

# POLYOLEFIN INSULATION DEGRADATION IN ELECTRICAL FIELD BELOW CRITICAL INCEPTION VOLTAGES

Ali Harlin<sup>\*</sup> — Michael G. Danikas<sup>\*\*</sup> — Petri Hyvönen<sup>\*\*\*</sup>

The degradation mechanism of polymeric materials is poorly predictable, and problematic to measure in the network. Polyolefins are widely used in the electric insulation of *eg* cables and capacitors due to their good dielectric properties and most competitive material price. The target for this paper is to explain the basic phenomenon related to the degradation of polyolefin in electrical discharge. Especially the reasons are reviewed why the material has such a sudden break down after a very long period of conservative electrical fields.

**Key words:** polymeric materials, dielectric properties, degradation, electrical discharge, polyolefin

## 1 INTRODUCTION

Polyolefins are a group of fully covalent bonded and non-polar hydrocarbons, and polyethylene is the simplest model for degradation. When inception discharge takes place, the expected lifetime of the insulation is very limited and a rapid decay leading to a break through has started. The paper is focused on the dry cable decay, important for the network with water blocked cable constructions.

### 1.1 Partial discharge and dielectric response diagnostics

The main goal of partial discharge (PD) diagnostics is to recognise the insulation defects which cause the discharges, *eg*, internal or surface discharges, corona, electrical treeing, *etc*, and to estimate the harmfulness of the discharge activity. The shape of a single PD pulse is not relevant for recognition of the type of PD but sampling a spectrum of PD. Equipment has been developed for the measuring the relative height and phase angle of the discharge. [IEC] A fingerprint technique TEAS has been developed for actual recognition [16].

The dielectric response (DR) can be measured in the frequency or time domain. Several methods are available. The return voltage (RVM) and polarisation and depolarisation current measurements (PDC) are suitable for measurements like detecting moisture content in transformer insulation. It has been shown that PDC measurement with one voltage level is not sufficient to detect a bad cable with water trees in polymer cable insulation.

There is proposed a discharge method that combines both the slopes of the decay voltage and the depolarisa-

tion or discharge-current value. Another method is the measurement of  $\tan \delta$  (complex permittivity or complex capacitance) as a function of frequency and its combination with non-linearity. Both of these methods give response due to water tree degraded XLPE cable insulation. [25]

Partial discharge PD and dielectric response can be used for recognition of degradation in oilpaper and polymer XLPE insulation. Combination of DR and PD measurements can improve diagnostic results. PD tests cannot identify the presence of water trees and may cause insulation failure. Typically both methods are effective only when the insulation has already been markedly damaged.

There are various types of partial discharges, not always detectable by conventional discharge detectors. The latter may detect mainly pulse-type discharges and not necessarily non-pulse discharges. There is still discussion as to whether there is material damage below the so-called inception voltage. Indications offered by Bruning et al. seem to point out that the nature of damage observed below inception is very similar to that observed above inception, an indication that even at very low applied voltages damage of the material is possible.

Moreover, even minute voids may be sites of partial discharge activity. It has been shown theoretically that small voids (of the order of 0.01 mm) may reduce the lifetime of insulation, but a further reduction of lifetime with voids of about 0.001 mm is rather unlikely. Thicker insulation needs more sensitive detecting equipment than the thinner one. This becomes even more pronounced when the insulation measuring system has to function in an industrial environment.

<sup>\*</sup> Technical Research Centre of Finland, PO Box 1602, FI 02044 VTT, Finland, E-mail: Ali.Harlin@vtt.fi

<sup>\*\*</sup> Democritus University of Thrace Democritus University of Thrace, Department of Electrical and Computer Engineering, Electric Energy Systems laboratory, 67100 Xanthi, Greece, E-mail: mdanikas@ee.duth.gr

<sup>\*\*\*</sup> Helsinki University of Technology Helsinki University of Technology P.O.Box 1000, FIN-02015 TKK, Finland, E-mail: petri.hyvonen@tkk.fi.

## 1.2 Water trees

Water trees are related to the degradation in moisture containing cable insulation. Polyolefins are able of uptaking 2000 to 5000 ppm of water depending especially on the crystallinity, which is in the case of polyethylene directly related to the material specific density.

Water-trees are well detectable indirectly by electrical spectroscopy especially through the high water contents evidently leading to treeing in longer times. Formed spongy structures filled with electrolyte are not limiting the usage of cable before over-tension of  $U_0$  to  $3U_0$  occurs [Whidsten]. Only water tree retardant like polyphenol compounds may hindrance the activation in wet conditions.

A real system is newer fully water or oxygen free. For instance, water is formed while cross-linking polyethylene and forming XLPE [7]. Water accelerates the degradation through providing free ions and forming electrolytes. At the same time also acetophenone and cumyl alcohol are formed in quantity of 1 wt% of the fresh vulcanised insulation, filling the minor cavities and increasing the impulse strength of the material by 20 to 25%. After degassing the insulation the residuals are in the magnitude of < 4000 ppm of peroxide residuals and < 150 ppm of water, which should not be considered a water tree issue [Mattila].

Water trees are formed in lower electrical field  $E < 10^7 \text{ Vm}^{-1}$  than the electrical trees  $E < 10^8 \text{ Vm}^{-1}$ , which makes it obvious to protect all insulation from water contamination. In Finland, based on the field studies by HUT High Voltage Institute, only one exceptional case has been found. Reasons for this should be the moisture blocked cable constructions applied.

## 1.3 Electric trees

Initiation of electric trees takes place in the micro cavities of the polymer. Initially, the discharge magnitude is 0.1 to 0.2 pC but it increases while the cavity enlarges through degradation up to 0.5 to 1 pC resulting in an actual PD. Finally cracks greater than 2 to 3 micrometers are formed where discharges and counter discharges may provide up to 10 eV of kinetic energies to the electrons. Energy 5 pC is enough for thermal runaway and extensive local thermal degradation of polymer [8].

Polymer insulation fails, sometimes in months, even if operated at voltages below the critical inception voltage (CIV, corona inception voltage, partial discharge inception voltage) showing the same physical appearance as PD induced failures. Similar chemical changes with both sub-corona and corona currents have been reported in the insulation cavities [5]. Minor cavity discharges could lead to an increase in the cavity size and discharge energies but the presence of free radical scavengers will limit the massive failure expansion until the antioxidant is consumed.

In the direct current (DC) field, the critical value for feeding space charges in the system is  $E_{SC,DC} \sim$

$10^8 \text{ Vm}^{-1}$  for polyethylene. In the alternating current (AC) field the critical value is  $E_{SC,AC} \sim 7 \times 10^8 \text{ Vm}^{-1}$ . This results in 3 to 4 eV kinetic energy for the electrons, which is the same magnitude as the chemical bonding energy in hydrocarbons.

## 1.4 Chemical bonding

The sharing of a pair of valence electrons between two atoms forms a typical covalent bond. The bond may dissociate in two ways. In the heterolytic both bonding electrons are retained by one of the atoms, and ionic species are formed. The other, less typical process is homolytic cleavage, when each atom involved receives one electron from the original shared pair.

An atom that contains an unpaired electron is called a **free radical**. Because free radicals contain an atom with an incomplete octet (desired noble gas electron structure), most free radicals are unstable and very reactive. In the table below some values are given for the change in enthalpy  $\Delta H$  while a large number of bonds dissociate, based on which the **bond dissociation energy** values are calculated, which is endothermic. Oxygen or chlorine, having substantially greater electron-negativity, takes larger share of electron density in the bond, increases polarity and weakens the bond [9].

Bond	Dissociation energy (kcal/mol)	Dissociation energy (eV)
CH <sub>3</sub> -CH <sub>3</sub>	88	3.8
CH <sub>2</sub> =CH <sub>2</sub>	163	7.1
CH <sub>3</sub> CH <sub>2</sub> -H	98	4.2
(CH <sub>3</sub> ) <sub>2</sub> CH-H	94.5	4.1
(CH <sub>3</sub> ) <sub>2</sub> CH-Cl	81	3.5

Macromolecules characterizing  $10^3$  to  $10^5$  covalently bonded molecules imply that very high energies are required to dissociate electrons from the nuclei and to form an extended orbital along the chain. Similarly, polyolefins may have sufficient energy to dissociate without dissociating in the first vibration. As a result the vibrations are distributed between the normal modes, and eventually vibration may lead to dissociation [15].

## 1.5 Ion production

Formation of electronically excited molecules is not typical for polyolefin, and formation of excited species can leads to molecular dissociation. The Heisenberg uncertainty principle and the typical mean time between the scattering  $10^{14}$  s imply that the bandwidth is  $W > 0.066$  eV, which is not typical for the low energy electrons [22]. Well-defined valence and conduction bands are unlikely to exist through the bulk of the polymer, and the hot electrons damage the polymer before they transport charge between polymer molecules.

Accelerated electrons in the material typically cause ionization. An electron does not necessarily deliver all of

its energy to the molecule it interacts with; typically it will only pass 0.6 eV of internal energy to the resulting ion.

Since organic molecules, almost without exception, contain electrons in pairs in filled orbitals, ionization of a molecule by removing an electron leaves behind an electron which is unpaired, *ie*, the product is a cation-radical (1). Electron capture to give an anion-radical (2) does not occur to a significant extent since the bombarding electrons have such high translation energies that they cannot be captured.



The molecular ions produced in the electron beam can fragment either by loss of radical, or by loss of the molecule with all its electrons paired. This fragmentation is extensive with pattern of fragment ions. Frequent absence of molecular ions is typical for organic compounds [26].

### 1.6 Thermal degradation

In temperatures below the actual melting point of the semi-crystalline polyethylene autocatalytic degradation takes place especially in the amorphous areas [18]. At higher temperatures the degradation mechanism is mainly according to Bueche's theory, when the molecular size becomes sufficiently small without necessity of chain rupture. Scission most probably occurs in the long polymer chains. Each thermal chain scission forms a polymer radical [15].

At polyethylene temperatures between 150 and 225 °C the free radical may attach to the backbone of the other polymers chains causing grafting, and thereafter a decrease in the mechanical strength, density and crystallinity. Higher than at 225 °C formation of trans-vinyl groups is observed, which indicates radical rearrangements.

In the case of polypropylene such a free radical rearrangement is not typical while the material follows  $\beta$ -scission through weakly bonded hydrogen next to the methylene group [20, 23]. At very high temperatures, 350 to 390 °C and higher, polyethylene degradation takes place through de-polymerization and incomplete thermal cracking forming coke [21].

In the presence of oxygen, initially formed free radicals will react with oxygen, forming per-oxy complexes and further **per-oxy radicals**. The per-oxy has a selfcatalytic effect on the degradation mechanism, accelerating the reaction through lower activation energies. Degradation products are oxy compounds like aldehydes and ketones [19].

### 1.7 Degradation mechanism

Polymer degradation reaction kinetics caused by the polymer radicals can be grouped in three main categories:

addition to polymer chain by branching or net formation (cross-linking), chain scission, and oxidation by absorbed oxygen [12].

*Addition:*

$$v_{addition} = k_p[\text{double bonds}][\text{polymer radicals}] + k_{tc}[\text{polymer radicals}]^2 .$$

*Scission:*

$$v_{scission} = k_d[\text{polymer radicals}] + k_{td}[\text{polymer radicals}]^2 .$$

*Oxidation:*  $v_{oxidation} = k_{ad}[\text{oxygen}][\text{polymer radicals}] .$

The polymer radicals are formed through various mechanisms in discharges, oxidation, and autocatalytic thermal scission. The effect of radiation able of ion formation, like UV and gamma should be neglected in normal operational conditions. The number of critical discharges in the material is related to the electric field, frequency, the number of cavities (and impurities) and their distribution.

Additionally, all the degradation reaction coefficients are increased while the temperature is increased and the mechanism is accelerated. While the radical recombination is markedly low and the activation energy of the double bond addition coefficient is less than that of scission, elevated temperature leads to an increased decay of molecular weight.

Hydrolysis is typical for, *eg*, polysaccharide polymers like cellulose in paper, but not marked in polyolefin. However, the dissociated water ions may form ions which react to form polymer radicals, resulting in irreversible polymer dissociation. When oxygen is present, the radicals may further react to carbonyls, hydroxides, and acids [13].

$$\text{Hydrolysis: } v_{hydrolyse} = k_{hd}[\text{water}] ,$$

$$\text{Hydroxidation: } v_{hydroxidation} = k_{ad}[\text{oxygen}]k_{hd}[\text{water}] .$$

The total effect of ageing is a sum of all these reactions. Addition route will harden the material, while scission and oxidation loss in molecular weight increase brittleness. Oxidation increases also the polarity and the loss factor of the insulation. Individual reactions are complicated or impossible to be measured directly. This means the whole net reaction kinetics has to be studied.

$$\begin{aligned} dn/dt = & (k_{thermal} + k_{oxidation}[\text{oxygen}]^k \\ & + k_{hydrolyse}[\text{water}]^l)(\text{polymer mass}) \\ & k_i = A_i e^{(-E_i/kT)} . \end{aligned}$$

Lifetime expectations can be made based on accelerated testing at elevated temperatures. Engineering of the insulation is typically enough to calculate simply the correlation between the electric field  $E_0$  and frequency  $f_0$  assuming the rest to be constant.

$$\text{Lifetime} = dn/dt (E/E_0)^n (f/f_0)^m .$$

Engineering calculations contain marked errors based on the morphology differentiation in the material and the balance of various sub-reactions in the system, but typically the safe factor approach takes care of the safety. The result is drastic simplification, and can only be made while the polymer system is stabilized with free radical scavengers reducing the system to controlled first order kinetics.

### 1.8 Degradation in the material

A semicrystalline polymer like polyethylene contains both crystalline areas and amorphous areas in between. Morphology of the high voltage cable insulation and the anomalies thereof have been reported in various publications [11].

In normal insulation systems micro voids of size typically from 1 to 5 micrometers are found [Kurioka]. Due to thermal condition in manufacturing and operation also markedly large gas expansion voids, 10 to 50 micrometers are observed. Another type of defects are various kinds of impurities in insulation. Both of these increase the local electric field strength.

The initial step for all polymer degradation is formation of a free radical in the polymer. The primary antioxidants are **free radical scavengers** which terminate free radicals forming stabile compounds with them. Hindered phenols and aromatic amines are examples of primary antioxidants. Phenols, bisphenols, polyphenols and thio-bisphenols are the primary antioxidants in greatest use today [2].

Both the initiation and propagation sequences of the degradation have to be controlled. Primary antioxidants interfere with propagation steps, typically producing highly coloured species indicating a protective decay of the antioxidant. When all antioxidant is consumed, a rapid decay of the polymer is expected [3].

Primary antioxidants when hindered phenols have synergism with organic phosphates. While free radical scavengers reduce free radicals, phosphates reduce hydro peroxy groups to alcohols [24].

## 2 EXPERIMENTAL

Measurements of the chemical structure of polymer insulation were made on certain samples collected from cables in use. A medium voltage cable (type SAMKA 73) was studied near to the terminal ending 30 years after installation (Sample Per30) and compared with the reference, a new installed cable (New).

In the terminal also a starting corona discharge was observed (sample Per30PD), failure of which is demonstrated in the attached picture. The reason for the damage was indicated to outer semiconductor protrusion in the insulation. Several scorch particles typically from extrusion were observed on the boundary layer before the area.

The SAMKA cable was described as follows:  $U_0/U = 11.6/20$  kV, cross section  $3 \times 70$  mm, stranded and compacted aluminium conductor, conductor screen semi conductive plastic, XLPE-insulation, outer screen semi conductive plastic, aluminium shield, PE-jacket, three single core cables are twisted around steel supporting rope. The cable was installed in 1973. Cable termination was installed to the wood pole face down.

The cable type was described as follows: 12/24 kV with a 19 core  $70 \text{ mm}^2$  stranded and compacted aluminium conductor and zero wired under HDPE jacket. The resistance value was  $R_{20^\circ\text{C}} = 0.435 \Omega/\text{km}$ .

Additionally also two samples of a 37 year old insulation of peroxide cured (Per37) and silane cross-linked (Sil37) were studied.

Insulation samples were collected in the middle of the insulations layer. The sample size was  $5 \times 5$  mm and sample thickness was 1.5 mm. IR spectra in the range from 600 to  $3000 \text{ cm}^{-1}$  were measured using the fibre assisted micro probe. In cable Per30PD the sample was collected under the corona area some 1 mm below the damaged area. Also 0.3 mm thick films were cut for testing, but the spectra were too weak for chemical analysis.

FTIR/UV-Vis has been measured from the samples. The observed concentrations are shown in the table: carbonyl at  $1745 \text{ cm}^{-1}$ , phenolic antioxidant at  $1301 \text{ cm}^{-1}$ , consumed antioxidant at  $1258 \text{ cm}^{-1}$ , and silane cross-linking side product at  $1117 \text{ cm}^{-1}$ .

### Spectra compared

ppm		New	Per 30	Per 30 PD	Sil 37	Per 37
Carbonyl	1745.0	440.0	810.0	1260.0	1460.0	970.0
AO (Ph)	1301.0	1730.0	1840.0	2020.0	470.0	1910.0
Phenol	1258.0	50.0	250.0	490.0	1100.0	380.0
MeSiO <sub>2</sub>	1117.0	0.0	0.0	0.0	1980.0	0.0

The results are supporting the following observations. A clear trend is seen of increasing carbonyl content when the cable is aging. Corona near the sampling point seems to promote oxidation observed also in the carbonyl content. The concentration of the consumed phenolic antioxidant increases when the carbonyl index increases. Carbonyl indication is present also in the new cable. The explanation could be in the curing process when the insulation material is placed for some 10 minutes at temperatures 250 to  $290^\circ\text{C}$ .

Additionally it can be noted that the silane cable insulation contains marked amounts of Monosil process side-products. The consumed phenolic antioxidant peak is unfortunately summed with the polysiloxane indication and conclusion in this point are not as clear as in the former cases. However, the antioxidant has been consumed markedly more and the carbonyl index is higher than that of the peroxide cross-linked samples. We have no reference what the carbonyl content of a new silane cable actually is but one can assume it could be 400 to 600 ppm.



**Fig. 1.** Please describe this picture in brief, also in the main text, thanks

### 3 DISCUSSION

There are two main alternatives for the initial degradation mechanism in polyolefin under discharge. Both of these are related to the formation of free radicals. Free radicals can be formed through various mechanisms like mechanical stress, radiation, thermally induced autocatalytic chain scission, thermal cracking and finally accelerated electrons.

Mainly in the electrical insulation the high energetic electrons are able of forming free radicals. In the case of polyethylene energies higher than 3.8 eV are certainly forming cation radicals and in lesser extent anionic radicals. The presence of oxygen accelerates the mechanism markedly forming per-oxy radicals and new intermediate degradation products with lower activation energies.

The thermal decay mechanism is a marked risk when the temperature is higher than 130 °C for a long time. The terminal decay phase leading to break through is described earlier in the text. This circuit is closing only in the end of degradation, when the energy formed in the discharges cannot be transferred from the system anymore due to poor thermal conductivity in the polymer.

#### 3.1 Strategies to measure the initial degradation

Various chemical compounds formed while polymer degrades are measurable by means of chemical analysis. FT-IR infrared and UV-Vis technologies are used for polymer long-term stability and cross-linking process studies, respectively. Unfortunately, the methods require sampling of the insulation.

Thermal degradation processes fingerprint excluding oxidation can be detected utilizing the vinyl content spectrum (vinylidene 888  $\text{cm}^{-1}$ , vinyl 910  $\text{cm}^{-1}$ , and trans-vinyl 965  $\text{cm}^{-1}$ ) which is indicating not only the amount of degradation but also the conditions in which it has taken place. The vinyl content will increase during the

degradation especially at the trans-vinyl. In polypropylene the methyl side groups in the polymer chain makes the measurement practically impossible. Carbonyl index is revealing information on the oxidation. Polymer reaction with oxygen is measurable in carbonyl index at 1710  $\text{cm}^{-1}$ , which is comparable with polymer backbone bonding of polyethylene or methyl groups of polypropylene 1470  $\text{cm}^{-1}$  and 1380  $\text{cm}^{-1}$ , respectively.

Radiation and 1 to 4.5 MeV proton bombardment cause cross-linking and oxidation in polyolefin films. The result of the processes are measurable at  $> 300$  nm UV/Vis spectra. Radical ions formed in heterolytic cleavage are detectable in the near infrared spectra and thus UV/Vis/NIR equipment can be utilized [4].

In advanced studies combined electron spin resonance ESR spectrometer enables measurement on reaction kinetics of radicals. ESR is a very sensitive and specialized technique which uses the electronic transitions taking place between Zeeman splitting levels for detecting and characterizing the paramagnetic centre and impurities in different materials. Electron paramagnetic resonance EPR is compatible with ESR in measurement of free radicals and transition complexes [17].

As a scientific tool, ESR has been powerful in order to directly associate the mechanical, thermal, environmental, UV radiation and electrical stresses to the formation of free radicals as the initial step for polymer degradation [1, 6, 27, 10], [Betteridge, Kahle]. The methods are too sophisticated and sensitive to be used in the field.

### 4 CONCLUSIONS

Polyolefin degradation in the electric field under discharge conditions can be understood especially through formation of free radicals, especially initiated by accelerated electrons with energy higher than 3.8 eV. The initial degradation phase is controlled mainly by decay of the primary antioxidant. While the hindered amines have typically strong coloured reactions when scavenging the free radicals, it is proposed to utilize this reaction as a measure of the initial degradation of the electrical insulation made especially of polyethylene.

Most interesting reaction related to the initial phase of polymer degradation is the decay of the primary antioxidant. Formation of the free radicals causes typical extensive coloured species formed through the free radical scavenger consumed. The change should be well measurable by means of UV/Vis spectra. The applied scientific tools are in consideration impractical to be used in field operations.

Access to the samples should be either collection of samples during the failure or other maintenance or through sampling at terminals. Collected samples are simple to be stored and sent to the laboratory for UV/Vis and also preferred FTIR measurements. Combined with grid service information and location, the chemical grid insulation mapping should provide a valuable additional tool for the asset management.

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**Ali Harlin** was born 1963 in Helsinki, Finland. He received MSc degree in Chemical Engineering (Polymer Science) in 1987 and the degree of Dr Tech in Polymer Technology (Extrusion technology) in 1996 at Helsinki University of Technology. During his doctoral studies he worked with polyolefin manufacturing and applications in Borealis (former NESTE Chemicals) as a project and development manager. Since 1997 he joined cable machinery development in Nokia-Maillefer as General Manager, Technology & Development, and till 2000 as Managing Director of Conex Cables. Finally in 2001 he was nominated Professor of fibre material science in Tampere University of Technology, 2003 docent of electric insulating materials in Helsinki University of Technology, and last 2004 Professor of smart materials in VTT Technical Research Centre of Finland.

**Michael G. Danikas**, born in 1957, Kavala, Greece, received his BSc and MSc degrees from the University of Newcastle-upon-Tyne, Department of Electrical and Electronic Engineering, England, and his PhD Degree from Queen Mary College, University of London, Department of Electrical and Electronic Engineering, England, in 1980, 1982 and 1985 respectively. From 1987 to 1989 he was a lecturer at the Eindhoven University of Technology, The Netherlands, and from 1989 to 1993 he was employed at Asea Brown Boveri, Baden, Switzerland. He researched in the fields of partial discharges, vacuum insulation, polymeric outdoor insulation, rotating machine insulation and insulating systems at cryogenic temperatures. From 1993 to 1998 he was Assistant Professor at Democritus University of Thrace, Department of Electrical and Computer Engineering. In 1998 he became Associate Professor in the same department. During the period 1999–2001 he was director of the Division of Energy Systems. He was invited as "Maitre de conferences" at the Laboratory of Electrostatics and Dielectric Materials, CNRS, in Grenoble, France, during the summer of 1994 and as professor at the Laboratoire de Genie Electrique, CNRS, in Toulouse, France, during the summer of 1995. He spent a sabbatical from February to July 1998 at Darmstadt University of Technology, High Voltage Institute, Germany. He was invited professor at Helsinki University of Technology, High Voltage Institute, Finland, during the summer of 2002. His current research interests are breakdown in transformer oil, simulation of electrical tree propagation in polymers, study of partial discharge mechanisms in enclosed cavities, study of circuit parameters on the measured partial discharge magnitude and surface phenomena in indoor and outdoor high voltage insulators.

**Petri Hyvönen** received his MSc degree in electrical engineering from Tampere University of Technology in 1997. After graduation he worked a few years at ABBs high-voltage testing laboratory as a laboratory engineer. He received a Lic Sc (Tech) degree in 2003 from Helsinki University of Technology. The focus was diagnostics of medium voltage cable systems especially using partial discharge measurement tools. He has been working as a senior researcher at the Power Systems and High Voltage Engineering laboratory of the Helsinki University of Technology since January 2000.