Received January 20, 2014, accepted February 25, 2014, date of current version March 10, 2014.

Digital Object Identifier 10.1109/ACCESS.2014.2308919

Aging of Silane Crosslinked Polyethylene

STEFAN HELLSTRÖM[1], FREDRIK BERGFORS[1], PAUL LAURENSON[2], AND JAMES ROBINSON[2]
[1]Borealis AB, Stenungsund 444 86, Sweden
[2]Borealis Polymers NV, Beringen 3583, Belgium

Corresponding author: S. Hellström (stefan.hellstrom@borealisgroup.com)

ABSTRACT Silane crosslinked polyethylene cable insulation occasionally fails to meet the aging requirements given in technical standards. The purpose of this paper is to investigate this phenomena and establish whether the safety margin of aging tests can be increased by changes in manufacture or test procedures. Using a number of cable types with different compositions and dimensions, the evolution of the absolute values of tensile strength and elongation at break upon aging was obtained. The results show that the major changes in mechanical properties happen within the first 24–48 h. This finding is valid both for ethylene vinylsilane copolymers and for grafted silane systems. In general, the effect is more pronounced for the 100°C compatibility test. Statistical analysis shows that insulation crosslinked in a hot waterbath will exhibit this behavior to a lesser extent, thus increasing the safety margin in aging tests, compared with ambient curing. This paper demonstrates that preconditioning at 70°C has no significant impact on aging properties. In addition, only small variations in mechanical properties were seen when changing the process parameters. It is concluded that further crosslinking is the principal cause of the phenomena under investigation.

INDEX TERMS Mechanical properties, silane crosslinking, thermal aging.

I. INTRODUCTION

Crosslinked low-density polyethylene is widely used for the insulation of power cables. The most commonly used crosslinking techniques are peroxide crosslinking and silane crosslinking. Using the peroxide route, the insulation is crosslinked above the melting temperature of polyethylene. During crosslinking the polymer chains are completely amorphous. This will result in a polymer material with a homogenous distribution of crosslinks. When a peroxide crosslinked polyethylene insulation is subjected to thermal aging tests, no further crosslinking will take place and potentially contribute to changes in mechanical properties. Silane crosslinked polyethylene (Si-XLPE) is, on the other hand, crosslinked at temperatures below the melting temperature of the polyethylene-based copolymer, often in ambient conditions. The crosslinking process can then result in a heterogeneous distribution of crosslinks because of the partial crystallinity [1], [2]. When a Si-XLPE insulation is subjected to thermal aging tests, hydrolysis and condensation of silanes in melted regions will give further crosslinking and changes to the crosslink distribution. These additional crosslinks will not decrease the performance of the insulation material. However, following the measurement procedures of IEC 60811-501 and IEC 60811-401, the decrease in elongation at break will on occasion result in silane-cured polyethylene insulation having problems meeting the aging requirements defined in the corresponding cable standards IEC 60501-1, HD 601 S1, and HD 626 S1. The purpose of the current study is to map the evolvement of the mechanical properties of Si-XLPE during the aging tests and to establish whether the safety margin of aging tests can be increased by changes in manufacture procedures.

In previous work, Miroslav Pastorek et al. have analysed tapes of crosslinked ethylene vinylsilane copolymer (XEVS) to study changes in mechanical properties during aging tests [3]–[5]. By using an ethylene vinylsilane copolymer (EVS) base resin and a catalyst masterbatch they followed the development of the carbonyl peak at 1700–1800 cm^{-1} using Fourier transform infrared spectroscopy (FTIR) and concluded that the material is not subjected to any thermooxidative degradation upon aging for 10 days at 90°C or 135°C. It is well known that thermooxidative degradation leads to degradation products containing carbonyl groups [6]. The carbonyl peak present in the FTIR-spectra originated from additives in the catalyst masterbatch. Since the intensity of the peak is unchanged upon thermal aging, this indicates that there is no thermooxidative degradation of the material. Furthermore, the increase in magnitude for the Si-O-Si peak at 1065 cm^{-1} proves that the material is further crosslinked upon accelerated aging. In addition, Celina et al. shows that thermooxidative degradation of silane crosslinked polyethylene will decrease the gel content resulting in the polymer rapidly losing most of its mechanical properties [7]. When further crosslinking is taking place during aging tests, the absolute values of tensile strength and elongation at break will stabilise after the initial drop, ruling out thermooxidative degradation [4].

Pastorek et al. also use differential scanning calorimetry (DSC) to show that aging at temperatures just below the melting temperature of the ethylene vinylsilane copolymer will, besides further crosslinking, result in an improvement in crystalline order, which in turn will impact the mechanical properties after aging. When a Si-XLPE material is subjected to temperatures just below the melting temperature of the copolymer, parts of the crystalline structure will melt and recrystallise as indicated by the evolvement of a new peak in the DSC thermogram at 90–100°C. This new peak is not noticed for material aged at 135°C. This is due 135°C being well above the melting temperature of the copolymer and after aging the DSC thermogram resembles that of a non-aged material. However, a silane crosslinked low-density polyethylene material aged at 135°C will give a reduction in crystal lamella thickness as indicated by a lower peak melting temperature compared to non-aged material. This will also have an impact on the mechanical properties of the insulation.

II. EXPERIMENTAL

The insulation materials used in the reported experiments are listed in Table 1.

TABLE 1. Insulation material – silane crosslinked polyethylene type (Si-XLPE).

	Base resin	Catalyst
1	Ethylene Vinyl Silane copolymer (EVS)	Sulfonic acid based (natural or black)
2	Grafted Silane LLDPE (Monosil process)	Tin based

For coloured samples 5% by weight of natural catalyst masterbatch was added. Exceptionally, the cables described in Table 3 were prepared by adding 7% by weight of the sulfonic acid black catalyst masterbatch. The catalyst masterbatches also contain other additives e.g. antioxidants. All tests have been performed according to IEC 60811-501 and IEC 60811-401.

Thermal aging tests have been performed using an Elastocon EB01 cell oven with an air flow of 0.6 l/min corresponding to 15 complete air changes per hour. Exceptionally, the results in Fig. 1 were obtained using a normal oven with calibrated air flow and temperature. All aging tests were performed on cable samples having a hot-set elongation (20 N/cm^2, 200°C, 15 min) below 100%.

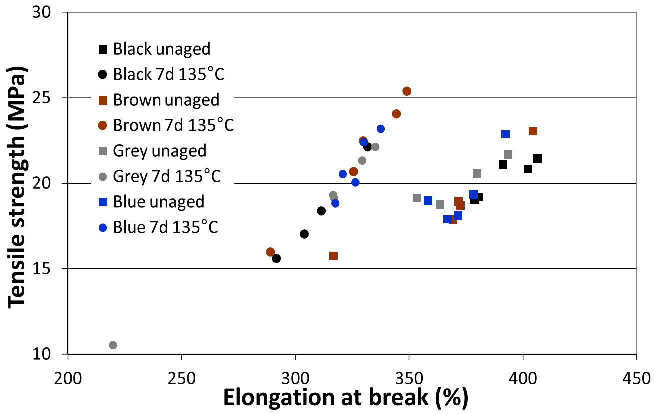

FIGURE 1. All tensile measurements of elongation at break for a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductor with XEVS insulation.

Mechanical properties were measured using a Zwick Z005 tensile tester. A gauge separation speed of 250 mm/min was used. Six samples per test were measured. Test specimens were, when necessary, milled to remove marking from stranded conductors. Tensile strength and elongation at break were obtained from median values.

III. RESULTS AND DISCUSSION

A. INFLUENCE OF COLOUR MASTERBATCH

In order obtain statistically significant data on the mechanical properties, the influence of colour masterbatch selection was analysed. For PVC-sheathed cables, normally the inside cores of different colours are measured one by one and due to the combined effect of big spread and few measurements, this creates a difference in the results between different sample colours. This variation is in many cases not statistically significant. In Fig. 1, all measurements of elongation at break of unaged and aged samples for a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductor with XEVS insulation are graphically illustrated.

The results show that the difference between colours is small compared to the variation between individual samples within one colour. A major part of the difference between colours can therefore in this case be explained by variation in the measurements. To be able to reduce the spread without a huge amount of measurements all colours are considered to be equal in the following analyses.

B. MECHANICAL PROPERTIES AFTER AGING

To study the changes in mechanical properties upon aging, cables with different dimensions, sheathing, and insulation were subjected to thermal aging. The evolution of the mechanical properties upon aging at 100°C (complete cable) or 135°C and 150°C (insulation alone) of XEVS insulation taken from a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductors are shown (Figs. 2 and 3). These test specimens were not subjected to any preconditioning prior to the tensile testing.

It is often noticed that as a result of aging, the elongation at break varies more than the tensile strength. However, this

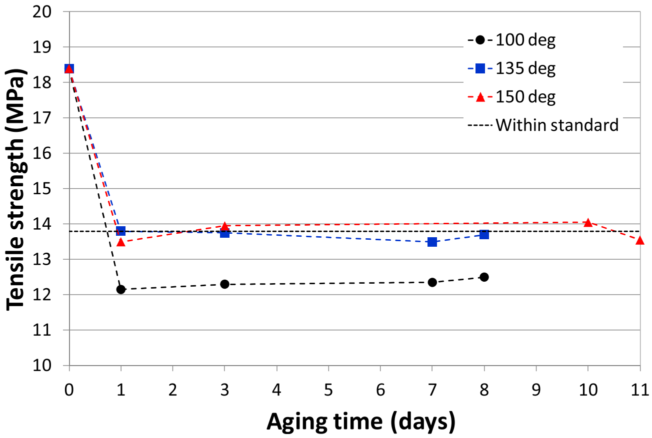

FIGURE 2. **Average values of tensile strength based on median values for two cores of a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductors with XEVS insulation.**

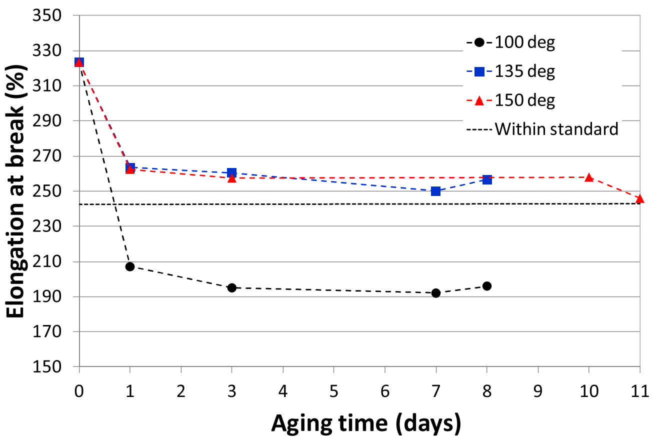

FIGURE 3. **Average values of elongation at break based on median values for two cores of a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductors with XEVS insulation.**

behaviour is not noted when comparing Figs. 2 and 3. Furthermore, it is evident that the major changes in elongation at break happen in the initial part of the aging test. After the first 24 hours, the absolute values of elongation at break and tensile strength stabilises. This is a clear indication that the material is not subjected to any thermooxidative aging. Due to space limitations, only results on elongation at break will be reported in the latter part of the paper.

The migration of plasticiser from PVC-sheathing and bedding can also influence the changes in mechanical properties during thermal aging of a complete cable. In order to investigate the effect of PVC-sheathing on mechanical properties, the 100°C compatibility test was performed both for a PVC-sheathed cable (4 × 35 mm^2 stranded copper) and a HFFR-sheathed cable (5 × 25 mm^2 stranded copper). Insulation is XEVS for both cable types.

The evolvement of the elongation at break is shown in Fig. 4. It is noticed that the difference in elongation at break is the same for the PVC-sheathed cable and the HFFR-sheathed cable. This indicates that plasticiser migration influence the mechanical properties after aging only to a smaller extent

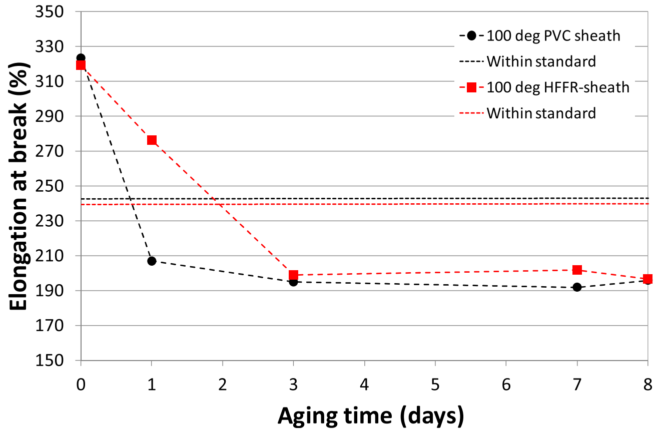

FIGURE 4. **Average values of elongation at break based on median values for two cores of the cables. Insulation is XEVS for both cable types.**

compared to the contribution from further crosslinking and improvement in crystalline order. For the compatibility test, improvement in crystalline order becomes a factor since 100°C is below the melting temperature of the EVS (110°C). This is not the case for thermal aging at 135°C as illustrated by DSC thermograms in previous publications [3]–[5]. The main decrease in elongation at break is once again concentrated to the first 24–48 hours.

It is evident that the insulation material is marginally close to or failing the standard requirements of ±25% change in mechanical properties upon thermal aging (Figs. 2–4). To broaden the scope of the work, aging test was repeated for a thinner XEVS insulation at 135°C. The insulation originated from a PVC-sheathed cable with three cores of 2.5 mm^2 solid copper conductor. This time the insulation clearly passes the aging requirements (Fig. 5).

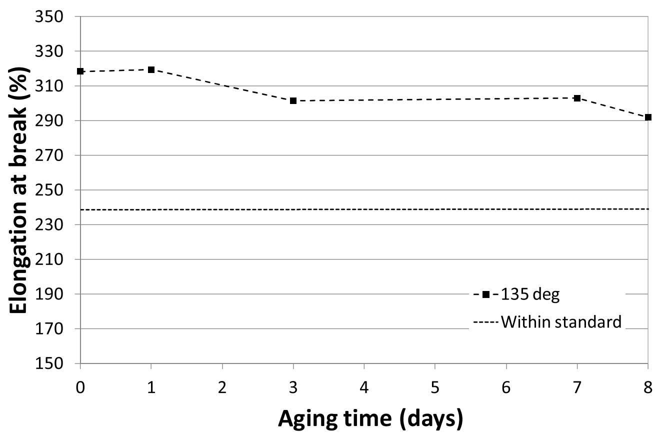

FIGURE 5. **Average values of elongation at break based on median values for two cores of a PVC-sheathed cable with 3 × 2.5 mm^2 solid copper conductors with XEVS insulation.**

It is important to note that when measuring the mechanical properties of power cable insulation, the results may vary greatly from day to day even though the samples are measured on the very same tensile testing machine by the same operator following the same routines. This will result in problems with outliers making it possible for the insulation material to fail the aging requirements due to measurements and not because of poor material. Performing a greater number of tests on the same insulation in order to obtain a more accurate median value would decrease this problem but generally only five or six measurements are made since sample preparation and tensile testing is quite time consuming and oven space is limited.

C. GRAFTED SILANE SYSTEMS

For comparison between insulation made from EVS and silane grafted polyethylene (Monosil process), aging test at 135°C were performed on insulation from a PVC-sheathed cable with 4 × 35 mm^2 stranded conductors with Monosil insulation. Although Monosil insulation with grafted silane is slightly more reactive and often has a different crosslinking catalyst compared to ethylene vinylsilane copolymer systems, the results in Fig. 6 show a similar evolvement of elongation at break as the previous graphs for XEVS.

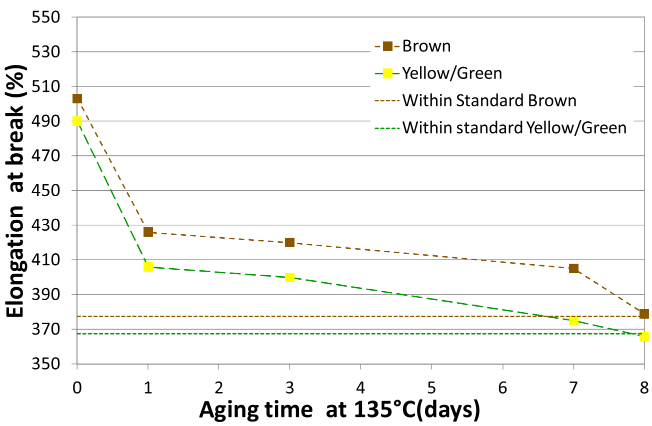

FIGURE 6. Elongation at break, based on median values, for two cores of a PVC-sheathed cable 4 × 35 mm^2 stranded copper conductors with Monosil insulation.

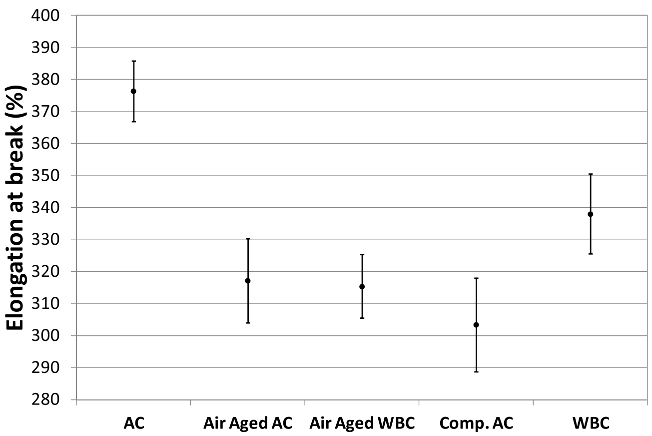

FIGURE 7. Statistical analysis (means with 95.0 percent confidence intervals) showing the effect of crosslinking conditions on elongation at break. AC: ambient cured, WBC: waterbath cured.

D. INFLUENCE OF CROSSLINKING CONDITIONS

The mechanical properties are highly influenced by the crosslinking conditions as temperature and diffusion of water

TABLE 2. Different extruders with characteristics used in the evaluation.

Name	Type	Characteristic
Maddox	Maddox mixer	High specific output rate
Medium	Conventional helical	Low specific output rate
Low shear	Megolon screw	Low shear, very high specific output rate
High shear	Davis Standard Barrier	High specific output rate

TABLE 3. Elongation at break for ethylene vinylsilane copolymer insulation prepared using different extruder screw design.

Extruder Screw	Maddox	Medium	Low Shear	High Shear
Treatment	Elongation at Break (%)	Elongation at Break (%)	Elongation at Break (%)	Elongation at Break (%)
Ambient curing, 120 h	342	334	354	356
Ambient curing, 120 h Aging 135°C, 240 h	295	287	295	319
Change	-14%	-14%	-17%	-10%
Ambient curing, 120 h Precon. 70°C, 24h	315	312	343	327
Ambient curing, 120 h Precon. 70°C, 24h Aging 135°C, 240 h	285	272	320	290
Change	-10%	-13%	-7%	-11%

TABLE 4. Correlation coefficients.

	DDR	DRB
DDR	1.00	0.49
DRB	0.49	1.00
Tensile Strength	-0.62	0.14
Elongation at Break	-0.84	-0.23
Shrinkage	0.41	-0.31
Adhesion	0.32	0.45

molecules are different between ambient cured and water-bath cured samples. A statistical analysis was completed on the measurements of elongation at break after different crosslinking and aging conditions for a PVC-sheathed cable with 4 × 35 mm^2 stranded copper conductor and insulation of XEVS. The analysis was made using the data of all the different colour samples. The mean values of the samples with different pre-treatments can be seen with 95.0% confidence intervals (Fig. 7).

TABLE 5. Results from aging test on 2.5 mm^2 stranded copper conductor with ethylene vinylsilane copolymer insulation using different draw-down ratios.

Catalyst	DDR	TS (MPa)	Difference	EaB (%)	Difference
Sulfonic Acid	4.4	20.9		266	
Sulfonic Acid	4.4	18.6	-11%	241	-9%
Tin based	4.4	19.2		279	
Tin based	4.4	19.3	+1%	261	-6%
Sulfonic Acid	1.8	16.9		272	
Sulfonic Acid	1.8	15.0	-11%	236	-13%
Tin based	1.8	16.6		284	
Tin based	1.8	16.9	+2%	278	-2%

It can be noticed that there is no statistically significant difference between the air aged ambient cured, air aged waterbath cured, compatibility cured and unaged waterbath cured samples. The samples that are ambient cured have a significant higher elongation at break compared to the rest of the samples. When the samples are crosslinked in 90°C waterbath, the level of elongation at break after aging is not significantly lower than before aging. However, when the samples are ambient cured the level of elongation at break after aging is significantly lower than before aging.

E. INFLUENCE OF EXTRUDER SCREW DESIGN

To evaluate if the safety margin of thermal aging tests could increased by changing process parameters, single wire cables with 1.5 mm^2 stranded copper conductor and XEVS insulation were produced using different extruder screw design (Table 2).

The cables were aged at 135°C for 7 days and elongation at break was measured (Table 3). Neither the absolute values of elongation at break nor the changes after aging are significantly influenced by screw design.

The influence of preconditioning the samples for 24 h at 70°C, as stated in IEC 60811-501 section 9.1.3 c, was also investigated. However, no significant improvement in aging properties was seen for the preconditioned samples. For Si-XLPE, 70°C is considerably below the melting temperature of the copolymer and the material will not to a greater extent be able to form further crosslinks or changes in crystalline order.

F. INFLUENCE OF DIFFERENT TOOLING

As a final step of the study, the influence of crosshead tooling was evaluated. The tests were performed on single-wire cables (insulation of XEVS, 2.5 mm^2 stranded copper conductor). Different tooling sets were applied which permitted a range of different draw down ratios (DDR) and draw ratio balance (DRB).

To aid the assessment of the data, a correlation analysis was completed (Table 4). As DDR increases both the elongation at break and tensile strength reduce (negative correlation) but shrinkage and conductor adhesion both increase to a lesser extent. The correlation between tensile strength and elongation at break is strongly positive.

Several cables, prepared using very different DDR were subjected to thermal aging at 135°C, followed by tensile measurements of the mechanical properties. Although the results in Table 5 show the anticipated loss in mechanical properties, there is no correlation with DDR.

IV. CONCLUSION

During aging the major change in mechanical properties occurs within the first 24–48 hours after which the absolute values of tensile strength and elongation at break stabilise. The changes in elongation at break are apparent after aging at either 100°C or 135°C but the effect is more pronounced after aging at 100°C (compatibility test). Previous studies showing that insulation of ethylene vinylsilane copolymer is not subjected to any thermooxidative degradation during thermal aging tests are confirmed. Similar behaviour is seen also for silane-grafted polyethylene insulation. Preconditioning of the reference samples at 70°C for 24 hours as defined in IEC 60811-501 has a limited impact on the change in mechanical properties. The influence of used colour masterbatches is small compared to the variation between individual samples within one colour. Process parameters e.g. extruder screw design and crosshead tooling will not significantly impact the results of aging tests. It is concluded that the phenomena can best be addressed by preconditioning the samples for 24h at the prescribed aging temperature i.e. 100°C, 135°C or 150°C.

REFERENCES

[1] R. M. Gohil and P. J. Phillips, "Crystallinity in chemically crosslinked low density polyethylenes: 3. Morphology of the XLPE-2 system," *Polymer*, vol. 27, no. 11, pp. 1687–1695, 1986.

[2] S. Venkatraman and L. Kleiner, "Properties of three types of crosslinked polyethylene," *Adv. Polymer Technol.*, vol. 9, no. 3, pp. 265–270, 1989.

[3] M. Pastorek, R. Cermak, J. Navratilova, M. Obadal, "Thermal ageing of crosslinked ethylene-vinyl silane copolymers," *Soc. Plastics Eng. Annu. Tech. Conf.*, vol. 67, pp. 1855–1859, Jun. 2009.

[4] M. Pastorek, "On silane crosslinking of polyethylene for wire and cable insulations," M. S. thesis, Dept. Centre Polymer Syst., Tomas Bata Univ., Zlín, Czech Republic, 2008.
[5] M. Pastorek, R. Cermak, J. Navratilova, and M. Obadal, "The effect of crosslinking and thermal ageing on the morphology of ethylene-vinyltrimethoxysilane copolymer," in *Proc. 3rd WSEAS Int. Conf. Eng. Mech. Struct. Eng. Geol.*, 2010, pp. 271–274.
[6] W. Schnabel, *Polymer Degradation; Principles and Practical Applications*. München, Germany: Carl Hanser Verlag, 1981.
[7] M. Celina and G. A. George, "Characterisation and degradation studies of peroxide and silane crosslinked polyethylene," *Polymer Degradation and Stability*, vol. 48, no. 2, pp. 297–312, 1985.

STEFAN HELLSTRÖM received the M.Sc. degree in chemical engineering and the Ph.D. degree in conjugated polymers for solar cells and electrochromic displays from the Chalmers University of Technology, Gothenburg, Sweden, in 2004 and 2011, respectively. He is currently a Lead Scientist for Borealis AB, Sweden, specialising in low-voltage cable insulation and high-pressure polymerisation.

FREDRIK BERGFORS received the M.Sc. degree in chemical engineering from the Chalmers University of Technology, Gothenburg, Sweden, and the M.B.A. degree in international business from the Gothenburg School of Economics, in 2001 and 2002, respectively. He is currently an Application Marketing Manager with Borealis AB, Sweden.

PAUL LAURENSON is a Senior Technical Service Manager of wire and cable with Borealis Polymers NV, Belgium. He received the Doctorate degree from the University of Clermont Ferrand, France, and has spent more than 15 years for working on the development and technical service of wire and cable products.

JAMES ROBINSON has been involved for more than 25 years in the development, manufacture, and technical service of polyolefin products for wire and cable applications. He represents Belgium as a Technical Expert on a number of ISO and CENELEC technical committees. He is currently a Senior Engineer with the Borealis Wire and Cable business.