BRNO UNIVERSITY OF TECHNOLOGY
FACULTY OF TECHNOLOGY IN ZLÍN
POLYMER CENTRE

# ELECTRICAL PERCOLATION THRESHOLD OF

# COMPOSITE MATERIALS

## (Elektrický perkolační práh kompozitních materiálů)

Short version of PhD Thesis

by

Jarmila Vilčáková

Zlín, Czech Republic, 2000

Doctoral study program: 2808-V Chemistry and Materials Technology

28-03-9 Macromolecular Substances Technology

Supervisor: *Prof.Ing. Petr Sáha,CSc.*

Reviewers: *Prof.Ing. František Schauer, DrSc.*

(Brno University of Technology, Faculty of Chemistry, Brno)

*RNDr. Petr Filip,CSc.*

(Institute of Hydrodynamics, Acad. Sci., Prague)

*Doc.RNDr. Miroslav Raab,CSc.*

(Institute of Macromolecular Chemistry, Acad. Sci., Prague)

Date of PhD thesis defense: October 6, 2000

The full version of the PhD thesis is available in the Department of Science and Research of the Faculty of Technology in Zlín, Brno University of Technology.

# CONTENTS

# ABSTRACT

The present thesis deals with electrical behaviour of composites of electrically conducting particles in a non-conducting matrix. The materials were investigated from the point of view of the percolation behaviour.

In the composites of short carbon fibres in polyester resin matrix a very low percolation threshold (1-2 wt.% fibres) was found. The relation between the pre-exponential factor and activation energy evaluated from the Arrhenius relationship from the conductivity–temperature dependences confirmed the validity of the Meyer-Nelder rule. When heated, the composites performed a distinct switching effect in the area of the percolation threshold.

A steep rise in conductivity with particle concentration at percolation threshold caused a great scatter of conductivity values due to the fluctuation in the material structure. From the point of view of technology, this concentration range may be considered a forbidden area.

Unlike the flow instabilities of the melts of the composites of hard metal carbide powder in the polymeric matrix the conductivity of solid composites continuously increased with particle concentration even at high filler contents. The switching effect, on the other hand, disappeared due to high particle interaction in this area.

Conductivity measurements during freezing and melting of the composites of polyaniline particles in 1,2,4-trichlorobenzene showed a different behaviour below and above the percolation threshold following from the different structure of the material after solidification. When particles in the melted suspensions were organized in the electric field, the conductivity both in suspensions and in the frozen composites was higher.

**Keywords:** composite, short carbon fibre, hard metal carbide powder, polyaniline particles, polyester resin, electrical conductivity, switching behaviour, percolation threshold, tunnelling effect.

# LIST OF PAPERS

This dissertation includes only short information about the following papers, referred to by Roman numerals:

I    ″Pre-exponential factor and activation energy of electrical conductivity in polyester resin/carbon fibre composites″

J. Vilčáková, P. Sáha, V. Křesálek and O. Quadrát

II    ″Electrical conductivity of polyester resin/carbon fibre in the area of percolation threshold″

J. Vilčáková, V. Křesálek, P. Sáha and O. Quadrát

III    ″Electric properties of composites of hard metal carbides in polymer matrix″

J. Vilčáková, P. Sáha, B. Hausnerová and O. Quadrát

IV    ″Conductivity of polyaniline/1,2,4-trichlorobenzene composites during freezing and melting transitions″

J. Vilčáková, P. Sáha, O. Quadrát and J. Stejskal

# INTRODUCTION

## 1. Electrical conductivity of composites

Generally speaking, composites are multiphase materials whose components are mechanically separable and which exhibit properties unattainable in any of the constituent phases [1]. The electrical properties of composite material are controlled through the material selection, volume fractions of components, conductivity, percolation behaviour and anisotropy.

In practice, electrically conductive composites are often used which consist of a non-conductive matrix filled by conductive particles of various shape (spheres, flakes, fibres, etc.). These materials can be used in many applications, such as electric heaters with self-adjusting power or small-size cutouts of current as temperature-dependent sensors [2]. They can also be utilized in the area of telecommunication and computer technologies of printed circuit boards. Besides, for various ecological applications and device protection against parasitic electromagnetic fields materials with high electrical loss (antistatic materials) are required [3]. The electrical conductivity of composites can be described by the theory of percolation [4-32].

### 1.1 Theory of percolation

The main factor influencing the composite conductivity is the concentration of the filler particles. At low filler content the conducting particles are separated and the electric current may flow only by means of hopping or tunnelling through a non-conducting medium between the neighbouring particles. The transport of charge carriers is inefficient and the overall conductivity of such a composite is low [33].

When particle concentration is increased, the gaps between particles diminish and conductivity slowly increases because charge transport gets easier. At the percolation threshold the conductivity steeply rises.

The percolation threshold is defined as a minimal concentration (volume fraction, $v_{crit}$) of the conducting filler at which a continuous conducting chain of macroscopic length appears in the system [5]. Sherman [6] described percolation threshold as the point at which a macroscopic length continuous chain first is formed.

#### *Percolation models*

There have been several attempts to model the percolation phenomenon, some of them are briefly described herein. The percolation threshold was first studied in 1957 by Broadbent and Hammersley [7], who proposed lattice models for the flow of a fluid through a static random medium. They showed that no fluid flows if the concentration of an active medium is smaller than a certain nonzero threshold value. The fraction of the filler required to achieve percolation can be modelled by the Monte Carlo method [8-10]. The essence of the percolation theory itself is to deter-

mine how a given set of sites, regularly or randomly positioned in some space, is interconnected.

Further statistical percolation models in the area of conductive binary mixtures were made in the 1970s, especially stimulated by the work of Kirkpatrick [11-14], and Zallen, Scarsbrick and Bueche [14].

The history of percolation models continued with those proposed by Sumita [14,15] and Wessling [14,16], which were based on thermodynamic principles. They both emphasize the importance of interfacial interactions between the individual filler particles and the polymeric host for the network formation. As a consequence, these models interpret the percolation phenomenon as a phase separation process.

Geometrical percolation models assumed by Slupowski et al. [14] expected that during the sintering process the insulating powder particles are deformed into more or less regular cubic shape and the conductive powder particles are arranged on the surface of these superparticles.

Bueche [7,14,22] proposed structure-oriented percolation model considering the problem of conducting particles in a nonconducting matrix analogous to the concept of polymer gelation, as suggested by Flory. Equations of the Nielsen model [7] made it possible to estimate the elastic moduli of the composite and to calculate the electrical and thermal conductivities of two-phase systems. McCullough's model [14] predicted the composite conductivity in either the longitudinal, transverse, or normal directions, and showed that a generalized rule for percolation transport mechanism performed a good agreement with experimental data for a polyester/aluminum powder composite. Ondracek [7,14] proposed a model for the field of properties of multiphase materials which are at equilibrium and whose microstructure is homogeneous. He obtained excellent agreement between the model predictions and experimental data. Nevertheless, the effective medium theory [7] did not predict a percolation threshold and was insensitive to changes in the fibre aspect ratio.

As apparent from the previous text, the problem of percolation can be seen from various angles and for different processing methods different models are used. The most promising from the engineer's point of view are the structure oriented ones, which explain the conductivity on the base of the material microstructure.

### *Composite behaviour above the percolation threshold*

The relation between the composite conductivity, $\sigma_c$, and the conductive filler concentration, $v_f$, above the percolation threshold is described by the power law

$$\sigma_c = \sigma_f \left(v_f - v_{crit}\right)^t, \qquad v_f > v_{crit} \qquad (1)$$

where $\sigma_f$ is the filler conductivity, $v_{crit}$ means the critical or threshold volume fraction of the filler, and $t$ is a critical exponent.

It is usually supposed that these values do not depend on the percolation character but on the dimensionality of space [17], therefore for various models t values have been calculated in two and three dimensions and are listed in Table 1
.

| Authors | t (2 D) | t (3 D ) |
|---|---|---|
| Kirkpatrick | 1.1 | 1.6 |
| Stauffer | 1.3 | 2.0 |
| Katsura | 1.1 | 1.73 |
| Straley | 1.1 | 1.7 |
| De Gennes | - | 1.83 |
| Lobb & Frank | 1.35 | - |
| Clerc et al. | 1.0 | 1.72 |

*Table 1. Calculated values of critical exponent, t, in two and three dimensional systems for conductive spherical particles in an insulating matrix* [34].

Eq.(1) has been used by a variety of researchers to fit experimental data and to obtain the values of $v_{crit}$ and $t$, which could be compared with the model predictions given in Table 1. For some composite systems the values of $v_{crit}$ and $t$ are given in Table 2.

| Filler / matrix | $v_{crit}$ | $t$ |
|---|---|---|
| Stainless steel fibres / LDPE | 1.0 | 2.40 |
| Stainless steel fibres / PP | 3.2 | 2.22 |
| Carbon fibres / ER | 4.5 | 3.10 |
| Carbon black / ER | 16.5 | 1.75 |
| Silver particles / Bakelite | 37 | 1.5 |

*Table 2. Experimental values of critical concentration, $v_{crit}$, and critical exponent, t* [34]. *(LDPE-low density polyethylene, PP-polypropylene, ER-epoxy resin)*

The composites reinforced with silver particles and carbon black have critical exponent in the range of 1.5 to 1.8, which is in agreement with the calculated values for three-dimensional systems. Weber [7] and Balberg [9] reported the *t*-values higher for the samples reinforced with fibres than those of compact particles, which is caused by the greater aspect ratio of the fibres. For the composite with carbon fibres [7,11,18] the highest *t*-value was about 3, and a similar value was also found for stainless steel fibres [7].

### *Composite behaviour at the percolation threshold*

Several researchers have investigated the area of the percolation threshold. Efros [17], Shklovskii [19] and Chmutin [20] described the behaviour of composites in this area and expressed the composite conductivity, $\sigma_c$, in terms of volume fraction as in Kirkpatrick's theory

$$\sigma_c = \sigma_f \left( \frac{\sigma_m}{\sigma_f} \right)^s , \qquad v_f = v_{crit} \qquad (2)$$

where $\sigma_m$ means the matrix conductivity, and *s* is a critical exponent for this area.

Chekanov's theoretical and experimental study [11] of the percolation behaviour of epoxy resin/carbon fibre composites was interpreted by Kirkpatrick's percolation theory [13]. Typically, the conductivity dependence on the filler content is an S-shaped curve, which also be seen Fig.1. Here, the percolation threshold was reached at about 7 vol.% of fibres.
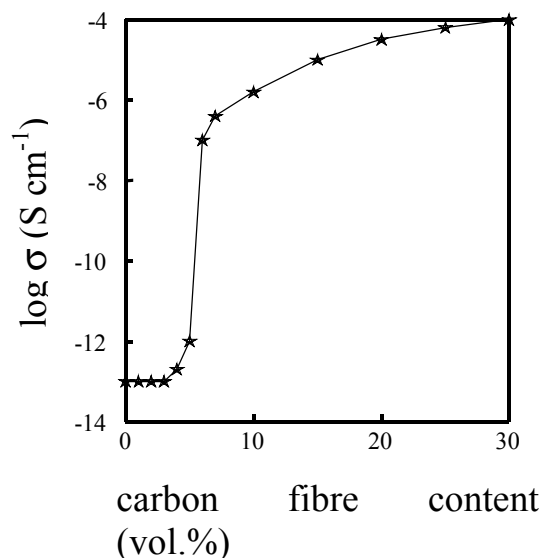


Fig.1Experimental dependence of conductivity on the filler content. Material: epoxy resin/carbon fibre [11].

*Composite behaviour below the percolation threshold*

When the volume fraction of the filler in the composite is smaller than the percolation value, the conductivity of the composite is a slowly varying function whose values approach those of pure matrix $\sigma_m$ [13]. The conductivity of the composite can thus be expressed

$$\sigma_c = \sigma_m \left(v_{crit} - v_f\right)^{-q}, \qquad v_f < v_{crit} \qquad (3)$$

where q is a critical exponent for this case.

The scaling hypothesis [17] gives the following relation between indexes *t*, *s* and

$$q = t\left(\frac{1}{s} - 1\right) \qquad (4)$$

*q*:

In the two-dimensional model (indicated by 2 in the subscript) $s_2 = 1/2$, and it follows from Eq. (4) that $q_2 = t_2$. In the three-dimensional model $q_3 \approx 1$, $t_3 \approx 1.6$ and from Eq.(4) we obtain $s_3 \approx 0.62$ [17].

## 1.2 Charge transport between composite particles

Charge transport in composites can be realized by tunneling [4-6,11,12,23,33-38], hopping [4,12,22,26], or some other mechanism in high electric field. The tunneling effect can be explained on the base of the band quantum mechanical theory as its special case [33].

Sherman [6] stated that between two conducting particles in a disordered system whose separation *d* is large (≥10nm), the resistance is controlled by the bulk resistivity of the matrix itself. However, when *d* is smaller (≤10nm), electrons may tunnel between conductive elements, which leads to a lower resistance of the composite than would be expected from the matrix alone.

Carmona [12] experimentally studied mechanisms of conduction in carbon black and carbon fibre composites and concluded that carbon-black-filled epoxy resin may exbihit two distinct dependences of conductivity on temperature. The first is caused by tunnelling of electrons between particles, in the composite in general, the other appears when carbon black particles are large. Due to different thermal expansion of the matrix and the filler the contact between particles disappears and tunneling sets up. The combination of these two mechanisms (change of tunnel junction width induced by thermal expansion) has been proposed to interpret a minimum in the resistivity - temperature dependence for polyethylene filled with carbon black particles.

The charge carrier tunnelling is predominant at low temperatures and low voltages [39]. Sodolski [40] described a case when conducting structure has not yet been created (low content of fillers), i.e. not all particles are sufficiently connected to one another. In such structure some "defects" can occur which become potential barriers for charge carriers. Since the electric force on these "defects" can be very high Sodolski suggests that the charge carriers can be additionally injected by field emission. From the previous it can be seen that percolation is quite a complex problem which is influenced by many factors. Those acting above the percolation threshold, in the area of conducting state, are analysed below.

## 2. Factors influencing electrical conductivity of composites

The electrical conductivity of composites mainly depends on the filler, matrix and temperature. From the filler point of view the type, size, volume fraction, and orientation of particles in the matrix are crucial here. According to Bigg [1], the fibrous fillers improve conductivity much more significantly than spheres, flakes or irregular particles, i.e. aspect ratio plays an important role here.

### 2.1 Aspect ratio of particles

The aspect ratio of particles is a proportion of maximum L and minimum D dimensions of a particle body. According to this classification $L/D \approx 1$ for symmetrical particles (spheres, cubes and ellipsoids), $1 < L/D < 1000$ for short fibres and flakes, and $L/D > 1000$ for long fibres [5]. It was found [8] that the larger the particle aspect ratio is and the more randomly the particles are oriented, the smaller value of the threshold filler content, $v_{crit}$, appears. Fig.2 shows that the dependence $v_{crit}$ vs. L/D is hyperbolic and that the larger values of L/D are more effective in enhancing the conductivity of the composite.
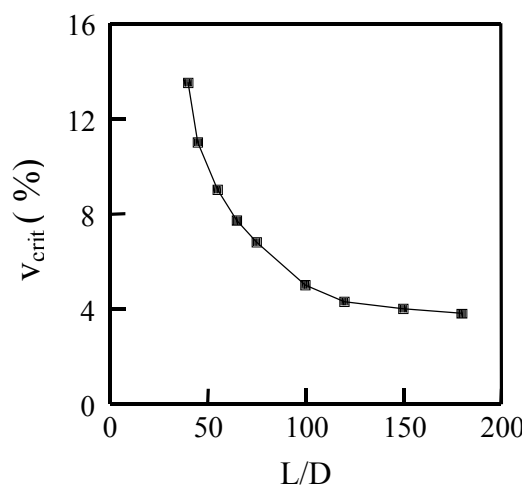


*Fig.2 Dependence of the critical volume fraction of fibres, $v_{crit}$, on the aspect ratio of particles L/D [8].*

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This was also proved by Lin and Chung [41], who compared conductivities of composites with 20vol.% of various fillers of different size in polyethersulphone matrix (Table 3). As can be seen, with increasing size of particles the value of the conductivity of the composites steeply rises.

| Filler (size) | $\sigma$ (S cm$^{-1}$) |
|---|---|
| Carbon fibres (0.2mm) | $7.10^{-4}$ |
| Carbon fibres (0.8mm) | $4.10^{-2}$ |
| Carbon fibres (3.0mm) | 2.0 |
| Aluminium flakes (1.2x1x0.03)mm | 86.0 |
| Nickel fibres (1.0mm) | 112.0 |
| Stainless steel fibres (1.6mm) | 242.0 |

*Table 3. Influence of the filler type and size on the composite conductivity.*
*Matrix: polyethersulphone* [41].

Similar results were achieved in work [35] for a polyvinyl chloride/carbon fibre composite where the initial length of carbon fibres also plays an important role in the conductivity of the network. It seems that there is a critical length of the fibre where a jump in conductivity can be seen. For carbon fibres (CF) it is 2 mm for L/D=285 and concentration 0.02 wt.%, and 3 mm for L/D=428 and 0.005 wt.%. According to [9,18,42,43] an spherical conductive filler, such as carbon black, would have to be added at higher quantities than carbon fibres having an aspect ratio greater than 1 because the interaction between fibres is stronger.

## 2.2 Continuous phase

The matrix (continuous phase) plays two very important roles in a composite material: it acts as a path for stress transfer between fibres, and protects the reinforcement from an adverse effect of the environment. The matrix has a major influence on the processing characteristics of composites [42-45]; its electric properties can be modified by various polymerization conditions. From this viewpoint unsaturated polyester resin with methyl-ethyl peroxide as an initiator and cobalt naphthenate as an accelerator was investigated [40,46]. Several types of matrix materials, such as glass, ceramics, metals and polymers have been used as matrices for reinforcement by carbon fibres [43].

The actual conductivity of the matrix is given by the material characteristics. In general its in the order of $\sigma < 10^{-11}$ S cm$^{-1}$ [46].

## 2.3 Temperature

The composite conductivity is influenced by temperature in various aspects; activation energy and switching effect are the most important.

### *Activation energy of conductivity*

The temperature dependence of conductivity, $\sigma$, can be expressed by the Arrhenius equation

$$\sigma = \sigma_o \exp\left(-\frac{E}{kT}\right) \tag{5}$$

where $E$ is the activation energy of conductivity, $k$ stands for the Boltzmann constant, $T$ means temperature, and $\sigma_o$ is a pre-exponential factor depending on mobility of charge carriers.

One case of temperature dependence of electrical conductivity was investigated by Jachym [46]. The materials were polyester resin polymerized with and without an accelerator and the results can be seen in Fig.3.

Resins have a thermally activated character of conductivity. A change of the curve slope is observed at the temperature above $T_g$ and can be formally connected with the changes of activation energy or pre-exponential factor. According to [2], this change is identical to that in the free volume-temperature dependence. It has been suggested that this is overwhelming evidence in favour of the ionic mechanism in the three polar polymers studied in this work in detail [polyester, polystyrene and poly (methyl methacrylate)], but there is really no reason for excluding the electronic mechanism.
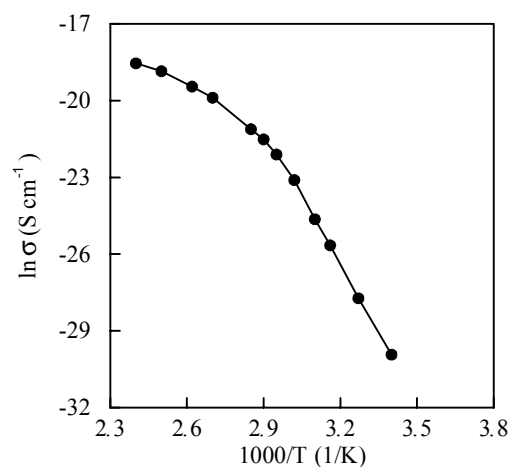


*Fig.3 Temperature dependence of the pure polyester resin conductivity* [46].

Experimental data for various semiconducting materials showed that the correlation between $\sigma_0$ and $\Delta E$ can be expressed by Meyer-Nelder rule [49], or according to Turvey as "the compenzation law" [48],

$$\ln \sigma_o = a + bE ,$$

(6)

which was first reported for semiconducting inorganic oxides; $a$ and $b$ (with $b > 0$) are constants. Several authors [47-49] stated that the compensation law was generally valid not only for inorganic substances but for many semiconducting materials as well.

### Switching effect in composite materials

An early study on switching effect in composite materials was carried out by Bueche [50], using a composite of carbon black (CB) in hydrocarbon wax (Fig.4). The material shows a distinct switching effect, i.e. sudden change in conductivity, at the temperature of 65 – 80 $^o$C.

Later, Gengcheng [24,25] described this effect in polyethylene/carbon black composite. This effect depending also on the concentration of the conductive filler was observed in polyester filled with silver powder or silver-coated glass spheres [51].

The phenomenon can be explained as a result of increasing distances between the conducting particles due to the thermal expansion of the matrix. Thus, separation of the particles which were originally in contact occurs and conductivity steeply decreases.
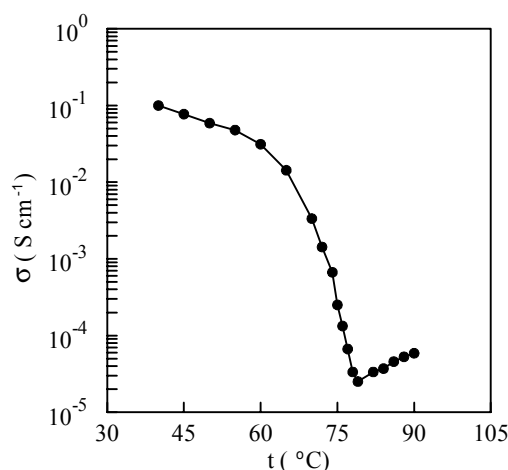


*Fig.4 Temperature dependence of the composite conductivity. Matrix: hydrocarbon wax, filler: 7.6vol % CB [50].*

# 3. Influence of electric field on composite conductivity

The composite conductivity is commonly measured as a current-voltage dependence.

## 3.1 Character of current – voltage dependences

Examination of current-voltage characteristics of composites is the main tool for investigating the mechanism of electrical conductivity [40]. For the given system the shape of current-voltage (I-V) characteristics predominantly depends on the filler content. There are two basic types of I-V characteristics: non-linear and linear.

The non-linear character of I-V dependences may be attributed to the temperature fluctuation caused by internal heating due to the current passing through the composite [34,36]. It can be supposed that more electrons are activated and permitted to junctions across the gaps, giving rise to an avalanche of tunnelling current through the material. With increasing intensity of electric field the probability of charge transfer through the insulating gap of matrix rises. Increasing content of the filler results in nearly linear I-V characteristics, implying that the conductivity obeys Ohm's law. The linear I-V characteristic indicates that conduction is achieved through contacts of the particles, the material behaves as a conductor.

Feng [54] studied I-V dependences and described an interesting phenomenon: when the electrical field strength is above a certain critical value, the current becomes highly unstable and oscillates. It should be noted that the threshold of electrical field strength depends on the filler content in composites, a higher filler content has a lower threshold electrical field strength values. These results suggest that the instability in the I-V curves may be caused by the thermal breakdown of the contact between the electrodes and the composite material due to heating of the composite by the current passing through a sample.

## 3.2 Polarization of particles

When an electric field is applied to a suspension of particles whose dielectric constant is higher than that of the surrounding fluid, an induced particle polarization sets in and particles become ordered in chains parallel to the stream-lines of the electric field [53, 54]. In other words, in the melt of the composite of non-conducting medium/semiconducting polarizable particles in the electric field an organized particle structure may arise (Fig.5) [55, 56]. In case of conducting particles, the conductivity of oriented particle chains is higher than that in perpendicular direction and after the melt solidification composites with anisotropic electrical properties could be obtained.
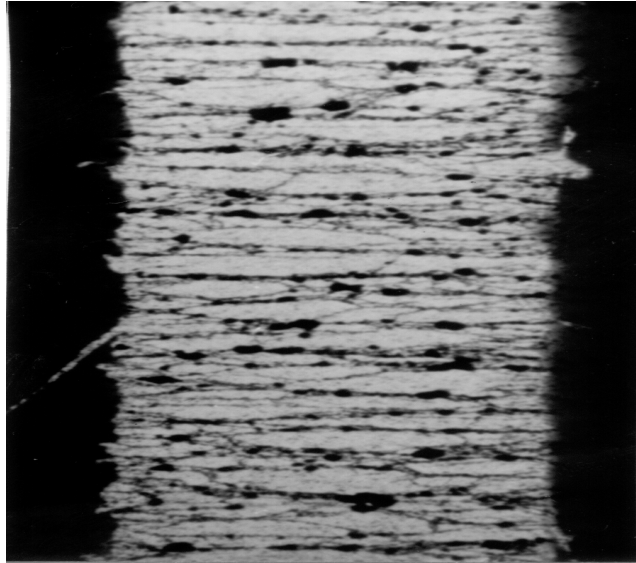
*Fig.5 Micrograph of 1 wt.% suspension of the acid form of polyaniline after application of electric field 1kVmm$^{-1}$ [55].*

During liquid-solid transition, however, particle chains may be interrupted and consequently, their conductivity decreases. The results suggest that such behaviour depends on the percolation limit of the composite.

The above given review suggests that the electrical conductivity in composites is quite a complex issue. Although it has been studied from different viewpoints, there are still some contradictions and discrepancies in the research results. One of them is the role of the filler a particles shape and temperature in the composite electric behaviour at the percolation threshold. Therefore in my thesis I investigate this area.

# RESEARCH RESULTS

Paper I *″Pre-exponential factor and activation energy of electrical conductivity in polyester resin/carbon fibre composites″* deals with the electrical behaviour of polyester resin filled with different contents of carbon fibres (0 - 10 wt.%). These composite materials can be classified by their DC conductivity as insulators or semiconductors (below the percolation threshold), or conductors (above the percolation threshold). At the percolation threshold reached at about 1-2 wt.% of the fibres in the resin, a switching effect has been observed. From the Arrhenius temperature dependence of electrical conductivity, the activation energy $E$ and the pre-exponential factor $\sigma_o$ were extrapolated. The linearity of ln $\sigma_o$ vs. $E$ confirmed the validity of the Meyer-Neldel rule for the investigated system.

A polyester resin (ChS POLYESTER 109) as a matrix was prepared by mixing a monomer with 1 wt.% of ChS accelerator IV and 3 wt.% of P-initiator XXII. All components are products of SINDAT Plzeň Co.Ltd., Czech Republic. Short carbon fibres (SCF), of average diameter 7 μm, length 3 mm, (Bestfight, HTA-7-12.000, Toho Rayon Japan) were used as conductive fillers. SCF as received mixed with 95 wt.% of NaCl particles (average diameter 135 μm ) were crushed using a mixer (EURO-ST-D, IKA LABORTECHNIK STAUFEN, Germany) at room temperature. Then NaCl was dissolved at 90 $^o$C in water and SCF were separated. Distribution of length of SCF evaluated statistically using an image analyser software corresponded to the logarithmic-normal distribution very well with the highest fraction of fibre lengths in the range 100 – 150 μm.

SCF were mixed with the polyester resin, accelerator and initiator in a mixer at room temperature. A series of 18 block composite samples with various SCF contents (0.1 - 10 wt.%) with dimensions 10x10x5 mm were prepared by cast moulding between two parallel copper electrodes with dimension 30x10x1 mm, while polyester resin was cured at room temperature for 24 h.

Measurements of current-voltage characteristics in the applied DC field were carried out using a Keithley 617 programmable electrometer, which also was used as a stabilized DC power source. The current - voltage measurements in the range $U = 0$-50 V, which corresponded to the electric field strength $U_o = 0$-100 V cm$^{-1}$, were performed continuously during the heating and cooling temperature cycles from 28 to 80 $^o$C. Conductivity $\sigma$ was calculated at $U = 10$ V.

Dependence the DC specific conductivity of composites on content of SCF shows a steep increase in this quantity between 1.0 and 1.3 wt. % of SCF corresponding to the percolation threshold. This critical content of SCF, at which first conducting contacts between the fibres are formed, compared with composites filled with carbon black or metal particles is very low and obviously is caused by a fibrous character of the filler. A low conductivity at this percolation threshold, which increases

only slowly further, indicates only a small number of contacts between fibres in the composite at a content of several per cent of SCF.

A semiconducting character of the composites in this transition area caused non-linearity of the current density – field strength dependences. This can be explained by a specific conductance mechanism of these materials, where even if a certain number of conducting paths are present, due to increasing voltage, more electrons are activated to hop over the nonconducting polyester resin barrier across the gaps between the conducting fibres. Thus the charge transfer is higher than that going through the fibre contacts and the current increases with the voltage more than linearly. At sufficiently high concentrations of SCF particles in the composite (such as 9 wt.%), conduction is predominantly achieved through the fibre contacts and the material behaves as a conductor. In this case the behaviour of the system is controlled only by the Ohm law. The shapes of plots of the conductivity on temperature for the neat polyester resin and for the composite below the percolation threshold (with 1 wt.% of the filler) were similar: after an initial slight increase from laboratory temperature at about 46 $^{o}$C corresponding to the glass transition temperature $T_g$ of the polyester resin, a steeper rise set. A similar dependence of conductivity on temperature, explained as a result of migration of ionic impurities through a polymer network.. On the other hand, at higher SCF contents in the composites, a specific behaviour was found. At low temperatures, the conductivity initially decreased while at $T_g$ (for 1.3 wt.% of SCF) or at somewhat higher temperature (for 2.5, 3 and 4 wt.% of SCF), its sudden drop followed by a subsequent slight increase appeared. This so called switching effect of the composite material is caused by breaking contacts between carbon fibres and increasing their distance due to thermal expansion of the matrix. The change in conductivity at the critical temperature was several orders of magnitude and, in fact, means a transition of semiconducting to non-conducting state of material. The sample with 4 wt.% of SCF contained more conducting paths and the switching effect took place more slowly. At 7 or 9 wt.% of SCF, the density of conducting paths is so high that the systems behaved as a conductor, the conductivity decreasing over the whole temperature range and the switching effect did not appear.

The temperature dependences of conductivity showed that up to 4 wt.% of SCF at temperatures above $T_g$ the composites or the neat polyester resin have a semiconducting character. In these systems, contacts between carbon fibres disappear and conductivity of composites is controlled by temperature-dependent hopping or charge tunnelling between conducting particles. The conductivity with temperature rises, which can be analyzed by activation energy of this process. For the purpose, the corresponding parts of ln $\sigma$ vs. 1/T plots were interpolated by straight lines and, from a slope and intercept, the activation energies and pre-exponential factors were estimated. The dependence of ln $\sigma_o$ on $E$ proved to be linear, which confirms validity of the compensation law for the semiconducting composite system under study.

Paper II ″**Electrical conductivity of polyester resin/carbon fibre in the area of percolation threshold**″ was arrived at the study of the electrical behaviour of composites of polyester resin filled with short carbon fibres in the area of percolation threshold. The percolation threshold was reached at about 1-1.1 wt.% of the filler. The dependence of electrical conductivity on the fibre content has been analysed on the base of Kirkpatrick percolation theory. A switching effect was studied in connection with conductivity - temperature dependence. The standard deviations of conductivity values were observed at percolation threshold, is increasing, as a consequence of great fluctuation in structure of fibre arrangement in this area.

Preparation of samples and measurement of conductivity were realized at the same conditions as in Paper I.

A steep conductivity increase between 1.0 - 1.1 wt.% of SCF indicated a percolation threshold in this material. This very low critical limit was obviously caused by a special structure of the fibre particle arrangement in the composites. The conductivity measurement of the set of five samples with an equal SCF concentration showed that at the percolation threshold the standard deviations of the results extremely increased. This effect can be explained as a consequence of especially high sensitivity of conductivity on small incorrectnesses in the fibre content during composite preparation.

The theoretical critical exponent of the Kirkpatrick´s relation lies between 1.35-1.6. A little higher values ranging from 1.6 to 2.0 were experimentally found for polymer-carbon black composites.

The temperature significantly influenced electrical behaviour of composite materials in the percolation area (1.0 - 1.5 wt.% of SCF). In the case of 1.0 wt.% of SCF (the lower boundary of the percolation area) the conductivity - temperature dependences for a set of all five samples with the same SCF content nearly linearly continuously increase, which suggests the semiconducting character of the composites, whose conductivity is controlled by tunnelling or hopping of charges between fibres through a non-nonducting polyester resin interlayer.

On the other hand at higher filler content a switching effect appeared. The initial conductivity (at 26 $^{o}$C) was much higher than in previous case, with increasing temperature at first it slowly decreased, between $40 - 60$ $^{o}$C fell down more than six orders of magnitude and then increased similar to for the 1.0 wt. % composites up to the maximum temperature used.

The semiconducting behaviour of all five samples under investigation with 1.0 wt.% of the filler in the composites manifesting a slowly increasing conductivity - temperature dependences was similar. At 1.1 wt.% of SCF, however, even if in five studied samples was the same SCF concentration, for two ones conductivity with temperature continuously increased as in previous case and in the three samples a switching effect appeared. Similar character of temperature dependences of conductivity was found for a set of five composites with 1.2 wt.% of the filler. For

composites with 1.3 wt.% of SCF the switching behaviour was not observed only for one from a set of five samples and at 1.4 and 1.5 wt.% of the filler the switching effect in all composite samples occurred.

Our results clearly demonstrate that in the percolation area it is difficult to prepare a set of homogeneous samples with demanded conductivity properties. Thus from the point of view of technology the area of percolation threshold could be called as a forbidden area.

In the paper III **″Electric properties of composites of hard metal carbides in polymer matrix″** electric conductivity of composites of a hard metal carbide powder in a non-conducting polymer matrix has been studied with a special attention to the behaviour at high filler concentrations $(\phi_p > 50$ vol. %), where flow instabilities of the melted composites have been observed.

A non-conducting polymer matrix was prepared by mixing 53 wt.% of low density polyethylene (Lacqtene 1200 MN 8 (Atochem), 21 wt.% of paraffin wax and 26 wt.% of block copolymer of ethylene and acrylic acid (5 %), Ex 225 (Exxon). The hard metal carbide powder was supplied by Sandvik Coromant (Sweden). It was a mixture of 77 wt.% of WC, 6.1 wt.% of TaC, 4 wt.% of TiC, 1.9 wt.% of NiC and 11 wt.% of cobalt employed as a metallic binder of the sintered product. The average density of the material was 13.2 g cm$^{-3}$, the average conductivity 3.9x10$^4$ S cm$^{-1}$.

The composites were obtained at 180 $^{o}$C in a laboratory kneader (Brabender Plasticorder PL-2000-6, mixer type W 50E). After cooling, a series of block samples of the 4x4 cm (for low HMC contents) and 1x 0.1cm profile (for high HMC contents) were prepared. The dependences of current density $I_o$ on field strength $U_o$ were measured using the programmable electrometer KEITHLEY 617.

The dependence of electric conductivity on the HMC content in the composites had a sigmoidal shape suggesting a percolation threshold between 20-30 vol.% of the filler, which is rather higher than the Scher-Zallen criterion (16-17 vol.%) calculated for a model system of randomly distributed conducting spherical particles. This may be caused by a rather broad particle size distribution and considerable rough surface of particles. In contrast, the percolation threshold of composites of short carbon fibres in a polyester resin was much lower (between 1.0 – 1.3 wt.%) as showed **Paper I**, which may be caused by a fibrous character of the filler making if possible to create small number of contacts even at relatively very low filler concentrations.

A detailed study of the influence of temperature on the conductivity of composites in the range 22 – 80 $^{o}$C revealed a specific dependence on the particle concentration. At low particle concentration, where only few conducting particle contacts are present, their breaking occurs already after a small temperature increase and a

subsequent conductivity decrease (switching effect) is low. For higher particle concentrations, where more contacts exist, the conductivity drop became more continuous and higher. On the other hand, close to maximum loading, the number of contacts between particles is so high that their interruption due to expansion of polymer matrix is negligible. Consequently, conductivity remains constant with temperature or decreases only a little.

It can be concluded that in a critical range of particle concentration, in which flow instabilities have been observed, electric conductivity continuously increased. This clearly demonstrated that no anomaly on the conductivity – particle concentration dependence appears. In contrast, the shape of the conductivity – temperature dependence suggests a qualitative difference at high particle loadings, following from composite structure with thin interparticle layers and a great number of conducting interparticle contacts.

Paper IV ″**Conductivity of polyaniline/1,2,4-trichlorobenzene composites during freezing and melting transitions**″ reports the results of the study of changes in conductivity during freezing and melting of composites of protonated polyaniline particles in the non-conducting 1,2,4- trichlorobenzene matrix.

Polyaniline (PANI) was prepared by oxidation of aniline hydrochloride with ammonium peroxydisulfate in hydrochloric acid. The green precipitate of polyaniline (emeraldine hydrochloride) was collected on the filter. After drying it was ground in an agate mortar and sieved to obtain particles with a maximum size 0.1 mm. As observed in the microscope, the particles were much smaller, typically 5–10 μm. The conductivity measured by four-point method on the compressed pellet was 5.0 S cm$^{-1}$.

1,2,4-Trichlorbenzene (TCB) was used as a non-conducting medium. According to DSC measurement, its freezing point was at about 18 $^{o}$C. Suspensions containing 2, 5, 9, 14 and 19 vol. % of PANI were prepared by mixing PANI powder with corresponding amounts of TCB at room temperature. As the density of 1,2,4-trichlorobenzene (1.455 g cm$^{-1}$ at 25 $^{o}$C) was close to that of PANI hydrochloride (1.34 g cm$^{-1}$), there was no sedimentation of particles in the liquid state and a only very slow flotation of PANI occurred on long-term standing. The solid PANI/TCB composites resulted when the suspensions had been frozen.

Conductivity was measured in a cell composed of aluminum coaxial-cylinder electrodes 20 mm and 18 mm in diameter, 30 mm high, separated by a gap of 1 mm. Two types of frozen suspensions with a different microstructure were investigated:

(1) After filling the cell at the laboratory temperature (about 22 $^{o}$C) with PANI/TCB suspension, the liquid content was cooled down to 1 $^{o}$C and froze. In this case, PANI particles and their clusters are randomly distributed in the frozen sample.

(2) Before cooling, a DC electric field of the strength 30 V mm$^{-1}$ was applied to the suspensions and kept during the whole cooling interval. This field strength was high enough to produce a fibrous organized structure of PANI particles in the suspensions due to the formation of chains of induced dipoles.

Conductivity has been monitored during the freezing of the samples. Both the random and oriented solid composites were then gradually heated at 2–3 °C steps until they melted again. A low current in the circuit using K104 conductoscope (Radelkis, Hungary) and a high measuring frequency (2 kHz) prevented any change in particle polarization.

The characteristic changes in the conductivity were observed during freezing and subsequent melting of the frozen composites at various PANI concentrations. For the initial suspension, the conductivity of oriented systems of polarized particles were higher than those with random non-polarized particle structure. The greatest difference between the oriented and non-oriented frozen composites was found in the suspension with the lowest particle concentration 2 vol.%. It is obvious that the particle organization, if produced by external electric field, does not disappear during freezing and melting the matrix, which allows the reorganization of conducting chains after the system becomes liquid.

When froze the original suspensions and melted the frozen samples, changes in the conductivity profile depended in the dependence on PANI particle concentration. At the lowest concentration 2 vol.% an initial conductivity of the original suspension fell down after freezing. When heating the solid composites conductivity steeply rose between 15 and 18 $^{o}$C (for a random particle structure for more than two orders of magnitude) and then only slightly increased again as before. For the composite comprising 5 vol.% of PANI the conductivity behaved similarly as in previous case, only its increases at the solid–liquid transition was steeper. The steepest conductivity increase in the narrow temperature range (17–18 $^{o}$C) appeared at the particle concentration of 9 vol.% PANI, while the difference between conductivity of the melted oriented and non-oriented suspensions was reduced.

In all three particles concentrations mentioned above, the conductivity of melted materials were several orders of magnitude higher than in the solid state. In contrast to this, at 14.1 vol. % PANI an increase in conductivity of melted material was much smaller and, at 19 vol.% PANI, the conductivity after melting was even significantly lower. This suggests that conductivity–temperature profiles are obviously related to the structure of the composite samples, and whether the PANI concentration is below or above the percolation threshold.

For both the oriented and non-oriented frozen samples, the steepest conductivity increase in the dependence on the PANI concentration indicated a percolation threshold between 9 and 13 vol.% PANI. It is lower than the theoretical value (16–17 vol.%) reported for a model system of randomly distributed conducting and nonconducting uniform spheres. This may be a result of a broad size distribution of

ground PANI powder which supports formation of paths of smaller conducting particles with irregular shape at relatively lower concentration than in the system of uniform spheres.

The results showed that preparation of composites of conducting particles in the non-conducting matrix with defined conducting properties by means of freezing of the liquid suspensions has to consider the changes in the particle organization which may occur during the solidification. If the particle concentration is low, conductivity of the resulting solid composite is lower than that of the basic liquid material. On the other hand, if the concentration of the conducting particles is higher than the percolation threshold, the resulting conductivity of the frozen composite was higher. Such behaviour is observed both for the original suspensions and those oriented in the electric field. The oriented liquid suspensions and solid composites produced from them had a higher conductivity compared with non-oriented ones due to the organization of the conducting particles.

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## SOUHRN

Předložená disertace se zabývá elektrickým chováním kompozitů na bázi elektricky vodivých plniv v nevodivé matrici se zaměřením na změny vodivostí v oblasti perkolace. Vodivé materiály byly klasifikovány podle perkolačního prahu, který představoval minimální množství plniva nutného k vytvoření první nepřetržité vodivé cesty v kompozitu. Pod tímto limitem se kompozit choval jako izolátor a vodivost byla převážně určována elektrickými vlastnostmi nevodivé matrice. Nad perkolačním prahem vodivost rostla v důsledku formujících se vodivých kontaktů mezi vodivými částicemi.

Hlavní myšlenky této práce jsou shrnuty ve čtyřech následujících článcích.

Článek I ″**Předexponenciální faktor a aktivační energie elektrické vodivosti kompozitů na bázi polyesterová pryskyřice/ uhlíková vlákna**″ se soustředil na elektrické chování kompozitů na bázi polyesterové pryskyřice a krátkých uhlíkových vláken. Tyto materiály byly klasifikovány na základě jejich stejnosměrné vodivosti jako izolátory a polovodiče (v oblasti pod perkolačním prahem) a vodiče (v oblasti nad perkolačním prahem). Hodnoty perkolačního prahu bylo dosaženo okolo 1-2 hm.% uhlíkových vláken v pryskyřici. V souvislosti s teplotní závislostí vodivosti kompozitů byl sledován spínací jev, kdy s rostoucí teplotou docházelo k oddálení vodivých vláken a přerušení vodivých cest v důsledku teplotní roztažnosti matrice. Z teplotní závislosti vodivosti (arrheniovského typu) byly extrapolovány hodnoty aktivační energie $E$ a předexponenciálního faktoru $\sigma_o$. Lineární závislost ln $\sigma_o$ na $E$ potvrdila platnost Meyer-Neldelova pravidla pro zkoumaný systém.

Článek II ″**Elektrická vodivosti kompozitů na bázi polyesterová pryskyřice/ uhlíkové vlákno na prahu perkolace**″ se zabýval výsledky studia elektrického chování kompozitů polyesterové pryskyřice s uhlíkovými vlákny v oblasti perkolace. Perkolačního prahu bylo dosaženo při plnění 1-1.1 hm.% plniva. Závislost elektrické vodivosti na podílu vláken byla analyzována na základě Kirkpatrickovy perkolační teorie. Spínací jev byl zkoumán v souvislosti se sledováním teplotní závislosti vodivosti kompozitů. Hodnoty standartní odchylky vodivosti pro kompozit se stejným plněním v oblasti perkolace vzrostly, což byl důsledek velké fluktuace ve struktuře uspořádání vláken. Z tohoto technologického hlediska lze perkolační práh považovat za oblast, kde je velmi obtížné připravit kompozitní materiál s předem požadovanými vlastnostmi.

Článek III ″**Elektrické vlastnosti kompozitů karbidů v polymerní matrici**″ byl zaměřen na chování elektrické vodivosti kompozitních materiálů, směsi karbidů WC, TaC, TiC a NiC v polymerní matrici. Hodnota perkolačního prahu v intervalu mezi 20-30 obj.% plniva byla vyšší než teoretická hodnota podle Scher-Zallen kritéria (16-17 obj.%) pro modelový systém náhodně distribuovaných vodivých sféric-

kých částic. Na rozdíl od toho významný vliv vyvolalo působení teploty na vodivost kompozitních materiálů. Pro nízké koncentrace částic, kde vodivých kontaktů bylo málo, se změna vodivosti jako funkce teploty (spínací jev) objevila již při nízké teplotě. Při vyšší koncentraci částic, kde existovalo více vodivých kontaktů, změna vodivosti byla výraznější. Naproti tomu, pro kompozity s maximálním plněním, bylo přerušení způsobené teplotní roztažností polymerní matrice zanedbatelné, neboť počet kontaktů mezi částicemi byl vysoký a pokles vodivosti se projevil nepatrně. V oblasti vysokého plnění, kde byly popsány tokové nestability tokových tavenin těchto kompozitů, vodivost rostla kontinuálně a žádné anomálie nebyly potvrzeny.

Článek IV ″**Vodivost kompozitů polyanilínu v 1,2,4-trichlorbenzenu během tuhnutí a tání**″ se zabýval změnami elektrické vodivosti po ztuhnutí a během tání v závislosti na koncentraci vodivého plniva. Pod perkolačním prahem byla vodivost tuhých kompozitů nižší než původních (kapalných) suspenzí. Naproti tomu nad kritickou hodnotou plnění, vodivost naopak po ztuhnutí suspenze vzrostla. Vodivost jak v kapalném tak pevném stavu byla vyšší, když polyanilínové částice v suspenzi byly polarizovány elektrickým polem a po spojení do řetězců vytvořily vodivé cesty mezi elektrodami.

# CURRICULUM VITAE

Jarmila Vilčáková (Horáková)    *1971

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|---|---|
| 1990 – 1995 | Engineer degree (equal to MSc.) at Brno University of Technology, Faculty of Technology in Zlin. |
| 1995 | Final thesis: ″Problematic of distribution of short carbon fibres and preparation of composite materials with different of content of conductive filler and their electrical properties″. |
| 1995- | Postgraduate doctorate study at the Faculty of Technology in Zlin, on subject matter ″Electrical percolation threshold of composite materials″. |
| 1997 | Research stay at Chalmers University in Gothenburg (Sweden), on subject ″Dielectric behaviour of composite material″. |
| 1999- | Research assistant at Polymer Centre, Faculty of Technology in Zlin. |

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1. VILČÁKOVÁ, J., SÁHA, P., KŘESÁLEK, V., QUADRÁT, O.: Pre-exponential Factor and Activation Energy of Electrical Conductivity in Polyester Resin/Carbon Fibre Composites, Synthetic Metals, 113 (2000) 83-87.

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