Title: CROSS-LINKED POLYETHYLENE USED FOR ELECTRICAL INSULATION APPLICATIONS

Figure 3

Comparison date penetration capacity

X-Ray-Gamma (Co60) plus ca. 50% Penetration

Cobalt-60

X-rays 5 MeV

E-beam 10 MeV

X-rays 7 MeV

0 5 10 15 20 25 30 35 40 45 50 55 60

Depth (micron)

Abstract: The present invention relates to a method for cross-linking thick layers of polyolefin by electromagnetic radiation. The invention relates further to a cross-linked polyolefin obtainable by the method and its use as electrical insulation material.
CROSS-LINKED POLYETHYLENE USED FOR ELECTRICAL INSULATION APPLICATIONS

The present invention relates to a method of cross-linking thick layers of polyolefin with electromagnetic radiation. The invention relates further to a cross-linked polyolefin obtainable by the method and its use as electrical insulation material, in particular for HV DC cable insulation.

TECHNICAL BACKGROUND

High voltage (HV) cables are used for electric power transmission at high voltage. HV cables of different types have a variety of applications in instruments, ignition systems, as well as AC and DC power transmission. In all applications, it is essential that the insulation of the cable does not deteriorate due to the high-voltage stress, ozone produced by electric discharges in air, or tracking. The cable system must prevent contact of the high-voltage conductor with other objects or persons, and must limit and control leakage current.

The polyolefin polyethylene, in particular low density polyethylene (LDPE), is widely used as insulation material in power devices, such as electrical cables and wires. LDPE is a branched polymer and is a partially (50-60%) crystalline solid with a melting point of about 115°C and a density in the range of 0.91 -0.94 g/cm³.

Besides its superior electrical properties such as low permittivity and low losses, LDPE stands out with its low material costs and its thermoplastic nature which makes it suitable for cost-efficient extrusion and injection moulding processes.

However, in many final electrical applications, such as medium (MV) and high voltage (HV) cables, cross-linked polyethylene (XLPE or PEX) is applied. The main purpose for cross-linking of LDPE is the improvement of dimensional and therefore thermo-mechanical stability while keeping the high flexibility. XLPE does not melt and therefore no large softening and loss of shape will occur above 110°C. This permits higher conductor operating temperature and reduces the level of short circuit and overload protection required. For that reason XLPE
is very well suited as main insulation in extruded HV AC cables, which operate with a rated maximum conductor temperature of 90°C and a 250°C short circuit rating.

Besides these significant benefits, cross-linking of thermoplastics may lead to further improved material properties such as increased hardness; increased stress at break and increased elastic modulus; improved creep resistance; improved resistance to stress cracking and to abrasion; higher chemical resistance, e.g. against organic solvents, acids, saline solutions; enhanced dimensional stability with higher heat distortion temperature; and higher glow wire resistance and flame resistance.

Material to be used for insulation of cables for DC power transmission requires high resistivity and absence of local high electric fields to prevent dielectric breakdown. High resistivity reduces leakage current and suppresses heat generation. Local high electric fields are generated by space charge formation and lower the insulation performance. Especially for high voltage DC applications, such as at a voltage >320 kV, low electrical conductivity is crucial in order to avoid thermal runaway effect and pre-mature breakdown (Nussin, N et al., Space charge accumulation and conductivity of cross-linking by-products soaked LDPE; Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), 2010 Annual Report, 17-20 Oct. 2010, 1-4).

The cross-linking of LDPE is carried out either chemically, such as by addition of cross-linking agents, for example peroxides or silanes, or physically via radiation. Chemical cross-linking of low-density polyethylene is commonly carried out by reaction of dicumyl peroxide (DCP) or silane cross-linking agents with the polyethylene during the cable manufacturing process.

In case of DCP and cable applications, the cross-linking reaction occurs during extrusion in the cable manufacturing process by reaction of LDPE with DCP. DCP decomposes and liberates a free radical that will abstract a hydrogen atom from the polyethylene chain. This abstraction site on the polyethylene chain then becomes a reactive radical and forms a cross-linked bond with another reactive radical of the same or a different polyethylene chain. The process
generates polar by-products, such as cumyl alcohol and acetophenone. These species impair electrical insulation properties such as space charge behaviour and electrical conductivity at very high voltages and limit the use of the material. The volatile polar by-products may generate charges due to high polarity. Further, inhomogeneous and continuously changing distribution of by-products due to volatility causes local concentration differences that leads to local electric field enhancements and finally breakdown. (Narkis M, et al., J Appl Polym Sci, 14 (1970) 65 and Kumar Sen, et al., J Appl Polym Sci, 44 (1992) 183).

Silane cross-linked polyethylene (Si-XLPE) is used as insulation material in low (LV) and medium voltage (MV) cables. Si-XLPE is manufactured in two steps: In the first step, i.e. during the actual cable extrusion, the silane coupling agent, usually a vinyl alkoxy silane (mostly vinyl trimethoxy silane), is grafted on the polyethylene. After cooling of the cable, the cross-linking reaction is carried out in the second post-extrusion step, where the cable is placed in a hot water bath or steam room. The cross-linking of the modified polyethylene is carried out by hydrolysis of the grafted alkoxy groups forming silanol units which reacts with each other to stable siloxane bonds and therefore cross-links. Similar to the polar by-products of the DCP route, the introduction of silanol and siloxane groups and especially water into the polymer also leads to increased polarity of Si-XLPE and therefore a decrease of insulation performance. Another disadvantage is the diffusion (water) controlled reaction leading to inhomogeneous cross-linking density and material properties.

The technology of physical cross-linking is based on electron beam radiation and the generation of free radicals and the recombination of these free radicals to C-C cross-links. This technology has been industrially established for low voltage (LV) and MV cables and wires, usually made of LDPE or EVA-copolymers. The use of electron beam technology allows similar cross-linking density compared to today's peroxide cured LDPE - but without generation of any volatile polar by-products. Only little oxidization phenomena - with generation of carbonyl groups - and formation of double bonds directly at the polymeric chains are side-effects of this cross-linking method.
However, cross-linking of thermoplastics via electron beam is limited to target products with thicknesses of up to 50 mm. There is a physical limitation given by discharge phenomena, in form of Lichtenberg patterns, that occur when the material is constantly charged with electrons until the dielectric breakdown strength is exceeded. (Matsuoka, S. et al. IEEE Transactions on Nuclear Science, (1976), 23(5), 1447-1452; Li, X. et al. Proceedings of the 5th International Conference on Properties and Applications of Dielectric Materials, 25-30 May 1997; vol.1, 311-314; and Sasaki, T. et al., Radiation Physics and Chemistry (1977), (1979), 14(3-6), 821-830).

The patent application US2010/0144916 describes different radiation methods, such as electron beam, X-ray and gamma-radiation, as possible methods for physical cross-linking of an organic polymer.

The use of physical radiation in general to manufacture XLPE is described in GB766802A, US2914450, and US3330748.

There is still a need for improving the manufacturing process as well as the performance of high voltage cables.

SUMMARY OF THE INVENTION

An object with the present application is to provide a method for cross-linking polyolefins in thick layers, wherein the cross-linking of the polyolefin is performed by electromagnetic radiation. The cross-linked polyolefin obtainable by the method is absent of polar by-products, which makes this insulation material suitable especially for high and ultra-high voltages (>500 kV) in DC applications, in particular for cable and HVDC applications.

A further object of the present invention is to provide a method for cross-linking a polyolefin to provide an insulation material without substantially increasing the DC conductivity compared with the DC conductivity of the corresponding non-cross-linked polyolefin that is that is used for cross-linking by the method.

BRIEF DESCRIPTION OF THE DRAWINGS
Figure 1 shows penetration depth curves of various electron beams in a material with a density of 1 g/cm³.

Figure 2a illustrates electromagnetic radiation of a standard HV cable (upper) and plate (lower) wherein the penetration depth of the radiation is greater than the sample thickness, and Figure 2b illustrates E-beam radiation of a standard HV cable (upper) and plate (lower) wherein the penetration depth of the radiation is smaller than the sample thickness.

Figure 3 shows penetration-depth curves of various radiations in a material with density of 1 g/cm³.

Figure 4 shows gel contents of 1 mm plates obtained from X-ray and E-beam radiation. Figure 5 shows gel contents along the height from X-ray irradiated 30 mm plates (from top surface to the middle) - before and after annealing.

Figure 6 shows free radical concentration of X-ray and E-beam irradiated 1 mm plates.

Figure 7 shows free radical concentrations measured on 30 mm plates irradiated with X-ray - not annealed and annealed for 2 h at 115°C and 5 h at 125°C.

Figure 8 presents a plot of DC conductivity of non-irradiated LDPE, E-beam cross-linked LDPE and X-ray irradiated LDPE (annealed and not annealed) versus free radical concentration.

DETAILED DESCRIPTION OF THE INVENTION

One aspect of the present invention is a method for cross-linking a polyolefin material, the method comprising subjecting a polyolefin material to electromagnetic radiation to obtain a cross-linked polyolefin, followed by annealing of the obtained cross-linked polyolefin material, wherein the irradiated polyolefin material has a thickness greater than 6 cm.
Throughout the present application the term "thickness" denotes the longest distance that the applied electromagnetic radiation has to go to pass through the polyolefin material that is irradiated. Figure 2a illustrates the exemplary case of irradiating a standard HV cable with a radial insulation thickness, \((d_1-d_2)/2\), of LDPE of about 40 mm - but maximum material thickness, \(D\), of about 80 mm next to the conductor - with X-ray radiation. For a polyolefin material where the applied radiation is submitted through a circular cross-section, the thickness of the material is the diameter. For a tubular polyolefin material where the applied radiation is submitted through a concentric circular cross-section, the largest thickness is the chord of the outer circle that tangent the inner circle (as illustrated with the distance \(D\) in Figure 2a).

The incoming radiation is preferably perpendicular to the surface of the material, but could also arrive at the surface of the material in other angles.

Throughout the present application the term "polyolefin" denotes a polymer produced from an alkene having the general formula \(C_nH_{2n}\) as a monomer. Examples of polyolefins are polyethylene (PE), such as ultra-high-molecular-weight polyethylene (UHMWPE), ultra-low-molecular-weight polyethylene (ULMWPE or PE-WAX), high-molecular-weight polyethylene (HMWPE), high-density polyethylene (HDPE), medium-density polyethylene (MDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and very-low-density polyethylene (VLDPE); polypropylene (PP); polymethylpentene (PMP); and polybutene-1 (PB-1).

Preferably, the polyolefin is polyethylene, preferably low-density polyethylene.

Preferably, the present invention relates to a method for manufacturing cross-linked polyethylene (XLPE).

The cross-linked polyolefin obtainable by the method according to the present invention can be used as an insulation material, preferably a dielectric material. An advantage of annealing the cross-linked polyolefin is that the number of free electrons, i.e. the concentration of free radicals, remaining after radiation is reduced and therefore electrical conductivity of the cross-linked polyolefin will
be in the same level as for the polyolefin before it was cross-linked, which is required especially for HV insulation applications. Preferably, the cross-linked polyolefin is annealed by heat treatment. The temperature to be used depends on the polyolefin used. For polyethylene, the annealing may be performed at a temperature of at least 115°C, preferably at a temperature between 120 and 140°C, such as at 125°C.

The time required for the heat treatment depends on the thickness of the material and also the method for application of heat. Preferably the heat treatment is performed for at least 1 h, preferably at least 2 h. In an alternative embodiment the annealing comprises a combination of different heating steps, such as heating at 115°C for 2h, followed by heating at 125°C for 5 h.

An indication of sufficient annealing time is that the cross-linked polyolefin becomes transparent, which indicates that crystallites in the polyolefin matrix are fully melted.

In one embodiment of the method according to the present invention, the electromagnetic radiation is X-ray radiation or gamma radiation, preferably X-ray radiation. Preferably, the overall radiation dose is in the range from 150 to 350 kGy, more preferably the overall radiation dose is about 150, about 250 or about 350 kGy.

The electromagnetic radiation according to the present invention may be performed during melt-processing and shaping of the polyolefin into a product or after the melt-processing on the solid polymer. Preferably, the electromagnetic radiation is performed after melt-processing and shaping of the polyolefin into a product. Preferably, the melt-process is an extrusion process.

More preferably, the extrusion process is a cable extrusion process.

In one embodiment of the method according to the present invention, the radiation cross-linking is performed directly on a product comprising the polyolefin, preferably a power product. The term "power product" as used herein denotes a product for use in electrical application, such as a power cable, a cable accessory, an insulating material, a bushing, or a wire. Also, the radiation cross-linking may be performed on a separate part that will be integrated into
the product afterward, such as an O-ring. Further, the cross-linking according to the present invention may be performed on a whole insulator as such, for example an already extruded outdoor insulation housing.

The product to be radiated with the method according to the present invention may, in addition to the polyolefin to be radiated, comprise parts that are not permeable to the electromagnetic radiation, such as the conductive core of a cable. In such cases the product may be radiated from more than one side of the product, or the product may be rotated during radiation, so that the electromagnetic radiation may reach all parts of the polyolefin that should be cross-linked.

When a material to be irradiated by an electron beam is thicker than the penetration depth of the electron beam, the electrons are not able to "pass through" the target material and electrons will be intentionally accumulated in the material. When the electrical breakdown strength of the material is reached, branching electric discharges (Lichtenberg patterns) occur. Figure 1 shows the penetration depths of an electron beam with a maximum of 6 cm in a material of 1 g/cm³ density - similar to LDPE - using a 10 MeV source. Furthermore, the use of an electron beam requires an extremely high level of safety measures due to generated radioactivity.

Figure 2b illustrates the exemplary case of irradiating a standard HV cable with a radial insulation thickness of LDPE of about 40 mm - but maximum material thickness of about 80 mm next to the conductor - with E-beam radiation using a 10 MeV source. Analogue to the observations mentioned above, discharge phenomena and destruction of the insulation material would occur with this technology disqualify its application for HV cables or any other electrical insulator product with thickness of > 50 mm.

An advantage with X-ray, in contrast to E-beam radiation, is that X-rays allows much higher penetration depths. This has the effect that electrons are not trapped in the irradiated material, which eliminates the risk of electrical breakdown due to accumulated space charge (see Figure 3). Thus, with the method according to the present invention it is possible to cross-link polyolefin
products, such as parts or layers, wherein the thickness of the irradiated polyolefin material is greater than 6 cm, preferably >10 cm, more preferably >20 cm, even more preferably up to 60 cm.

A problem with E-beam accelerated electrons is that they interact directly with the electron conformation of the target molecules. This gives rise to an avalanche like formation of free secondary electrons, excitation of molecules and creation of heat and possibly radiation. Free electrons acting as charge carrier in an insulation material can highly influence electrical properties, specifically the resistivity.

An advantage with the use of X-ray or gamma radiation as in the method according to present invention is that photons are generated interacting with the electrons of the target molecules in different processes: 1) a photoelectric effect, i.e. the electron absorbs energy, the conformation is changed, and photoelectrons are released; 2) Compton scattering, i.e. release of photons; and 3) pair production, i.e. electron-positron pairs. Thus, electron avalanches are avoided and therefore breakdown phenomena are prevented.

Further, the secondary electrons and/or positrons produced in any of the three processes have enough energy for radiation chemistry and cross-linking reactions. However, the overall energy absorption of gamma and X-ray used for the final radiation chemistry is much lower and slower compared to E-beam radiation, which leads to longer treatment time but also the advantage of a higher penetration depth.

X-rays are emitted by electrons outside the nucleus while gamma rays are emitted by the nucleus. X-ray is usually generated as Bremsstrahlung (braking radiation) originated from a high energy electron beam (Rhotodron accelerator) colliding on a metal target. Gamma radiation is generated from radioactive gamma decay - alongside other forms of radiation such as alpha and beta - by using a radioactive source such as cobalt-60. Gamma ray from a Co$^{60}$ source is emitted with 1.17 MeV as given by its radioactive decay, while with X-ray higher energy levels are possible which are determined by the electron accelerator, e.g. 5 or 7 MeV Rhotodron.
When cross-linking a polyolefin with electromagnetic radiation according to the present invention, carbonyl groups (in presence of oxygen) or double bonds from carbon radicals are formed in the polymer chain. These functional groups could act as charge traps in insulating materials and thus be beneficial for insulation performance, especially for DC applications. Their presence in polymeric samples can be identified and quantified by FT-IR spectroscopy.

An advantage with the method according to the present invention is that polar by-products are avoided. This has the effect that space charges can be eliminated.

Another aspect of the present invention is a cross-linked polyolefin obtainable by the method according to the present invention.

A further aspect of the present invention is an electrical insulation material comprising the cross-linked polyolefin obtained with the method according to the present invention. A further aspect of the present invention is a power cable, preferably a high voltage DC cable, comprising the cross-linked polyolefin obtained with the method according to the present invention.

Another aspect of the present invention is the use of the cross-linked polyolefin obtained with the method according to the present invention for electrical insulation, preferably in a DC-application, preferably a high voltage DC application. Suitable DC-application is a power cable, a cable accessory, a bushing, or a wire; or a separate part that will be integrated into an end product.

Yet another aspect of the present invention is the use of electromagnetic radiation for cross-linking polyolefin in a power application, such as in a power cable, a cable accessory, a bushing, or a wire; or a separate part that will be integrated into an end product.

Further advantages with the method according to the present invention is that thermal and mechanical properties are improved and increased resistance to chemicals and fire (see above), compared with DCP cross-linked XLPE.

EXAMPLES
Materials
LE4147 from Borealis - LDPE with Melt Flow Rate (MFR) of 2.0 g/10min (ISO 1133)

Methods
Plate samples (18x18 cm) of 1 and 30 mm thickness were manufactured from polymer granules using a hot press. The sample plates were cross-linked via X-ray by radiation of the sample plates from two sides using overall doses of 150, 250 and 350 kGy - meaning 75, 125 and 175 kGy from each side. The radiations were carried out at the X-Ray facilities of LEONI Studer Hard AG in Daniken (CH).

As reference, sample plates of 1 mm thickness were cross-linked via E-beam by irradiating from using overall doses of 50, 100, 150 and 250 kGy. The radiations were carried out at the E-Beam facilities of LEONI Studer Hard AG in Daniken (CH).

The irradiated sample plates were annealed by heat treatment for 2 h at 115 °C and other 5 h at 125 °C.

Gel content
The gel content, reflecting the degree of cross-linking, was measured by determining the residual polymer (by weight percentage) after Soxhlet extraction in xylene for 24 hours. The gel contents for 1 mm plates irradiated with 150, 250 and 350 kGy X-ray as well as a non-irradiated sample are shown in Table 1. With increasing dose level a higher cross-linking is achieved indicating that a plateau will be reached at higher doses above 350 kGy. A standard DCP cross-linked XLPE used for HV cables has a gel content of 65-80 %.

Table 1

<table>
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<tr>
<th>X-ray</th>
<th>0 (non)</th>
<th>150 kGy</th>
<th>250 kGy</th>
<th>350 kGy</th>
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<tr>
<td>Gel content</td>
<td>0 %</td>
<td>39 %</td>
<td>65 %</td>
<td>68 %</td>
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</table>
Table 2 presents the gel contents for 1 mm plates irradiated with 50, 100, 150 and 250 kGy E-beam.

**Table 2**

<table>
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<tr>
<th>E-beam</th>
<th>50 kGy</th>
<th>100 kGy</th>
<th>150 kGy</th>
<th>250 kGy</th>
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<tbody>
<tr>
<td>Gel content</td>
<td>0 %</td>
<td>43 %</td>
<td>56 %</td>
<td>64 %</td>
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</table>

5 The gel contents of 1 mm plates in dependence of the dose level obtained from X-ray as well as E-beam radiation is shown in Figure 4. Overall similar cross-linking densities are achieved.

The gel contents were measured also on 30 mm plates along the height from the surface (0-1 mm) to the middle (15-16 mm) showing the distribution of the cross-linking density along the height of the plate (first half from the top surface to middle). The results are presented in Figure 5. The tests were carried out on the samples directly after irradiation and after additional annealing.

All irradiated and non-annealed plates showed a similar behaviour with maximum gel content / cross-linking density around 8 mm from the surface. This behaviour may be due to X-ray distribution in the 30 mm plate when irradiating from two sides.

The increase in cross-linking density shows that post-reactions occur, i.e. recombinations of carbon radicals in the polymeric chains. It is known that especially in the crystalline phase generated radicals remain non-reacted due to very low flexibility in the ordered structure. The decreasing gel content values of annealed samples (along the height) are due to the poor heat transfer in the material and higher temperatures at the outer surface.

**Free radical concentration**

Free radical concentration was measured via determination of the number of non-paired electron spins per sample weight using electron spin resonance spectroscopy.
In Figure 6 the free radical concentrations - as measured with electron spin
resonance (ESR) - of X-ray irradiated 1 mm plates are shown in dependence of
the dose level - in comparison with E-beam irradiated 1 mm plates. The
measurements were also carried out on annealed samples - with two different
conditions 2 h at 115 °C and 2 h at 115 °C / 5 h at 125 °C.

From these measurements, it is seen that for both E-beam and X-ray cross-
linking the free radical concentration increases with radiation dose. After
annealing the free radical content is remarkably reduced to a constant value for
all dose levels. A further decrease towards the value of non-irradiated LDPE is
obtained with longer annealing at higher temperatures. The reduction of free
radicals of irradiated polymers via heat treatment is based on radical consuming
reactions: post-cross-linking, oxidization (in presence of oxygen) or elimination
reaction leading to double bonds or chain scission.

Free radical concentrations were also measured on 30 mm plates along the
height (first half from the top surface to middle) as shown in Figure 7. Similar to
the observations on 1 mm plates, the free radical concentration increases with
radiation dose. Along the height, the free radical content slightly decreases.
Again, with sufficient annealing time (2 h at 115 °C / 5 h at 125 °C) the free
radical concentrations in the irradiated LDPE can be reduced to the low level of
the non-irradiated LDPE.

**DC conductivity and correlation with free radical concentration**

DC conductivity was determined by applying a DC voltage of 20 kV/mm to a
three electrode system (40 mm round electrode diameter with guard electrode)
and the leakage current was measured with a sensitive picoamperemeter
(Keithley 6485). The measurements were performed on 1 mm thick plates at
70 °C for up to 120 hours.

The DC conductivity was measured on 1 mm samples irradiated with X-ray or
E-beam. As shown in Figure 8, there is a strong correlation between the free
radical concentration and the DC conductivity proving that free radicals
remaining in the insulation (after irradiation) act as charge carrier. This is the
case for both E-beam and X-ray treatment. Hence, annealing of the irradiated
samples leads to a reduction of conductivity - towards a value close to non-irradiated LDPE.

**Discharge phenomena**

No discharge phenomena were observed on the 1 mm and 30 mm plates - neither directly after irradiation nor after additional heat treatment / annealing.
CLAIMS

1. A method for cross-linking a polyolefin material, the method comprising subjecting a polyolefin material to electromagnetic radiation to obtain a cross-linked polyolefin, followed by annealing of the obtained cross-linked polyolefin material, wherein the irradiated polyolefin material has a thickness greater than 6 cm.

2. The method according to claim 1, wherein the polyolefin is polyethylene.

3. The method according to claim 2, wherein the polyethylene is low-density polyethylene.

4. The method according to claim 1, wherein the radiation is X-ray radiation or gamma radiation.

5. The method according to claim 1, wherein the overall radiation dose is from 150 kGy to 350 kGy.

6. The method according to claim 1, wherein the annealing is performed at a temperature of at least 115°C.

7. The method according to claim 6, wherein the annealing is performed at a temperature of from 120°C to 140°C.

8. The method according to claim 1, wherein annealing is performed during at least 1 h.

9. The method according to claim 1, wherein the electromagnetic radiation is performed after melt-processing and shaping of the polyolefin into a power product.

10. The method according to claim 8, wherein the melt-processing is an extrusion process.

11. The method according to claim 9 wherein extrusion process is a cable extrusion process.

12. The method according to claim 1, wherein the electromagnetic radiation is performed on a power product.

13. The method according to claim 12, wherein the power product is a power cable, a cable accessory, a bushing, a wire, or a separate part that will be integrated into an end product.
14. A cross-linked polyolefin obtainable by the method in any one of claims 1-13.
15. An electrical insulation material comprising the cross-linked polyolefin according to claim 14.
16. A power cable comprising the cross-linked polyolefin according to claim 14.
17. A power cable according to claim 16 wherein the power cable is a DC cable.
18. Use of the cross-linked polyolefin obtained according to the method in claim 1 as an electrical insulation material in a DC application.
19. Use according to claim 18, wherein the DC application is a power cable, a cable accessory, a bushing, or a wire.
20. Use of electromagnetic radiation for cross-linking polyolefin in a power application.
Figure 6

This figure shows a graph with the x-axis labeled "Dose level [kGy]" and the y-axis labeled "Free radicals [spins/g]." There are multiple curves indicated with different markers and annotations:

- X-ray - not annealed
- X-ray - 2 h @ 115 °C
- X-ray - 2 h @ 115 °C + 5 h @ 125 °C
- E-beam - not annealed
- E-beam - 1 h @ 115 °C

The graph illustrates the relationship between dose level and the number of free radicals for different treatment conditions.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F10/02  C08J3/28  H01B3/44  H01B9/00

ADD.

According to International Patent Classification (IPC) and both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F  C08J  H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

A* document defining the general state of the art which is not considered to be of particular relevance

E document earlier application or patent but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited in the publication date of another citation or other special reason (as specified)

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

A* document member of the same patent family

Date of the actual completion of the international search

20 February 2013

Name and mailing address of the ISA

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Authorized officer

Knutzen-Mi es, Karen
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