the milling process on the crystallization kinetics of XLPE, three different kinetic models, the Avrami, the Ozawa and the Mo, were applied to systematically study the non-isothermal crystallization kinetics of XLPE, de-XLPE and LDPE based on the DSC technique. All three models were found to describe the experimental data very well.

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![Fig. 10. Thermal conduction behaviors of chemically cross-linked high-density polyethylene melts (HDPEs). Reprinted with permission from [72]; (a) DSC thermograms of pristine and crosslinked HDPEs via a heating scan; (b) A synchrotron WAXS patterns of HDPE and crosslinked HDPEs. Top and bottom insets show high magnification of (110) diffraction and amorphous halo B resolved peaks of HDPE, and C crystallite size of HDPE and crosslinked HDPEs; (c) gel contents and bulk densities of the pristine and crosslinked HDPEs with various DCP contents; (d) polarized optical micrographs of A HDPE and B crosslinked HDPE with DCP 3.0 wt.%; (e) characteristics of the pristine and crosslinked HDPEs with various DCP contents including thermal diffusivity, density and specific heat data.](http://carbonlett.org)
XLPE was found to be lower than that of XLPE, which also indicated that the de-cross-linking effect of mechano-chemical milling could accelerate the overall crystallization process (Fig. 11).

### 2.3. Silane

Silane coupling agents are silicon-based organic chemicals that contain two types of substituent (inorganic and organic) in the same molecule [74,75].

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 the cross-linking of polyolefins and some other polymers [76-78].

Since the silane groups are polar they provide compatibility in PE based blends, where the PE is non-polar in nature [79]. Vinyl alkoxy silanes (e.g., vinylmethyldimethoxysilane, vinyltrimethoxysilane [VTES], vinylmethoxysilane) are suitable compounds for these kinds of reactions due to their double

![Fig. 11. Non-isothermal crystallization kinetics of peroxide-cross-linked polyethylene (XLPE): effect of solid state mechanochemical milling. Reprinted with permission from [73]; (a) DSC thermograms of non-isothermal crystallization for XLPE A, de-XLPE B, and LDPE C at the cooling rate of 2.5 °C/min; (b) effect of mechanochemical milling on the gel content of XLPE; (c) characteristic data of nonisothermal crystallization exotherms for XLPE, de-XLPE, and LDPE at different cooling rates; (d) non-isothermal crystallization kinetic parameters based on the Ozawa method.](image)

![Fig. 12. Principal reactions involved in silane cross-linking of polyethylene [82].](image)
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Fig. 13. Characterization and mechanical properties of cross-linked high density polyethylene (HDPE) by silane. Reprinted with permission from [83]: (a) yield strength and Young’s modulus as a function of processing conditions of HDPE, PEX-3% silane, and PEX-4% silane; (b) yield strength and Young’s modulus as a function of processing conditions of HDPE; (c) FTIR spectra of HDPE and PEXs crosslinked with 3% and 4% silane; (d) DTG curves of HDPE and PEX with 3% and 4% silane; (e) gel content and solvent uptake factor values of the extraction carried out with trichloroethylene for crosslinked samples at crosslinking time of 90 min.

Silane-grafting by water-cross-linking method consists of at least two stages that also proceed consecutively [81]. In the first stage, a proper silane (vinylalkoxysilane) is grafted via its vinyl groups on PE through a peroxide initiated free radical reaction; it should be noted that during the grafting reactions, new PE radicals are formed (Fig. 12) and the required amount of peroxide is relatively low. In the second stage, the resultant copolymer is crosslinked via exposure to hot water or steam with the aid of a catalyst. Moisture leads to hydrolysis of the alkoxy groups of silane and thereafter, these hydroxyl groups condense to form stable siloxane linkages (the crosslinks). Fig. 12 illustrates the reaction mechanism during peroxide induced melt grafting of vinyl silane onto PE, followed by the hydrolysis and condensation step during the silane crosslinking reaction [82].

Oliveira and Costa [83] found that, after optimization of the cross-linked PE (PEX) process conditions by extrusion, the process speed did not significantly affect tensile mechanical properties such as modulus of elasticity and yield strength, although an increasing trend was observed for materials processed at temperature range B. This trend was greater when combined with 60 rpm speed, which made it possible to define the optimum PEX extrusion condition. Infrared analysis allowed the PEXs development to be confirmed, and the
siloxane crosslinks present in their structures were observed in the spectra of HDPE cross-linked with 3% and 4% silane. Those crosslinks did not significantly change the crystallinity of the PEXs, as confirmed by X-ray diffraction analysis. However, they ensured an improvement in the cross-linked HDPE thermal stability and creep resistance when compared to non-cross-linked HDPE (Fig. 13).

Sirisinha et al.’s [84] investigation of the silane grafting of HDPE indicated that the studied silane carriers (EVA, EB, and EO) could not improve the efficiency of grafting. The presence of bulky groups and steric side chains in the carrier molecules caused melt grafting difficulty. However, the silane carriers showed a positive influence on the water–cross-link reaction. The rate of cross-linking and density of the crosslink network increased with carrier addition. This was due to an increase in the amorphous region brought about by the siloxane crosslinks present in the silane carriers.
Fig. 15. Non-isothermal crystallization kinetics of peroxide-cross-linked polyethylene: effect of solid state mechanochemical milling. Reprinted with permission from [85].

Sirisinha and Chimdist [85] also investigated silane-water cross-linked ethylene–octene copolymer (EOR) and EOR/LDPE blends for their degree of cross-linking. The characterization techniques used were the standard gel content determination method, the solvent uptake factor method, and FTIR analysis. The results showed that the cross-linking time and the content of the crystalline portion in the materials have an important effect on the degree and rate of cross-linking reaction. Comparing the three techniques investigated, it can be summarized that the measurement of gel content is a direct way to yield results on the degree of cross-linking. However, care must be taken when analyzing samples with low gel content by these techniques. Quantitative characterization of the FTIR data, especially a decrease in the absorption intensity of the methoxysilane groups, may not provide a direct cross-linking value, but the technique is non-destructive and presents meaningful information on the progress of the silane-water cross-linking reaction. The test is also less time consuming and needs no solvent, so is more environmentally friendly compared to the gel content determination and solvent up-
for reactions performed in the presence of peroxide. Final torque did not change at all with the changing concentration of VTES, but after a few months’ storage a significant gel fraction was observed, probably due to post-reactor combination reactions (Fig. 16).

2.4. Sulfuric system

Ihata [86] demonstrated the cyclization formation of PE via the cross-linked reaction of sulfuric acid in 1988. The reaction mechanism of the sulfuric acid with PE is represented take factor methods (Fig. 15).

Fabris et al. [70] found that VTES easily grafted to melted LDPE in the presence of peroxide, up to 86% of conversion. The degree of functionalization increased with VTES and peroxide concentration though no functionalization was observed in the absence of peroxide. The absolute degree of functionalization could be determined by simple infrared analysis after relating them to Rutherford backscattering spectrometry results, with a good correlation factor ($r = 0.995$). Torque measurements and molecular weight determinations indicated the occurrence of chain combination reactions performed in the presence of peroxide. Final torque did not change at all with the changing concentration of VTES, but after a few months’ storage a significant gel fraction was observed, probably due to post-reactor combination reactions (Fig. 16).

**Fig. 16.** Free radical modification of low density polyethylene (LDPE) with vinyltriethoxysilane. Reprinted with permission from [70]; (a) infrared spectra of LDPE and PE–VTES; (b) correlation between degree of functionalization ($F$) determined by RBS and ratio $A958 / A2020$ obtained from FTIR ($r = 0.995$); (c) degree of functionalization as a function of VTES concentration for two DCP concentrations; (d) molecular weights of PE; (e) gel fraction of PE-VTES; (f) crystallinity, melting temperature ($T_m$) and crystallization temperature ($T_c$) of PE and PE–VTES; (g) mechanical properties of PE and PE–VTES.
Using density functional theory and transition state theory, the author determined the rate constants for the internal elimination and radical chain reaction mechanism for the pyrolysis of H$_4$S.

Nonlinear Arrhenius plots were found for all bimolecular reactions. To report and interpret rate constants, we used the Kooij equation. For reactions with low activation barriers, nonlinearity was traced to conflicting trends between the exponential temperature dependence of the energetic term and the vibrational partition function of the transitional modes. For reactions with high activation energies, the exponential term was dominant, and the Arrhenius plot approached linearity. This work represents the first study of E$_i$ elimination in alkane sulfonic acid derivatives. Two different reaction barriers were found (50 and 60 kcal/mol), depending on the placement of the HO-group in the sulfonic acid. R–CHSO$_3$H rotation from the reactant to the transition state yielded a cis-alkene. The decomposition of the product, H$_2$SO$_3$, was aided catalytically by H$_2$O, with a barrier of 16 kcal/mol. Following the radical abstraction of the α-H from H$_4$S, first order decomposition of the radical intermediate yielded the trans-alkene and HOSO$_2$. At temperatures <440 K, the amount of H$_4$S converted to the olefin was insignificant. At higher temperatures, HOSO$_2$ underwent decomposition to OH + SO$_2$, which allowed for rapid α-H abstraction by OH. Given the reported BDEs for the resulting olefin, we predicted that the increasing presence of unsaturated bonds during the course of pyrolysis will augment the amount of OH, and

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**Fig. 17.** Reaction mechanism of sulfuric acid with low density polyethylene, introducing sulfuric groups and carbon-to-carbon double bonds [86].

below as Fig. 17. In the reaction mechanism, the surface of PE was sulfonated by reaction with gaseous SO$_3$. It was confirmed that PE and SO$_3$ gave unsaturated sulfonic acids and that, as the reaction proceeded, the elimination of sulfuric acids took place to form sulfonic acids having highly conjugated C=C unsaturated bonds.

Younker et al. [87] sought to understand the pyrolysis pathways of sulfonated PE with the present Author, and studied the decomposition reactions of the model compound H$_4$S.

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**Fig. 18.** Pyrolysis pathways of sulfonated polyethylene, an alternative carbon fiber precursor. Reprinted with permission from [87]: (a) scheme showing E$_i$5 elimination (top) and the radical chain reaction (bottom) for H$_4$S; (b) M06-2X/6-311++G(3df,3pd)/M06-2X/6-31G** BDEs in kcal/mol at 298 K; (c) binned minima from R–SO$_3$H rotational coordinate. Reactant A is in purple, B is in green, and C is in blue; (d) A TGA thermogram of partially functionalized PE fiber (inset: scanning electron micrograph of pyrolyzed fiber from a partially sulfonated polyethylene). B TGA thermogram of fully functionalized PE fiber (inset: scanning electron micrograph of pyrolyzed fiber from a fully sulfonated polyethylene).
different mechanisms. At temperatures >600 K, a concerted unimolecular reaction was present that produced a \textit{cis}-alkene. At temperatures from 440 to 550 K, a radical reaction produced a \textit{trans}-alkene. In this region, the maximum rates of change in % mass occurred from 440 to 480 K, depending on heating rate. At these temperatures, \text{HOS}_2\text{O} decomposed and \text{H} became the radical responsible for propagation of the chain reaction.

Younker et al. \cite{87} have used kMC, in conjunction with density functional theory (DFT)/threshold testing (TST) determined rate constants, to simulate thermosgravimetric analysis (TGA) simulations. We found two regions in the TGA that were dominated by \textit{H} radicals. At higher temperatures, \text{OH} became the dominant radical.

**Fig. 18.** Continued: (a) M06-2X/6-311++G(3df,3pd)//6-31G** Kooij Parameters from 300 to 1000 K for Various Reaction Steps; (b) A experimental TGAs based on sulfonated PE at heating rates of 2.5 (red), 5 (green), 10 (blue), and 20 (pink) °C/min. B H4S kMC simulations (1.6 ng mL\(^{-1}\) 20 °C/min) detailing TGA dependence on \text{O}/\text{H4S} ratio: 3.3 × 10\(^{-1}\) (red), 3.3 × 10\(^{-2}\) (green), 3.3 × 10\(^{-3}\) (blue), 3.3 × 10\(^{-4}\) (pink), 6.7 × 10\(^{-5}\) (aqua), 1.3 × 10\(^{-5}\) (orange), 2.7 × 10\(^{-6}\) (gray), and experimental (black, based on sulfonated PE). C H4S kMC simulations (20 °C/min) detailing TGA dependence on H4S density (first number) and high \text{O}/\text{H4S} ratio (second number): 1.6 pg mL\(^{-1}\) 6.7 × 10\(^{-7}\) (red); 16 pg mL\(^{-1}\) 3.3 × 10\(^{-3}\) (green); 160 pg mL\(^{-1}\) 2.7 × 10\(^{-3}\) (blue); 16 ng mL\(^{-1}\) 2.7 × 10\(^{-3}\) (pink); 16 ng mL\(^{-1}\) 2.7 × 10\(^{-3}\) (aqua); and experimental (black, based on sulfonated PE). D TGA (1.6 ng mL\(^{-1}\) 20 °C/min) mole ratio of H4S and \text{O}/\text{H} as a function of temperature/time with \text{O}/\text{H4S} ratio: 3.3 × 10\(^{-1}\) (aqua), 3.3 × 10\(^{-2}\) (pink), 6.7 × 10\(^{-3}\) (blue), 1.3 × 10\(^{-3}\) (green), and 2.7 × 10\(^{-4}\) (red). See the Supporting Information for all TGAs.
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The elongation at break was extremely high, up to 3%. The carbon yield of the process was 72% to 75% (Fig. 19).

Penning et al. [111] researched the pronounced effect of the diameter of LLDPE-based CFs on their strength and modulus, and these properties could be improved considerably by using thin precursor fibers. Thin LLDPE filaments were obtained by application of elevated spinline temperatures in the melt-spinning process, which led to an improvement of the maximum attainable draw-down ratio. Careful carbonization of these filaments gave 17 µm thick CFs with a tensile strength of 1.90 GPa and a modulus of 148 GPa. By additional hot-drawing of the melt-spun filaments, even thinner precursor fibers were obtained, that could be converted to 13 µm CFs, with a strength of 2.16 GPa and a modulus of 130 GPa. It was necessary to anneal chain reactions. The maximum rates of change in the radical region of the TGA agree with what was observed experimentally (440-460 K). Low-scale pyrolysis of sulfonated PE utilizes temperatures <620 K, making the radical mechanism the dominant pathway in the production of carbonaceous unsaturated hydrocarbon that, subsequently, undergoes carbonization at very high temperature. Such carbonization studies will be conducted in future investigations, as shown in Fig. 18a and b [96-109].

Postema et al. [110] researched melt-spun LLDPE fibers which were made infusible by treatment with chlorosulfonic acid. The cross-linked fibers were pyrolyzed within 5 min at temperatures between 600°C and 1100°C under tension, in a nitrogen atmosphere. CFs prepared at 900°C, had a tensile strength of 1.15 GPa and a Young’s modulus of 60 GPa. The elongation at break was extremely high, up to 3%. The carbon yield of the process was 72% to 75% (Fig. 19).

Penning et al. [111] researched the pronounced effect of the diameter of LLDPE-based CFs on their strength and modulus, and these properties could be improved considerably by using thin precursor fibers. Thin LLDPE filaments were obtained by application of elevated spinline temperatures in the melt-spinning process, which led to an improvement of the maximum attainable draw-down ratio. Careful carbonization of these filaments gave 17 µm thick CFs with a tensile strength of 1.90 GPa and a modulus of 148 GPa. By additional hot-drawing of the melt-spun filaments, even thinner precursor fibers were obtained, that could be converted to 13 µm CFs, with a strength of 2.16 GPa and a modulus of 130 GPa. It was necessary to anneal chain reactions. The maximum rates of change in the radical region of the TGA agree with what was observed experimentally (440-460 K). Low-scale pyrolysis of sulfonated PE utilizes temperatures <620 K, making the radical mechanism the dominant pathway in the production of carbonaceous unsaturated hydrocarbon that, subsequently, undergoes carbonization at very high temperature. Such carbonization studies will be conducted in future investigations, as shown in Fig. 18a and b [96-109].

Fig. 19. Morphology and mechanical properties of amorphous carbon fibers from linear low density polyethylene. Reprinted with permission from [110]: (a) IR spectra of LLDPE films treated with chlorosulphonic acid for different periods of time, At = 30 min, bt = 1 h, ct = 2 h, dt = 4 h; (b) SEM micrograph of the surface of a chlorosulphonated LLDPE fibre showing longitudinal and perpendicular cracks (fibre B); (c) tensile strength and Young’s modulus of carbon fibres obtained from precursor B (chlorosulphonation time 12h) as a function of applied stress (heat-treatment temperature 900°C; heat-treatment time 5 min); (d) SEM micrograph of the surface texture of a carbon fibre made at 900°C from precursor A (heat-treatment time 5 min, stress 0.10 MPa); (e) SEM micrograph of the surface texture of a carbon fibre made at 900°C from precursor B (heat-treatment time 5 min, stress 1.3 MPa).
Fig. 20. Mechanical properties of amorphous carbon fibers from linear low density polyethylene, due to diameter. Reprinted with permission from [111]: (a) effect of chlorosulfonation time on the mechanical properties of carbon fibres, prepared from fibre A (●) and fibre B (○); (b) effect of fibre stress during pyrolysis of fibre B on the mechanical properties of the resulting carbon fibres. Heating rate: 26 °C/min; (c) effect of carbon fibre diameter on the ultimate mechanical properties; (d) optimal chlorosulfonation time as a function of precursor fibre diameter; (e) effect of heating rate during pyrolysis of fibre B on the mechanical properties of the resulting carbon fibres. Fibre stress: 2.8 Mpa; (f) scanning electron micrograph of the fracture surface of a 1.90 GPa carbon fibre.

the hot-drawn fibers in order to remove the residual stresses induced by hot-drawing. Most likely, the diameter effect arises from the presence of a strong and stiff outer sheath, whose contribution to the mechanical properties is more dominant in thinner CFs (Fig. 20).

Zhang and Sun [54] have shown that CFs can be manufactured from partially drawn PE and highly oriented PE precursors. Both precursor fibers could be stabilized by sulfonation and the stabilization time decreased to 45 min from 130°C to 170°C compared with highly oriented PE fibers. The stabilized fibers were carbonized at 1100°C for 2 min. Tensile properties of the CF, at this stage, were reasonably good with a tensile strength of 2 GPa and Young’s modulus of 200 GPa. The elongation at break was less than 1%. These precursors are quite promising and, by controlling tension during stabilization, CFs with superior mechanical properties may be produced (Fig. 21).

Kim et al. [48] have shown that LDPE could be used as a precursor and cross-linked by sulfuric acid to obtain a high degree of carbonization. The cross-linking behaviors of the samples were clearly observed with increasing reaction temperatures in sulfuric acid from DSC results. From the TGA results, the residues of the samples increased gradually up to 150°C of reaction temperature, then were dramatically enhanced at 170°C. This result indicates that the cross-linking reaction of the LDPE in sulfuric acid can occur at low temperature, but high temperature (over 170°C) can radically accelerate the cross-linking reaction. The final residue of ‘PE-S-170’ was over 50%. In addition, the fibrous states of the samples were clearly observed to be carbonized fibers from the SEM results. From the results, LDPE can be a potentially advantageous material as a CF precursor (Fig. 22).

3. Conclusion

This review study, besides focusing on details of PE-based
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Effects of cross-linking methods for PE-based CFs were investigated. The sulfonic acid cross-linked method resulted in XLPE with a high cross-linking density, but it lacked cross-linking uniformity and produced surface destruction. The sulfonic acid cross-linking method can achieve a high carbonization yield (over 50%) for the manufacture of CFs. When producing a CF using the sulfuric acid cross-linking method, hollowness and fractures were generated in the CF due to non-uniform cross-linking. The PE based CF production process required multiple cross-linked (1st low cross-linking density and a 2nd high cross-linking density) and precision in the cross-linking process.

Fig. 21. Structure and properties during the conversion of polyethylene precursors to carbon fibers. Reprinted with permission from [54]: (a) burning Testing for Stabilized Fibers; (b) DSC scans of fiber samples stabilized at different temperatures and time. (1) Precursor, (2) 150°C and 30 min, (3) 160°C and 45 min, (4) 170°C and 60 min; (c) DSC scans for differences between highly oriented polyethylene and partially drawn polyethylene. (1) Highly oriented polyethylene, (2) partially drawn polyethylene, (3) HOPE stabilized at 150°C for 60 min, (4) PDPE stabilized at 150°C for 30 min; (d) TGA scans (in nitrogen) of fiber samples stabilized at different temperatures and time. (1) Precursor, (2) 150°C and 30 min, (3) 160°C and 45 min, (4) 170°C and 60 min; (e) tensile properties of resultant carbon fibers; (f) SEM photographs of resultant carbon fibers from a) insufficient stabilization and b) sufficient stabilization; (g) X-ray diffraction photographs of fiber samples. a) precursor, b) partially stabilized.

Low cost CF, was also intended to introduce and investigate the different methods of preparing XLPE. The descriptions provided here of the available methods of XLPE, by sulfonic acid, peroxide, silane and radiation methods, demonstrate that all methods provide a common and efficient approach to XLPE. The cross-linking behaviors of PE were clearly observed with increasing reaction time for all methods, based on thermal properties and gel content results. But, the silane, radiation, and DCP cross-linked methods were inappropriate as PE stabilization methods for CF, because of their low cross-linking density. The sulfonic acid cross-linked method resulted in XLPE with a high cross-linking density, but it lacked cross-linking uniformity and produced surface destruction. The sulfonic acid cross-linking method can achieve a high carbonization yield (over 50%) for the manufacture of CFs. When producing a CF using the sulfuric acid cross-linking method, hollowness and fractures were generated in the CF due to non-uniform cross-linking. The PE based CF production process required multiple cross-linked (1st low cross-linking density and a 2nd high cross-linking density) and precision in the cross-linking process.


Fig. 22. Mechanical properties of amorphous carbon fibers from linear low density polyethylene, due to diameter [48]: (a) DSC curves of the cross-linked LDPE fibers treated by sulfuric acid with different temperatures. A heating B and cooling scan; (b) TGA curves of the cross-linked LDPE fibers treated by sulfuric acid with different temperatures; (c) SEM image of the cross-linked LDPE fibers treated by sulfuric acid: A As-received, B cross-linked LDPE fibers, C carbonized LDPE fiber; (d) TGA curve parameters of the cross-linked LDPE treated by sulfuric acid with different temperatures.

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