

The influence of matrix composition on electrical properties of polymer composites

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Master Thesis
2007



Tomas Bata University in Zlín
Faculty of Technology

Děkuji své vedoucí Ing. Michaele Pelíškové, PhD. a také RNDr. Janu Prokeši, CSc. za odborné vedení diplomové práce, poskytování rad, materiálových podkladů k práci a návrhy při získávání a zpracování výsledků.

Ráda bych také poděkovala Jiřímu Kadleci, Doc. Ing. Josefu Špačkovi, CSc., za pomocnou ruku a vlídné slovo.

Prohlašuji, že jsem na celé diplomové práci pracoval/a samostatně a použitou literaturu jsem citoval/a.

Ve Zlíně, 15. 05. 2007,

.....
jméno diplomanta

Odstraněno: 09. 05. 2007

Univerzita Tomáše Bati ve Zlíně
Fakulta technologická
Ústav inženýrství polymerů
akademický rok: 2006/2007

ZADÁNÍ DIPLOMOVÉ PRÁCE

(PROJEKTU, UMĚLECKÉHO DÍLA, UMĚLECKÉHO VÝKONU)

Jméno a příjmení: **Bc. Jitka HRNČIŘÍKOVÁ**
Studijní program: **N 2808 Chemie a technologie materiálů**
Studijní obor: **Inženýrství polymerů**

Téma práce: **The influence of matrix composition on electrical properties of polymer composites**

Zásady pro vypracování:

1. Prepare the background research on the given subject.
 2. Prepare composite materials with two component matrix and electro-conductive filler: with several separated filler concentrations and several different ratios of both of the matrix components.
 3. Using SEM, evaluate electrical properties of the composites prepared this way in DC electrical field as well as their morphologic properties.
 4. Discuss obtained results and make the diploma work conclusions.
-
-

Rozsah práce:

Rozsah příloh:

Forma zpracování diplomové práce: **tištěná/elektronická**

Seznam odborné literatury:

STRUMPLER, R., GLATZ-RECHENBACH, J., Conducting polymer composites. *Journal of Electroceramics*. April 1999, no. 3

MILES, D. C., BRISTON, J. H., Polymer technology. New York: Chemical Publishing Co., 1979. 707 p. ISBN 0-8206-0255-8

GOOSEY M., *Plastics for Electronics*, Dordrecht/Boston/London: Kluwer academic Publisher, 1999, p. 404, ISBN 0-412-72560-6

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Datum zadání diplomové práce:

11. listopadu 2006

Termín odevzdání diplomové práce:

10. května 2007

Ve Zlíně dne 5. února 2007


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Abstract

Conducting polymer composites (CPC) still constitute an ongoing topic of great scientific and commercial interest. While the utility of CPCs is well established, a new generation of efficient CPCs possessing a low percolation threshold concentration and high conductivity continues to be sought. Lately two main strategies of improving the conductivity at a given filler concentration have been followed: the double percolated networks induced by immiscible blends as well as multicomponent fillers in a single polymer matrix.

In many previous studies conducting immiscible blends of thermoplastic polymers were investigated, the novelty of this diploma work consists in the use of thermosetting immiscible blends. Three types of epoxy/silicone rubber blended composites differing in the content of the second polymer were prepared and filled with various amounts of carbon black. Electric properties of such multicomponent composites were measured and compared with electrical properties of single polymer composites filled with carbon black. The hardness of prepared composites was evaluated too. The conductivity enhancement about 2 – 3 orders of magnitude of composites containing even only 25 % of silicone rubber and from 15 – 25 wt.% of carbon black was found comparing to single epoxy with the same amount of filler.

Abstrakt

Vodivé polymerní kompozity (CPC) stále představují téma značného zájmu vědců i komerce. Zatímco užitečnost CPC je dobře známá, nová generace efektivního CPC majícího nízkou hodnotu perkolační prahu a vysokou vodivost se stále hledá. Poslední dobou jsou sledovány především dvě hlavní strategie zlepšování vodivosti s danou koncentrací plniva: vytvoření dvojité perkolační sítě vytvořené nemísitelnými směsmi matric, a druhou strategií jsou mnohosložková plniva v jedné polymerní matici.

V mnoha předchozích studiích byly zkoumány vodivé nemísitelné směsi termoplastických polymerů, novinkou této diplomové práce je použití nemísitelných směsí termosetů. Tři druhy kompozitů z epoxidové pryskyřice/silikonového kaučuku byly připravené, lišily se ve svých poměrech a byly naplněny různým množstvím sazí. Elektrické vlastnosti těchto mnohosložkových kompozitů byly měřeny a srovnávány s elektrickými vlastnostmi čistých polymerních kompozitů plněných sazemi. Také tvrdost připravených směsí byla

hodnocena.

U kompozitů obsahující jen 25 % silikonového kaučuku a 15 – 25 hm.% sazí došlo, ve srovnání s čistou pryskyřicí obsahující stejné množství plniva, ke zvýšení vodivosti o 2-3 řády.

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INTRODUCTION

Conducting polymer composites (CPC) are commonly consisting of a polymer matrix into which conducting filler is incorporated. These multifunctional materials are a part of various commercial applications due to their high electrical conductivity, light weight, corrosion resistance and enhanced mechanical properties. Their applications include battery and fuel cell electrodes, antennas, wave guides, as well as antistatic layers, electromagnetic wave absorbers, corrosion resistant or optical materials.

Lately a new generation of efficient CPCs connecting advantages of a low percolation threshold (PT) and high conductivity has been investigated. The main objective of these efforts is to optimize application properties with regard to processibility, cost and lowering of environmental pollution. The addition of large quantities of solid fillers into a polymer matrix is thus the limiting factor for development of commercially applicable CPCs. Strategies developed to improve electric conductivity at a given concentration have relied on double percolated networks, structural and electrical, induced by immiscible blends, as well as on the multicomponent fillers in a single polymer matrix.

It has been proposed by Mamunya that conducting fillers can be forced to segregate in polymer blends as the particles either reside within one of the polymer blend in the random distribution prior mixing or migrate to the polymer-polymer interface after mixing.

Recent studies of immiscible conducting polymer blends demonstrated that the PT can be in this manner substantially reduced for given filler.

Some studies demonstrated that conducting immiscible polymer blends are also promising chemical sensitive materials.

In the general, results arising from previous studies of conducting immiscible polymer blend composites filled with carbon black were established. Carbon black (CB) locates preferentially within a phase in which it has a higher PT. The double percolation concept, requiring continuity for the CB network, has been introduced and found to be necessary to obtain conductivity in such immiscible polymer blend. The PT and resistivity of the blend are lower than those of the corresponding CB-filled individual polymers.

Most studies using polymer blends have involved melt blending combinations of thermoplastics, or thermoplastics with rubbers or thermoplastics elastomers. Nevertheless, one type of phase separated polymer systems, which does not essentially require high processing temperature is use of reactoplasts with catalysts.

Only limited number of studies deals with carbon black filled interpenetrating polymer networks (IPN). Carbon black is used in such immiscible blends as a flame retardant or to improve mechanical properties and heat and corrosion resistance. The electrical properties of only few IPNs have been reported in literature and even lower studies deals with undoped IPN polymer systems.

The main goal of this diploma work is a proposal of new unconventional material by use of immiscible reactoplastic blend. Three types of blended composites differing in the content of the second polymer were prepared and filled with various amounts of carbon black. Electric properties of such multicomponent composites were measured and compared with electrical properties of single polymer composites filled with carbon black. The hardness of prepared composites was evaluated too.

The work should bring new knowledge about the relation between morphology and conducting properties of such blends. Moreover, the orientation on thermosetting multicomponent polymers provides a new unexplored possibility of CPCs construction under controllable conductivity and mechanical properties improvement as well as cost reduction; therefore also reduction of the impact on environment can be obtained.

1 THEORETICAL PART

1.1 Electrical properties of polymer composites

Electrical properties of polymers subject to low electric field strengths can be described by their electrical conductivity and dielectric constant, volume resistivity, surface resistivity, dissipation, power and loss factors, arc resistance and dielectric strength. [1,2]

Electrical conductivity is a measure of how a material accommodates the transport of electric charge. SI derived unit is the siemens per metre (S/m). It is the ratio of the current density to the electric field strength. Symbol for electrical conductivity is kappa (κ), but also sigma (σ) or gamma (γ).

Conductance is an electrical phenomenon where a material contains movable particles with electric charge, which can carry electricity. When a difference of electrical potential is placed across a conductor, its movable charges flow, and an electric current appears, as sketched in the Figure 1. Electrical conductivity is the reciprocal of the electrical resistivity. [3]

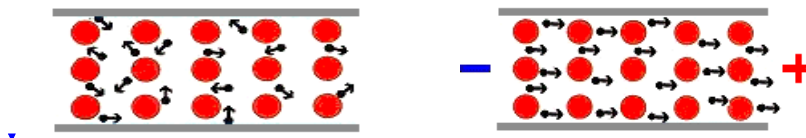


Fig. 1 Connecting a voltage source to conductor gives rise to free electron movement and the electric current is established. [4]

The relative dielectric constant of insulating materials (ϵ) is the ratio of the capacities of a parallel plate capacitor with and without the material between the plates. A correlation between the dielectric constant and resistivity R at 298 K: $\log R = 23 - 2 \epsilon$. [1]

Materials can be classified by their conductivity in $(\Omega \cdot \text{cm})^{-1}$ as follows:

- conductors 10^{-5} ,
- semiconductors $10^{-5} - 10^{-12}$,
- insulators 10^{-12} or lower.

The resistivities of a number of materials are given in Table I. [2]

Table. I Electrical resistivity of different materials in ($\Omega \cdot \text{cm}$)[2]

Resistivity ($\Omega \cdot \text{cm}$)	Material	Classification
10^{18}	Polytetrafluoroethylene	Insulators
10^{17}	Polystyrene, polypropylene	
10^{16}	Polyethylene, silicone rubber	
10^{15}	Amine-cured epoxides	
10^{14}	Diamond	
10^{13}	Polyamides	
10^{12}		Semiconductors
10^{11}		
10^{10}	Glass	
10^9		
10^8	Silver bromide	
10^7		
10^6		
10^5		
10^4	Silicon	Conductors
10^3		
10^2	Germanium	
10^1		
1		
10^{-1}		
10^{-2}	Quinolinium salts	
10^{-3}		
10^{-4}	Bismuth, mercury, graphite	Conductors
10^{-5}	Polypyrrole and polythiophene	
10^{-6}	Silver, copper	

Polymers generally have resistivities of $10^{12} \Omega \cdot \text{cm}$ or greater and some fluorinated polymers have resistivities in excess of $10^{18} \Omega \cdot \text{cm}$. However, it should be noted, that intrinsically conducting polymers such as polyaniline and polypyrrole have been the

subject of many studies and development over the last decade or so and it is now possible to produce these materials with conductivities approaching those of the metals. [1,2]

To describe the difference between conductors, insulators and semiconductors, the energy band theory can be used. If an electric field is applied to a solid, electrons in the valence and conduction bands can be accelerated by the field and gain energy. However, this can only happen if the electrons can move from their own energy level within the band to an unoccupied level of higher energy.

In conductors such as metal solids the valence band is only partially filled and the valence and conduction bands overlap as shown in Fig. 2 (a). Thus, valence electrons are free to move in both the valence and conduction bands. Hence conductors have low electrical resistance and allow current to flow when a potential difference is applied across them.

In insulators the valence band is completely filled, moreover the energy gap between it and the conduction band is very large as shown Fig. 2 (c). Thus, electrons cannot move under the influence of an applied potential difference. Insulators therefore have very high electrical resistance and do not conduct electric current.

In semiconductors there is a small forbidden gap between the valence band and the conduction band as shown Fig. 2 (b). At absolute zero the valence band is completely full with electrons and the material acts as an insulator. As the temperature increases some electrons gain sufficient thermal energy to escape from the valence band and cross the forbidden gap into the conduction band. Once sufficient electrons have crossed the gap conduction of electric current becomes possible and conductivity increases with temperature. [5]

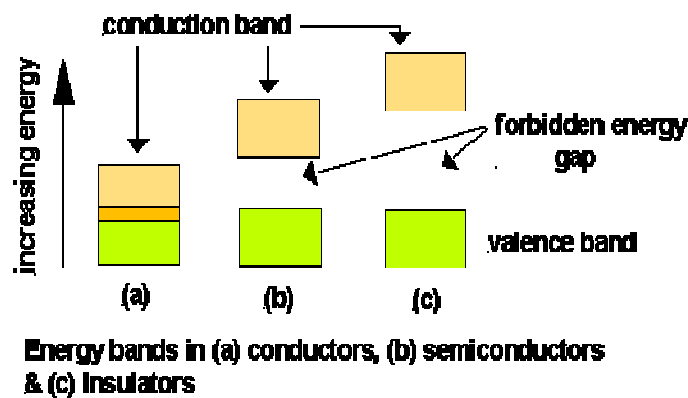


Fig. 2 The illustration of energy band theory [5]

1.1.1 Charge transport

Electrical behaviour is presented by charge transport. [6] However, conductive polymers generally exhibit very low conductivities. The conductivity of the composite is given by a conducting structure of particle chains above the percolation limit. The charge transport in the composite can be realized by hopping or tunnelling mechanism. [7-9]

Odstraněno: ¶

Hopping

Hopping is a variety of charge transport between localised electronic states, thus it is the process most likely to proceed in heterogenous materials. It is asserted only in the potential barrier with a width lower than 10nm. [9]

The temperature dependence of hopping conductivity can be sufficiently described by the energy band theory. According to it, there are localized states in the gap, randomly distributed in space and in energetic level. Charge transport can only occur here through thermally activated hopping, across potential energy barriers between localized states. The forbidden band is approximately at the centre of the gap, the states below are occupied and those above are empty like is shown in Fig.2 (b). Electrons will hop from the occupied to the empty states, although most of the hops will have to be upward in energy. At high temperatures there are many phonons available that can assist in upward hopping, but as these phonons freeze, the electron has to look further to find an energetically accessible state. Consequently, the average hopping distance will decrease as the temperature decreases. Thus, the hopping probability decreases exponentially with the distance and the conductivity also decreases. [9, 10]

Tunneling

Another mechanism of charge transport is tunnelling. This process depends on the potential barrier width and height, the charged particle on one site may hop or tunnel to the other site as shown Fig. 3. According to classical theory, the electron cannot penetrate into or across the potential barrier of height which is greater than its energy. However, according to quantum mechanics, there is a finite probability for the electron to appear on the other side of a sufficiently thin (<1 nm) barrier. [7, 8, 10, 11]

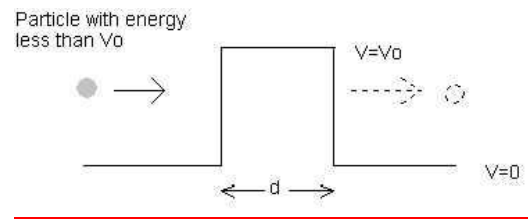


Fig. 3 Potential barrier width d , and height V_0 . [11]

1.1.2 The percolation theory

It is generally known that the electrical resistivity for polymer composites does not increase continuously with increasing electroconductive filler content, but there is a critical-composition (percolation concentration) at which the resistivity drops magnitudes from the insulating range to values in the semiconductive or metallic range. For efficiency, in order to decrease the difficulty of the process and economic costs, the amount of the conductive phase for achieving materials with high conductivity should be usually as small as possible. [12]

The conductivity of heterogenous material thus critically depends on the volume content of the filler. For very low filler fractions, the mean distance between conducting particles is large and the conductance is limited by the polymer matrix which is typically in the order of $10^{-15}(\Omega \cdot \text{cm})^{-1}$. When a sufficient amount of filler is loaded, the filler particles get closer and form chains, which result in an initial conducting path through the material. The corresponding filler content is called the percolation threshold. In this concentration range, the conductivity can change drastically by several orders of magnitude for small variations of the filler content. Finally, at high loading of the filler, the increasing number of conducting paths forms a three-dimensional network. In this range the conductivity is high and less sensitive to small changes in volume fraction. In order to create a well conducting polymer composite, the filler's conductivity has to be much higher than that of the matrix. [7]

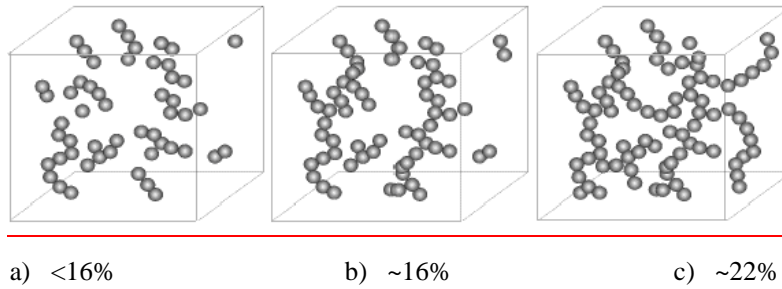


Fig. 4 Illustration of critical fraction in the percolative network of spherical inclusions in the random distribution: a) without percolation; b) critical volume fraction percolative network; c) percolative network cluster. [13]

Electrical properties of polymer composites depend upon factors such as filler content, aspect ratio, conductivity of filler and the processing conditions. The amount of electrically conductive filler required to impart conductivity to an insulating polymer can be dramatically decreased by selective localisation of the filler in one phase, or better at the interface of co-continuous two-phase polymer blend. This subject will be interpreted in topic 1.2 – Blends. An experimental example of a percolation curve is demonstrated in Fig. 5. [15]

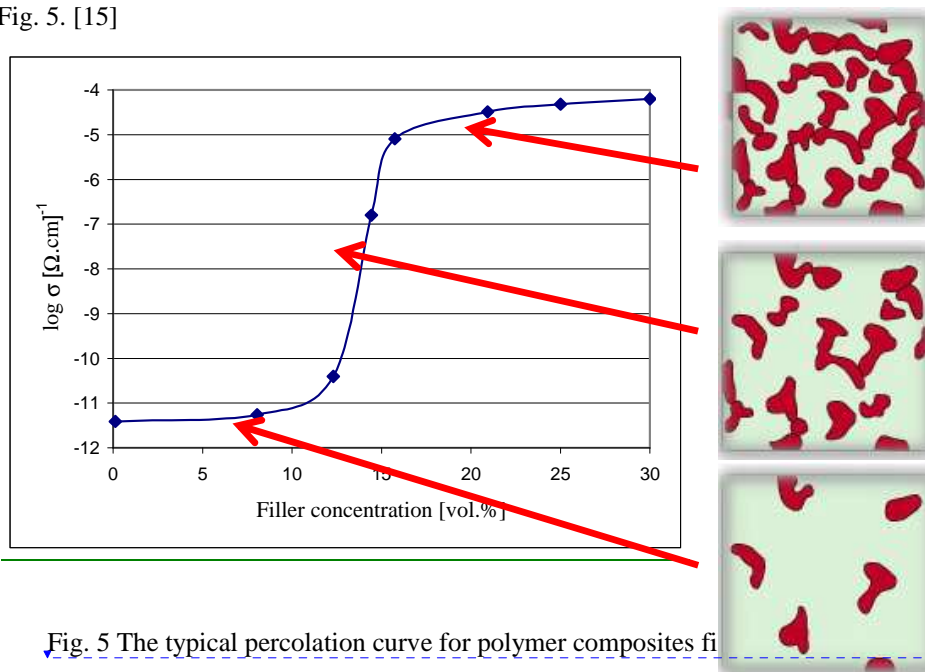


Fig. 5 The typical percolation curve for polymer composites with conductive filler. [15]

Odstraněno: ¶

Random resistor networks, such as filled polymers, typically obey a power-law conductivity relationship above the percolation threshold of the form:

$$\sigma_c = \sigma_f (v_f - v_{\text{crit}})^t \quad v_f > v_{\text{crit}} \quad (1)$$

where σ_c is the composite conductivity, σ_f is the intrinsic conductivity of the filler and v_f is the volume fraction of filler at the percolation threshold. Critical exponent t describes the rate of conductivity change.

The conductivity of composites at the percolation threshold is given by

$$\sigma_c = \sigma_f (\sigma_m / \sigma_f)^s \quad v_f = v_{\text{crit}} \quad (2)$$

where σ_m means the conductivity of the matrix and s is a characteristic exponent.

Under the percolation threshold, at low volume fraction of filler, the composite conductivity is expressed as

$$\sigma_c = \sigma_m (v_{\text{crit}} - v_f)^{-q} \quad v_f < v_{\text{crit}} \quad (3)$$

and its value approaches that of the pure matrix, q is the critical exponent for this case. [16]

Many approaches are now being explored to reduce the percolation threshold, thereby achieving near-maximum conductivity at much lower concentrations of conductive filler.

Percolation thresholds have already been successfully reduced using ternary composite systems in which carbon black has been incorporated into a mixture of two immiscible polymers. [17]

Sumita and coworkers were the first to exploit the use of matrix blends and were able to significantly reduce the percolation threshold. Carbon black was found to aggregate at the interface of the two polymers, which led to more efficient formation of conductive pathways. The surface energies of the two polymers seem to determine where the carbon black will localize. The critical volume fraction (v_c) required to reach the percolation threshold is now determined by a “double percolation effect.” Double percolation results from the dependence of electrical conductivity on both the connectivity of carbon black within a given polymer and the connectivity of that polymer within the blend. [17]

1.2 Polymer composites

The term composite is often used to describe polymer matrix: as continuous part and containing filler as discontinuous part.

1.2.1 Polymer matrix

Composite matrixes are usually polymers because they are light weight, inexpensive, and are easy to process and mould. The matrix serves two main purposes: it transfers forces to the reinforcing phase, and it protects the reinforcing material. They can be created by pure polymers or blends. [18]

Pure polymers

Pure polymers can be classified as thermosets and thermoplastics or elastomer.

Thermosets

Thermosetting plastics are polymer materials that cure, through the addition of energy, to a stronger form. The cure is initiated by heat, light, or the addition of other chemicals. It is not a reversible process resulting in materials which cannot be recycled. [18]

Thermosetting materials are generally stronger and brittle than thermoplastic materials and are also better suited to high-temperature applications. Their conductivity should be very low. A variety of polymers is used – for example: polyester resin, epoxy resin, urea-formaldehyde foam. [19]

Epoxy resin

Epoxy or polyepoxide is a material that cures when mixed with a catalysing agent. Most common epoxy resins are produced from a reaction between bisphenol-A and epichlorohydrin. [20]

Epoxy resins that may be of widely different structures but are characterized by the presence of the epoxide group [21];

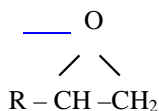


Fig. 6 The chemical formula of the epoxide group [21]

Odstraněno:

There are a number of ways how epoxies can be modified by adding mineral fillers, flexibilizers, viscosity reducers, colorants, thickeners, accelerators or adhesion promoters.

The applications for epoxy-based materials are extensive and include coatings, adhesives and composite materials, such as those using carbon fiber and fiberglass reinforcements. In general, epoxies are known for their excellent adhesion, chemical and heat resistance, excellent mechanical properties and very good electrical insulating properties, but almost any property can be modified (silver-filled epoxies with good electrical conductivity are widely available even though epoxies are typically electrically insulating). [22]

Epoxy resins protect electrical components from dust, humidity and other environmental factors that could damage the electrical equipment. In the electronics industry, epoxy resins are the primary used in over-moulding integrated circuits and transistors and making printed circuit boards. Epoxy resins are also used in bonding copper foil to circuit board substrates. [22]

Thermoplastics

Thermoplastics are materials that are plastic or deformable when they heated and freeze to a brittle, glassy state when they are cooled sufficiently. Most thermoplastics are high molecular weight polymers whose chains associate through weak Van der Waals forces (polyethylene), stronger dipole-dipole interactions and hydrogen bonding (nylon) or even insert in aromatic rings (polystyrene). Thermoplastics are elastic and flexible above glass transition temperature T_g . [22]

Elastomer

Elastomers are long polymer chains, amorphous, above their glass transition temperature. Elastomeric polymer chains can be crosslinked, or connected by covalent bonds. This process is sometimes called vulcanization. Crosslinking is initiated by heat, light or the addition of chemicals. They are easily formed. [18]

Their special property is advantage for many using. They will stretch rapidly under tension, reaching high elongations (500 to 1000%) with low damping. It has high tensile strength and high modulus when fully stretched. On the release of stress, it will retract

rapidly, exhibiting the phenomenon of snap or rebound, to recover its original dimensions. Elastomers and synthetic rubbers are unlike thermoplastics in that they can be repeatedly softened and hardened by heating and cooling without substantial change in properties. Elastomers such as carboxyl-terminated butadiene-acrylonitrile (CTBN) copolymers form a discrete second phase, when added to a thermoset or thermoplastic resin, to serve as a toughening agent. The rubber particles improve the polymer ability to craze, form shear bands and to terminate them before total failure.[23]

Common elastomers include polybutadiene, natural rubber, polyurethane, polyisobutylene, and polyisoprene. [18]

Silicon rubber

Silicon rubber is a polymer that has a “backbone” of silicon-oxygen linkages, the same bond that is found in quartz, glass and sand. Its chemical formula is shown in Fig. 7.

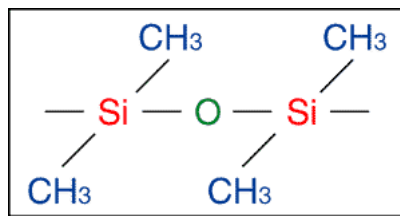


Fig. 7 The chemical formula of silicon rubber [24]

Usually, heat is required to vulcanise silicone rubber. This is normally carried out in a two-stage process at the point of manufacture into the desired shape and then in a prolonged post-cure process. Further type of cure is chemical vulcanisation, for example by orthosilicic acid. In this process only room temperature is used. [22]

Silicone rubber offers excellent resistance to extreme temperatures, being able to operate normally from -100 °C to +500 °C. In such conditions, the tensile strength, elongation, tear strength and compression set can be far above conventional rubbers. [22]

This can leave them susceptible to ozone, UV, heat and other aging factors that silicone rubber can withstand well. This is why it is the material of choice in many extreme environments. [22]

There are also many specialist grades of silicone rubber that offer the following qualities: steam resistance, metal detectable, electrically conductive, low smoke emission, and flame retardant. It has resistance to: chemicals, oils, acids, and gasses. [22]

Silicones are excellent electrical insulators with grades available with volume resistivities as low as $0.004 \Omega \cdot \text{cm}$. Their thermal stability means that properties such as volume resistivity, dielectric strength and power factor are not affected by changes in temperature. [25]

Blends

Materials made from two polymers mixed together are called blends. Their various morphologies are shown in Fig. 8.

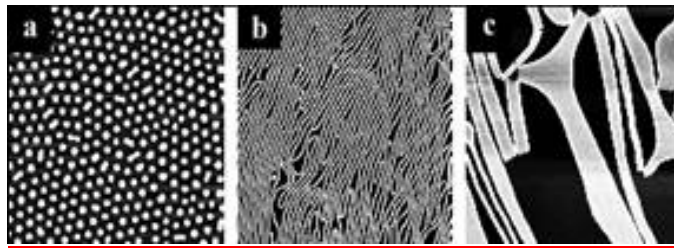


Fig. 8 – Scanning electron microphotographs of matrix a, matrix b and their blend c [26]

Miscible and immiscible blends

Blends span the entire range from fully miscible to completely immiscible. Polymers are usually mixed together in order to get a material with properties somewhere between those two polymers. Immiscible (phase-separated) blends are what you most often get when you try to mix most polymers. [27]

The thermodynamic drive towards phase separation increases with increasing inherent incompatibility and as with increasing average molecular weights of polymer chains. This is a direct result of the low entropy of mixing of two polymers, and often positive heat of mixing. [27]

The blend morphology can be affected significantly by many factors. These factors include the incorporation of compatibilizers, the kinetic "freezing in" of nonequilibrium morphologies by the application of shear during processing, and annealing at an elevated temperature in order to release the kinetically frozen-in morphological features and thus approach thermodynamic equilibrium. [27]

The most significant way can be the morphology of an immiscible blend affected, is to control the relative amounts of the two used polymer. Let's consider to make an immiscible blend from two polymers, polymer A and polymer B. If there is more

of polymer A than of polymer B in the blend, polymer B separate into little spherical globs. The spheres of polymer B will be separated from each other by polymer A, like you see in the picture below. In such a case we call polymer A the major component and polymer B the minor component. [28]

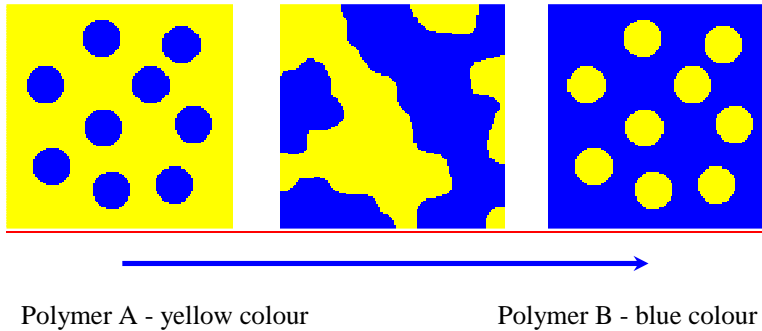


Fig. 9 Relative amount of polymer B in the immiscible blend [28]

But if it is put more of polymer B into the immiscible blend, the spheres become bigger and joined together. Consequently, these are not isolated spheres anymore, but a continuous phase. The immiscible blend looks like the middle picture above. When this happens we say that the polymer A phase and the polymer B phase are co-continuous. [28]

But if polymer B is kept adding, eventually there will be so much of polymer B in the immiscible blend, that polymer A will become isolated spheres surrounded by a continuous phase of polymer, just like it can be seen in the picture above on the right. Polymer B become the major component and polymer A is the minor component, and the situation is reversed from what we had at first. [28]

There are some types of morphology phases for example:

- Spheres:

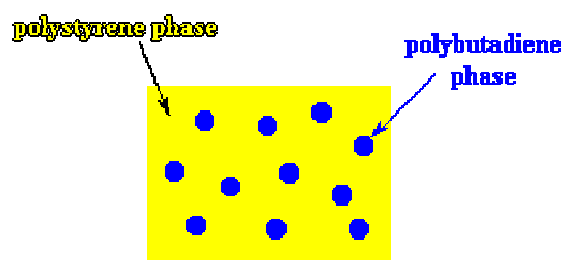


Fig. 10 High-impact polystyrene (HIPS) contains polystyrene and polybutadiene (the little spheres) [28]

- Lamella:

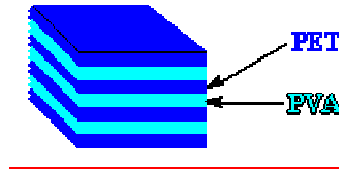


Fig. 11 Poly (ethylene terephthalate) (PET) and poly(vinyl alcohol) (the layers PVA). [28]

Sometimes the way in which a product is processed affects the morphology of the material. Soft drink bottles are made by the technique called blow moulding. When it is being inflated, it is put under stress in two directions. This is called biaxial stress, and it causes the domains of PET and the domains of PVA to flatten out. [28]

- Rods:

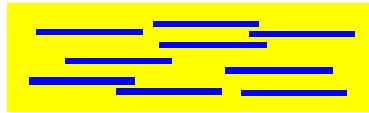


Fig. 12 Processing under flow in one direction turns the spheres into rods. [28]

Another interesting morphology you can get is one of rod-like domains of one polymer surrounded by a continuous phase of the other. This happens when the immiscible blend is put under stress in only one direction, such as during extrusion. [28]

Properties of Immiscible Blends

An unusual property of immiscible blends is that these made from two amorphous polymers has two glass transition temperatures. Since the two components are phase separated, their separate glass transition temperatures retains. If two glass transition temperatures are found, then the blend is immiscible. If only one glass transition temperature is observed, then the blend is likely to be miscible. [28]

Considering an immiscible blend of a major component polymer A and a minor component polymer B, whose morphology is that of spheres of polymer B dispersed in a matrix of polymer A. The mechanical properties of such this immiscible blend are going

to depend on those of polymer A, because the polymer A phase absorbs all the stress and energy when the material is under load. In addition, the immiscible blend is going to be weaker than a sample of pure polymer A. [28]

It turns out, there are some tricks how can be immiscible blends made strong. One is to process them under flow. If they are processed under flow in one direction, the minor component forms rods instead of spheres. These rods act like the fibers of a reinforced composite material. They make the material stronger in the direction of the rods. [28]

Another way to make a strong immiscible blend is to use roughly equal amounts of the two polymers. This means both phases bear the load of any stress on the material, so it is stronger. [28]

But one of the most interesting ways to make immiscible blends stronger is to use a compatibilizer. It helps bond the two phases to each other more tightly. In an immiscible blend, the two phases are not so strongly bonded to each other, because they do not like each other. But if stress and energy are transferred between the components, they have to be bound in some fashion. [28]

This is good for the mechanical properties of the immiscible blend. The smaller the spheres are, the greater area of the phase boundary between the two phases is. The greater the area of the phase boundary is, the energy is more efficiently transferred from one phase to the other, meaning better mechanical properties. [28]

Crystalline-amorphous(C-A) and amorphous-amorphous(A-A) blends

In semicrystalline polymers small fillers can be segregated into amorphous formation regions. In such polymers the critical concentration required to achieve network formation is less than in a purely amorphous polymer where uniform dispersion is achieved. These composites have lower resistivities, suggesting that in this case a conductive network is formed by the concentration of filler in amorphous regions, while in amorphous part will be distributed through the polymer matrix as explained by Reboul et al. [29]. Polymers with a semicrystalline microstructure will also lower the percolation threshold, in a manner similar to that of a two-polymer blend. [30] This aspects can be used to C-A (Fig. 13) and A-A blends, too.

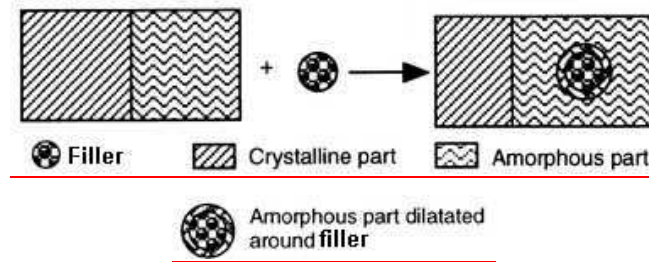


Fig. 13 – General schema crystalline-amorphous blends with filler [31]

When filler is added to a crystalline-amorphous blends, an accumulation in amorphous part is preferred. By amorphous-amorphous blend a part with higher amorphous manner for filler is determined. [32]

Interpenetrating polymer networks (IPN)

A combination of two polymers is created with a network form. There are many types of them in which at least one of the polymers is synthesized and/or cross-linked in the immediate presence of the other without any covalent bonds between them as shown in Fig. 14 (a,b) [23]. The three conditions for eligibility as an IPN are: (1) the two polymers are synthesized and/or crosslinked in the presence of the other, (2) the two polymers have similar kinetics, and (3) the two polymers are not dramatically phase separated. [33] These polymers are closely related to other multicomponent materials, containing completely entangled chains, such as polymer blends, grafts and blocks. But, the IPN can swell in solvents without dissolving and can suppress creep and flow. Most IPNs are heterogeneous systems comprised of one rubbery phase and one glassy phase which produce a synergistic effect yielding either high impact strength or reinforcement, both of which are dependent on phase continuity. There are same types of IPNs, including full-IPNs, semi-IPNs and homo-IPNs. These systems differ mainly because of the number and types of crosslinks that exist in the system. [23]

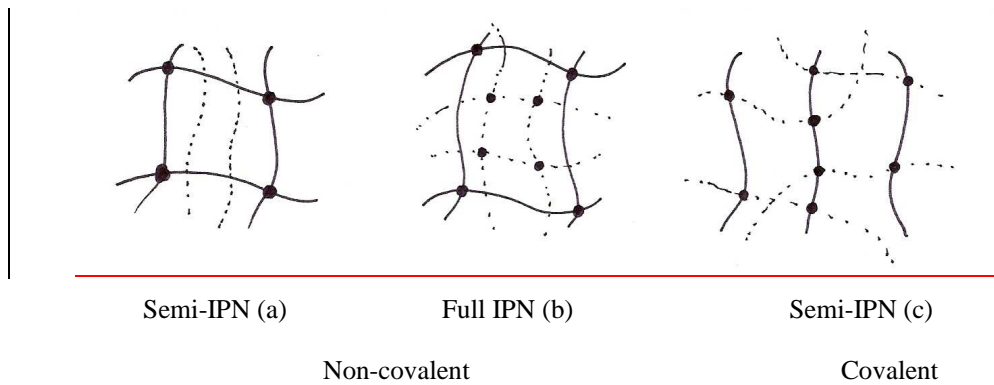


Fig. 14 A depiction of a simple IPN materials. Solid lines represent one network, while the other network is shown by a dotted. The circles represent points at which the chains are crosslinked. [33]

A non-covalent semi-IPN is that in which only one of the polymer systems is crosslinked. A non-covalent full-IPN is that in which the two separate polymers are independently crosslinked. A covalent semi-IPN contains two separate polymer systems that are crosslinked to form a single polymer network [33]. IPN Classification by Structure:

Full-IPNs

This type of IPN is comprised of two networks that are ideally juxtaposed, which generates a lot of entanglements and interaction between the networks. The structure depiction shows the ideal intermeshing of the two networks. This type of network can be by either a sequential or simultaneous process. [34]

Homo-IPNs
 This IPNs are a special type of full-IPNs, where both polymers used in the networks are the same. They are usually sequential IPNs. [34]

Semi-IPNs

One of the components of these IPNs has a linear structure instead of a network structure. The linear component changes some of the properties of the IPN. One thing to keep in mind is that the linear component of the IPN can be removed from the network if the material is swollen in the appropriate solvent. These types of IPNs can be formed by either a sequential or simultaneous process. [24]

1.2.2 Fillers

Fillers are most often low-molecular materials which are added to polymer matrixes. The reasons for their use are: improvement of mechanical properties, non-toxic, non-

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irritating, without odour, easy dyeable and miscible with polymers. They must have a good stability in a wide range of temperatures.

Fillers are not essential for every polymer compound, but some are vitally necessary for specific end-uses. [19]

The following are some requirements on potential filler for polymer modification:

- Low cost
- Low specific gravity and heat stability
- Easily and readily obtainable
- Neutral-should not be acidic or alkaline
- Easy to handle
- Low water and oil absorption
- Suitable for wetting by the polymer binder
- Must not absorb the polymer
- Must not prevent flow of the polymer [35]

In addition to the above properties, the fillers must also confer certain advantages on the final product. These include enhancement of:

- Heat resistance and thermal stability
- Dimensional stability
- Mechanical strength, e.g., impact and tensile
- Mold shrinkage
- Surface finish of the molding [35]

There are many types of fillers that can be divided in following:

- By their geometric conformation:

Spheres, cubes – chalk, dolomite, glass spheres

Fibres – glass fibres, carbon fibres, graphite fibres, aramide

Platelets – feldspar, kaolin, talc, mica [35]

- By the material type:

Organic - cellulosic - cotton fabric, wood powder, lignin, sisal, paper

- noncellulosic - wool, cork dust

Inorganic - metal or ceramic, glass-fibre, calcium carbonate, kaolinit, feldspar, talc or other clays, mica

- electroconductive - carbon black, carbon fibres, metal powders, carbon nanotubes, graphite, electroconducting polymers (polypyrrole, polyacetylene, polyaniline, polythiophene), aluminium powder, fullerene

Miscellaneous – soya flour, walnut shell flour, coconut shell flour [19, 35]

○ By the function:

Fillers can basically be divided into two groups, according to their effect on the properties: reinforcing and non-reinforcing (extender). In this work carbon black as a filler of multicomponent polymer composite has been investigated. [19, 35]

Carbon black (CB)

CB is a common polymer additive used for reinforcement and enhancing physical properties, such as conductivity or density.

It consist of powdered forms of highly dispersed elemental carbon manufactured by controlled vapour-phase pyrolysis of hydrocarbons. There are a number of different types of carbon black, produced by different industrial processes, including acetylene black, channel black, furnace black, lamp black and thermal black. Average particle diameters in several commercially produced carbon blacks range from 0.01 to 0.4 micrometres (μm), while average aggregate diameters range from 0.1 to 0.8 μm as shown in Fig 15. Because of their materials source, the methods of their production and their large surface areas and surface characteristics, commercial carbon blacks typically contain varying quantities of adsorbed particularly aromatic compounds as a product from the production processes. [36]

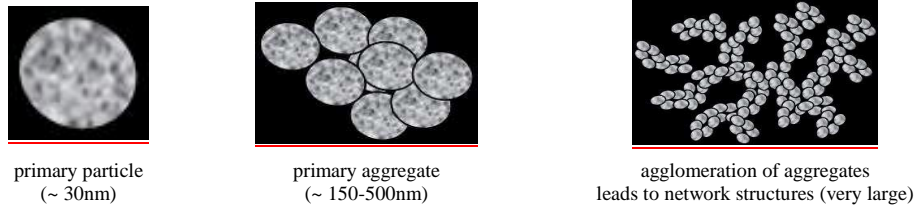


Fig. 15 Carbon black particles [37]

The principal uses of carbon black are:

- to give colour to the material
- to give higher temperature insulating to the material
- to control electrical conductivity - conductive and antistatic rubber
- to enhance abrasion resistance
- to increase the tensile strength
- to increase modulus
- to provide a reinforcing to agent in rubber products such as tires, tubes, conveyer belts, cables and other
- to impart electromagnetic interference shielding to the material. [2, 36, 37]

1.2.3 Conductive composite

When an electrically conducting phase is dispersed in a sufficient quantity of polymer resin, a conductive composite is formed. [1]

The spherical particles are separated from the matrix by the surface of contact conductance. A cross-section of the composite material is shown in Fig. 16. [38]

Carbon-based fillers (carbon black, graphite, carbon fibers, carbon nanotubes or fullerenes) are the most frequently used conductive fillers because of their high conductivity, relatively low price, and good ultimate and processing properties of the [39].

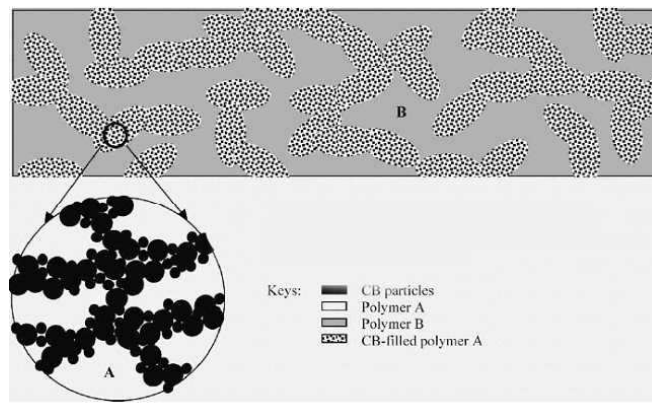


Fig. 16 Schematic of the microstructure of the proposed CB/polymer blend composite. Note that CB particles are preferentially distributed in one polymer phase and both polymer phases are continuous in 3D space. [38]

Electrical properties of polymer composites filled with conducting fillers are explained by the percolation theory, as was represented in topic 1.1.2

Mainly, the electrical resistivity, the extent of mechanical properties and processing characteristics of conductive composites depends on proximity of neighbouring conductive particles and the volume fraction of the conducting filler particles. [14, 32, 39]

1.3 Effect of filler on the conductivity

There are several aspects which decide about the effect of filler on the composite conductivity. In the following we will deal with three of them: electrical contacts, distribution, size, shape and hardness of filler particles.

1.3.1 Electrical contacts between filler particles

The resistance of the contact spots is the leading contribution to the overall composite resistivity, particularly for good conducting filler materials [40]

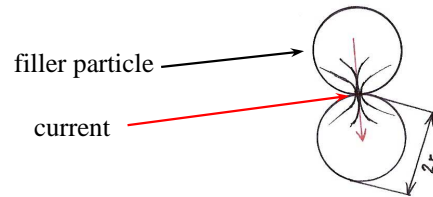


Fig. 17 - Sketch of two adjacent filler particles. The current through the grains is constricted at the contact point. [7]

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The spheres show contact to each other at only one point. This results in singularities of the contact resistance and the current density, without any dependence on an applied external force. [7]

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1.3.2 Filler Distribution

The value of percolation threshold is significantly influenced by the distribution of filler particles in a composite. It was observed, that the segregated distribution of the conductive filler phase in a polymer matrix leads to the formation of conductive network at a rather low critical concentration of conductive filler. [41]

This distribution depends strongly on the processing technique. For industrial production, extrusion or injection moulding processes are used quite often.

An attention must be taken, if the composite parts are made by compression moulding of polymer and conductive powders. Figure 18 shows a cut through a press-sintered composite high-density polyethylene powder and carbon black were mixed and then compressed at elevated temperature [42]. The carbon black particles are much smaller than the polymer particles. This results in a core-shell structure, which is clearly visible in Fig. 9. The polymer particles are surrounded by shells of carbon black, forming a percolating network. The percolation threshold of a core-shell structure is considerably lower than that

of homogeneous composite. Of course, the conductivity cannot be isotropic in such parts [43].

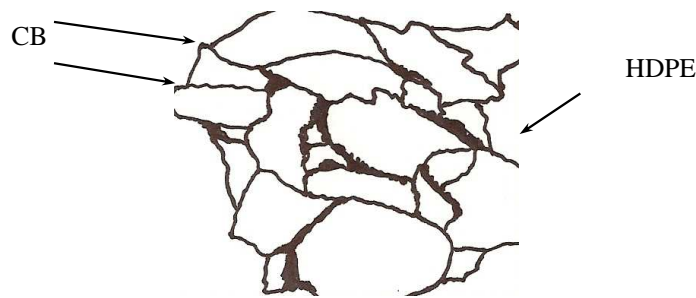


Fig. 18 Cut through a compressed plate made out of high-density polyethylene powder mixed with carbon black. In ratio scale 500 μm [42].

In the filler distribution can be found that all these factors are rooted; by changing thermodynamic and kinetic factors, including interfacial energy, melt viscosity matching, blending ratio, melt mixing time, and sequence of blending, as well as filler concentration, the composites' PTC performance can be tailored. [17, 44]

1.3.3 Particle size

Other important processing parameter for composite system can be particle size.

It is generally known that the constriction resistance decreases with increasing particle radius. If the protrusions, which form the contacts, are assumed to be larger in radius with increasing particle size, larger filler particles should result in a lower composite resistivity. This is supported by experimental data. [7]

Strümpfer et al. explain this problem by their own measurements of the specific resistivity of TiB_2 filled high-density polyethylene for different particle size distributions. The filler content is 55 vol. % for 1- 5 μm particles and 50% for all other sizes. TiB_2 is a good conducting material with conductivities between 9 and 35 $\mu\Omega\text{cm}$. The Fig. 19 shows that the resistivity decreases for increasing particle size. The strongest effect is observed between

1- 5 μm and 10 - 30 μm . In this range the resistivity changes by about one order of magnitude. If 50 vol. % is occupied by the 1-5 μm particles, the difference would be even larger. [7]

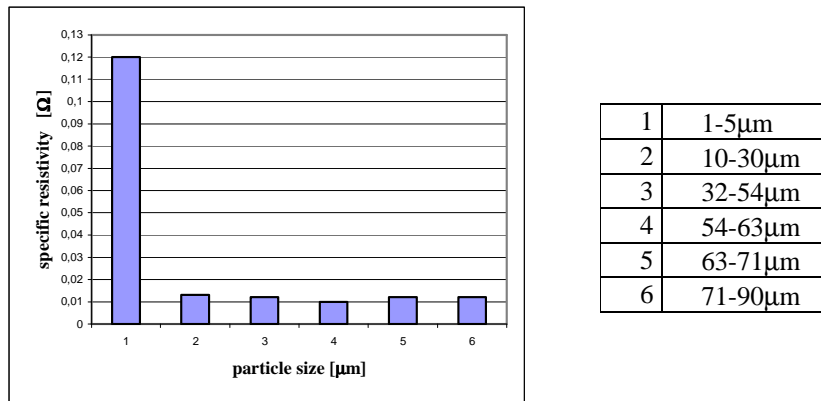


Fig. 19 – Specific resistivity of HDPE/TiB₂ for different particle size distributions. [7]

Particles of 100-200 μm have a four times smaller resistivity than 50 μm particles. The same trend has been reported by Ruschau et al. [40] for fine silver powder in a silicone rubber. Again, the resistivity decreases for increasing particle size.

The filler size also has a strong influence on the heating of a composite by an electrical current. A reduction of the particle size leads to a larger number of contacts and smaller volumes of polymer matrix material embedded within the network of metal filler particles. Due to a reduced mean distance of the matrix material to the next neighboring particle contacts, where the energy is generated, the heating of a composite with smaller filler particles should occur faster. Together with the properties of polymer matrix it is important for nonlinear changes of resistivity with temperature. [45]

1.3.4 Filler hardness

The contact resistance depends on the physical properties of filler and its surface. This means the softer the filler material, the larger is the contact spot area due to deformation. Hard fillers such as ceramic silicides, borides or carbides, lead to small point-like contact spot areas. If no surface oxide layers are formed, even these small contacts can provide relatively high conductivities. [7]

One main advantage of hard particles is that they do not stick together. Hence, the contact is easy to release by reducing the contact pressure. On the other hand, the particles of a ductile metal give rise to a larger contact area with good adhesion to next neighbors and show therefore an even lower contact resistance. Relatively soft materials

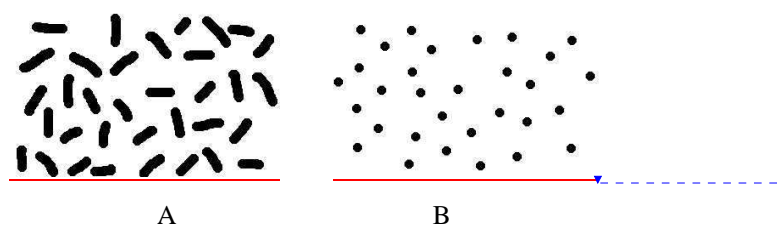
however, tend to stick together and maintain a soldered-like connection. Even for large applied external forces it is hard to separate the particles. [7, 12]

1.3.5 Filler Shape

Some of reductions in the percolation threshold can be achieved by changing the shape of the conductive filler and modifying the microstructure of the matrix polymer. Changing the shape of graphite filler from spheres to rods will reduce the percolation threshold, although preferential alignment of the rods tends to create anisotropic conductivity. Polymers with a semicrystalline microstructure will also lower the percolation threshold, in a manner similar to that of a two-polymer blend. [30]

In the previous studies, spherical particles were usually assumed in modeling the composites. In practice, however, fillers are often used which have a shape very much different from a sphere. Examples are aluminum flakes, stainless steel fibers, carbon fibers or carbon black. As mentioned earlier, the percolation threshold can be drastically reduced for particles with an aspect ratio larger than one. This effect is illustrated in Fig. 5 for the statistical distribution of two-dimensional fillers on a two-dimensional plane [42].

In the Fig. 20, the left picture shows a particle-like filler, the right picture a fiber-like filler with an aspect ratio of 200. The filler content is 10% of the area in both cases. By visual examination, one can easily observe connecting paths of the fibers. The particles, however, are isolated and no percolation can be observed. This illustrates that fillers with high aspect ratio can drastically reduce the percolation threshold. [7]



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Fig. 20 Two-dimensional statistical distribution of powder-like particles (B) and fiber-like particles (A). The aspect ratio of the fibers is 200. The filler content is 10% of the area in both [7]

Bigg et al. [46] studied experimentally, the influence of the aspect ratio for different kinds of carbon fibers. Carbon fibers with an aspect ratio of 1000 need only 1 vol. %, whereas fibers with an aspect ratio of 10 need a volume fraction of about 10% in order

to achieve the same resistivity. In the same study, the percolation of aluminium fibers and flakes with aspect ratios between 12.5 and 35 have been reported. Again the percolation threshold decreases with increasing aspect ratio. [46]

1.4 Effect of polymer matrix on conductivity

The influence of mechanical and thermal properties of the polymer matrix on the electrical behavior of conducting composites requires further elucidation. Different materials like soft elastomers and rubbers, linear or branched thermoplastics or hard materials as epoxies cover a wide range of mechanical properties. [7]

As was already mentioned, the constriction resistance between filler particles depends on the forces between the grains. Higher contact forces may improve the conductivity. Hence, internal stresses in the polymer matrix caused by shrinkage, external mechanical actuation or thermal expansion play an important role for the conductivity of composites. [7]

1.4.1 Elastic properties

A shrinkage of the polymer during processing can induce high internal stress. This reduces the interparticle resistance, but may also induce cracks and lead to failure during application. The origin of the shrinkage stress differs for thermosets and elastomers on the one hand, and thermoplastics on the other. The curing and cross-linking of thermosets and elastomers gives rise to a free volume reduction, which is responsible for the build-up of internal stresses. Thermoplastics are commonly processed above melting temperature and used for applications below this temperature limit. In this case, the thermal shrinkage during solidification creates the internal stress. [7]

During gelation the resistivity of epoxy generally increases. Secondly, a separation of the particles can occur due to the expansion of the epoxy. In the succeeding 10 min. the resistivity is reduced by eight orders of magnitude. This is caused by a shrinkage of the epoxy, which increases the particle-particle pressure. The temperature increases in the meantime to a maximum of 106°C due the heat of reaction [45]. After a curing time of 75 min, ρ has stabilized at about 0.04 Ω .cm and the temperature at 102°C. These values remain stable and unchanged until the completion of curing after 15 h. During the slow

cool-down, a further reduction of the resistivity down to 0.01 $\Omega\cdot\text{cm}$ is caused by the thermal contraction of the composite. [7]

This example shows that the thermal contraction of a composite can have a huge influence on the electrical resistivity. Since a filler fraction of 46% is far beyond the percolation threshold for particles, this effect cannot be explained in terms of percolation theory. Instead, the observed strong resistivity change is caused by a release of particle-particle contact pressure and a change in gap distance. It should be noted that the resistivity change during curing is the smallest for Ag, medium for Ni and highest for TiB_2 . This reveals again the influence of the filler hardness. Due to the hardness of TiB_2 , the particles do not stick together and make the resistivity of the composite sensitive to small micro-mechanical changes. In addition the influence the particle size shall be mentioned again. If the particle size is reduced, the internal stress generated during processing is distributed to a larger number of contacts. That means a reduction of the contact forces and a further increase of the resistance. [7]

1.4.2 Thermal properties

Polymers can show three significant reversible structural transitions, which are thermally induced: crystallization and melting in a semi-crystalline phase and a glass transition in the amorphous phase. All three transitions are related to a relative large volume change or to a pronounced change in the thermal expansion (Table II). The thermal expansion of the polymer matrix exerts a considerable influence on the electrical conductivity. [50]

Table II. Properties of phase transitions in polymers

Transition	Important property of interest
Crystallization	Shrinkage, densification
Melting	Expansion
Glass transition	Freezing, introduction or release of internal stress

Below the polymer melting temperature conducting filler particles are in a state of close packing with intimate contact to next neighbors, forming conducting paths throughout the composite. During heating polymer expands much more than the filler particles themselves. The contact pressure between adjacent filler particles is reduced leading to

a moderate resistivity increase for $T < 120^{\circ}\text{C}$, as for 50 vol.% TiB_2/HDPE composite. The effect is strongly enhanced when approaching the melting temperature of the polymer matrix. There the filler particles and the conducting paths are obviously interrupted due to the enhanced thermal expansion of the polymer. [50]

This leads to the huge jump in the resistivity. This fact is supported by similar results for carbon black dispersed in polyethylene [47]. The transition from low resistivity to high resistivity can be utilized for current limitation. Such limiters are presently available as small elements for the protection of circuit boards at rated currents between fractions of an Ampere to several Amperes [48]. As a three-phase current limiting module [49], they are used in low voltage distribution systems for ratings up to 63 A. Even for very fast current limitation, it could be shown by optical methods that the origin for the resistivity increase is the expansion of the composite material. [50]

Most of the resistance of the positive temperature coefficient (PTC) material (is defined in next clause) in the conducting state originates from constriction resistance at the contact points. Therefore, the contact points are the dominant sources of heat in the material. The thermal conductivity of most of the conducting filler materials ($1\text{-}10^2\text{W/Km}$) is at least one order of magnitude higher than that of the polymer matrix ($<0.3\text{W/Km}$). Consequently, one can show from the heat equation that the generated heat dissipates first, within $1\text{-}10\ \mu\text{s}$, into the filler particles. Then, with a time delay of $0.2\text{-}0.5\ \text{ms}$, the matrix is heated as well. Therefore the temperature distribution inside the filler particle will be quite homogenous, except in the close vicinity of the contact spots, where temperatures up to $3000\ \text{K}$ can be expected. [45]

Temperature coefficient of resistance is defined as the amount of change of the resistance of a material for a given change in temperature. There are three types of relation between temperature and electrical resistivity of conductive composites:

- o negative temperature coefficient (NTC),
- o low positive temperature coefficient (L-PTC),
- o high positive temperature coefficient (H-PTC).

The resistivity increase upon increasing temperature is described by a positive temperature coefficient (PTC), whereas the resistivity decrease is described by a negative temperature coefficient (NTC). [51]

Crystalline polymers are usually used as matrices of PTC materials, in which there is an abrupt resistivity increase at the melting point of the polymer matrix. The shorter the melting region is, the more precipitous is the PTC effect. After crystalline melting is complete, the resistivity decreases quite rapidly, which means an obvious NTC effect. [51] PTC effect was significant when the acicular filler was added rather than spherical ones. PTC phenomenon is attributed to the separation of conductive pathways by thermal volume expansion that is due to the difference in the expansion coefficient between the polymer matrix and conductive filler. [52]

With the increase in CB loading, there is an increase in the number of conductive networks and average inter-particle gap becomes smaller. Therefore, the contact pressure of particle becomes higher for higher CB loading and the network breakdown process becomes less efficient. As a result, the rate of increase in resistivity is reduced for higher CB filled composites. In contrast, when the total conductive particle was increased by the addition of 5 wt.% of TiO₂, PTC intensity was remarkably increased as than the addition of CB. TiO₂ has a relatively high-linear thermal expansion coefficient ($7.14 \times 10^6 \text{ K}^{-1}$) than CB ($1.19 \times 10^6 \text{ K}^{-1}$). The conductive CB aggregation may easily break apart by volume expansion of TiO₂. [53]

1.4.3 Stability and Endurance

In addition to the long-term properties of polymers and polymer composites, as they are known in general, conducting composites are very sensitive to changes in the inter-particle resistance due to environmental influences. If the composite is operated or aged at elevated temperature, metal filler materials can easily oxidize, drastically reducing the conductance [54]. Also for carbon blacks a strong resistivity increase has been observed by Meyer [55] in the presence of oxygen at elevated temperature. In addition, the mechanical properties of the polymer are changed up on continuous heating. Meyer reported that the total expansion of polyethylene/carbon black is considerably reduced after aging at 150°C

for 39 days. During the same time the degree of crystallinity is reduced by about 50%. As a considerable part of the expansion is due to melting of crystalline areas, this must consequently have a strong influence on the PTC anomaly. Therefore, it is not surprising that Meyer also found a reduction of the resistivity ratio $\log(\rho_{\max}/\rho_{25^\circ\text{C}})$ of the PTC effect from 4 to about 0.2. [7]

Active heating of the composite by a current can lead to similar aging phenomena. In particular for high power applications this is especially important since it can change the operational characteristics of a device. For PTC devices it is known that the resistance increases by at least 20% after the first fast self-heating by a current [5]. The recovery of the resistance to its initial value takes place very slowly during several days. The origin of this process probably involves secondary recrystallization of the polymer and reorganization of the filler chains. [7]

Most polymers used for conducting composites show decomposition when they are exposed to temperatures above 300°C. Consequently, heating by over-currents to such temperatures can lead to irreversible changes of the polymer which alter the mechanical and electrical properties of the composite. [7]

1.5 Applications of conducting polymer composites

Conducting polymer composites have been studied extensively because of their numerous high technological electrical and electronic applications in a variety of areas such as self-regulating heaters (thermistors), ideally suited for electromagnetic interference shielding, antistatic layers, chemical vapor sensors, rubber contact switches, include battery and fuel cell electrodes, antennas, wave guides, corrosion resistant or optical materials.[12, 52]

Plastics capable of conducting provide inherent EMI shielding to protect business machines, automotive and aerospace components and computers from electromagnetic interference. In addition to the consideration that a device should not emit radiation that interferes with others, electronic devices must be capable of functioning under EMI from other sources, i.e., they must exhibit electromagnetic compatibility, and must be shielded in such a way so that both incoming and outgoing interferences can be filtered. Plastics are widely used to make shellac for electronics equipment. However, their volume

resistivities are approximately 10^{13} - 10^{17} Ω .cm, so they are transparent to electromagnetic waves [32]. A range of options is available for introducing conductivity to plastics housing and enclosures: these options broadly fall into three categories.

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Intrinsically conductive polymers such as polyacetylene, polyaniline, polythiophene and polypyrrole can be produced, but are expensive and difficult to process. [14]

Coating methods are the predominant choice for EMI shielding operations. Despite a growing number of potential applications, these composites are plagued by a serious drawback as they involve an extra production process, can be subject to delamination, and difficult to recycle. [32]

The third approach is to produce plastics composites containing conductive fillers. These materials are relatively cheap and have good processibility. Also, the conductivity of a composite can be adjusted relatively easily to meet product requirements. [32]



Fig. 21 Exemplary products of SAS Industries carry a wide selection of EMI shielding materials with excellent conductive properties. [56]

Conducting polymer composites are ideally suited for antistatic layers, chemical vapor sensors, and thermal resistors (low-temperature heaters), and electric field grading.

Elastomers loaded with electrically conductive fillers are commonly used as contact point materials, for electrostatic charge dissipation, as surface heaters, and rubber contact switches. [12, 30, 52]

As was already indicated electroconductive polymer composites exhibit a positive temperature coefficient of resistance effect. The distinguishing characteristic of all PTC thermistors is an abrupt increase in electrical resistance within a narrow, distinct temperature range. Traditionally, PTC thermistors (as shown fig. U) have been composed of ceramic materials, most notably donor doped BaTiO_3 compounds. The use of traditional

ceramic thermistors has been confined because of the high room temperature (RT) resistivity that severely limits the current flow. The breakdown voltage shows also a temperature dependence that cannot be closely controlled or eliminated, restricting the application of thermistors.

An inorganic semiconductor with relatively large negative temperature coefficient of resistance can be used for sensing of temperature; the mechanism involves an increase in temperature, thermally activates more charge carriers over the band gap and the conductivity of the material increases. But the magnitude of the change in resistivity is limited to several percent per degree [6]. On the other hand, polymer composites can exhibit much stronger increase in electrical resistivity with the increase in temperature.

Recently, ceramic-polymer and carbon-polymer conducting composites have been successfully employed in PTC thermistor fabrication. The ceramic-polymer and carbon-polymer thermistors can withstand much higher temperatures and have a much lower RT resistivity. Such polymer composites are used in both low and high current applications. [7, 8, 41]



Fig. 22 Exemplary products of Alibaba.com [56]

2 AIMS OF THE MASTER THESIS

The amount of conductive filler required to achieve a sufficient level of electrical conductivity often leads to processing difficulties. Lowering the percolation threshold of a composite system appears to be an effective way to reduce the amount of filler required to produce adequate conductivity and thereby minimize problems with mechanical performance.

In this work a study of the influence of filler concentration and the amount of second polymer on the electrical resistivity of immiscible blend composites is reported:

- Pure silicone rubber
- Pure epoxy resin
- Silicone rubber with epoxy resin in these rates 25:75, 50:50, and 75:25.

An electrically conducting grade carbon black Vulcan XC 72R is used as a conductive filler. It is added into the matrixes in the amount 0 wt.%, 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, and 25 wt.%. To complete the percolation threshold curve more concentrations of CB were lately added as shown in tab. I.

The present work is focused on the effect of lowering the percolation threshold by use of immiscible blend as a matrix composite. Lowering of the PT of prepared composites containing CB, is evaluated by DC (direct current) conductivity measurements with 4-points or 2-points methods. Further materials hardness is measured by hardometer Shore A and Shore D to examine the influence of silicone rubber addition on the mechanical properties of epoxy composites. The morphology of composites is investigated with means of scanning electron microscope. It is demonstrated, that the PT concentration strongly depends on distribution of CB in matrixes as well as it is supposed to depend on the amount of the second polymer in the immiscible blend.

3 EXPERIMENTAL PART

3.1 Chemical materials and their characteristics

3.1.1 Lukopren N1000

It is silicon two-component rubber, so called condensation type. When a paste with a catalyst is compounded, the vulcanization start up during few minutes in this whole mass. The silicon rubber arises which do not have adhesion to the bottom. Dosing of Lukopren catalyst is 1,5 weight %.

Properties of vulcanizer:

- Resistivity to climatic influences, solar radiation and ozone
- Separative properties toward non-porous surfaces
- Resistivity to bacteria and fungi
- Excellent separative properties, resistivity to weak acid and alkalis, polar solvent and most of salts
- Low shrinkage, good thermostability

Applications: This silicon rubber is suitable for flexible form production. [57]

3.1.2 Epoxy resin ChS Epoxy 531

It is low molecular weight material modified with bi-functional reactive diluent.

By mixing of epoxy and curing agent in the correct ratio (100:4), completely homogenous consistency is obtained. For the optimal parameters of final system choice of the right curing agent up to application temperature is important. If these principles are not kept, it will result in hardening time prolongation and the system would not provide the optimum properties for usage.

Properties:

- Excellent penetration on cement-based substrates
- Solvent free
- Certified for contact with food and drinking water
- Short waiting times before subsequent solvent free coatings
- Good mechanical resistance
- Good chemical resistance

Limits on application:

Minimum air and substrate temperature: +15°C /+15 °C

Maximum air and substrate temperature: +30°C

Maximum waiting time between coats: 24 hours [58]

Table III. Main parameters of matrixes [57, 58]

Name of matrix	Epoxy resin ChS Epoxy 531	Lukopren N1000
Producer	Spolchemie company, Czech Republic	Lučební závody, Kolín, Czech Republic
Cured with	Polyakylepolyamine	4 wt. % of orthosilicic acid
State	Liquid	Liquid
Color	Yellow, yellow-brown	Transparent
Smell	Weak characteristic	Intensive characteristic
Flash point (°C)	> 150	Not information
DC conductivity (S.cm ⁻¹)	<10 ⁻¹⁴	<10 ⁻¹²
Density (g/cm ³)	1.150 (25°C)	0.98
Solubility in water (g/l)	Immiscible	Immiscible
Solubility in grease	Immiscible	Immiscible
Viskozity (Pa.s)	30 - 80 (23°C)	0.8 - 1.2 (25°C)
Hardness (°Sh A)	-	< 30

3.1.3 Carbon black (CB) Vulcan XC 72R (GP-3909)

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Naformátováno: Odrážky a číslování

CB is a particulate form of elemental carbon, similar to graphite in its microstructure.

Table IV. Main parameters of filler [59]

Name of filler	Carbon black Vulcan XC 72R
Producer	CS Cabot Spol s.r.o, Valašské Meziříčí, Czech Republic
State	Powder
Color	Black
Smell	None
Flash point (°C)	Not applicable
DC conductivity (S.cm ⁻¹)	550
Density (g/cm ³)	1.7-1.9
Solubility in water (g/l)	Insoluble
pH	2 - 4
Viskozity (Pa.s)	Not determined

Incompatible materials: Strong oxidizers such as chlorates, bromates, and nitrates.

Conditions to avoid: Do not expose to temperature above 300°C. Keep away from oxidizing agents in order to avoid exothermic reactions. [59]

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3.2 Measuring device

- Current source SMU Keithley 237– high voltage source measure unit for Four-point method
- Multimeter Keithley 2010 with a 2000 SCAN 10-channel scanner card for Four-point method
- Vacuum coating unit VEB Hochvakuum Dresden R HVG 32, typ B 30.2 (1987) for low conductive materials (coated by gold Au), made in NDR
- Keithley 6517 electrometer for Two-point method
- Digital scale A&D GF-300-EC, Schoeller instruments s.r.o., made in Japan
- Vacuum drying device for CB
- Dessicator
- Ultrasonic homogeniser UP 400s, Schoeller instruments s.r.o., made in Japan
- Thickness meter
- Mixing scales for preparation of materials
- 2 spoons
- Moulds with thickness 2 mm
- Scanning electron microscope
- Hardness tester Shore A (for silicon rubber matrix) and Shore D (for epoxy resin matrix) HHP-2001, Bareis, supplier JD Dvořák, s.r.o. Praha

3.3 Preparation of polymer matrixes with carbon black

3.3.1 Pure matrix

CB was dried in drier at 90°C for about 30 minutes. Simultaneously a matrix polymer was weighed in the amount of 8g. Then the relevant amount of CB (as shown in tab. I) and appropriate matrix was carefully mixed together during 10 min by hands.

Then corresponding quantity of cure agent was added, according to the recipe of matrix producer. The vulcanisation process started and mixture was immediately transferred into the mould form, where the cure was finished during 24 hours at the room temperature.

3.3.2 Two matrixes

Before CB was mixed with matrixes, it was dried like in case of pure matrix.

Matrixes were weighed in proportions 2g:6g (for 25:75), 4g:4g (for 50:50), 6g:2g (for 75:25). Next, polymers were blended in an ultrasonic under standard conditions of the experiment in each case for 10 min. Not longer, because there was a danger of overheating and material degradation. Then CB in different amounts (as shown in tab. I) was added and this mixture was slowly and carefully mixed by hand during 10 min. The relevant quantity of cure agents was added afterwards, according to the recipe of matrixes producer. The vulcanisation process started and mixture was immediately transferred into the mould form, where curing was finished during 24 hours at the room temperature.

Table V. CB amounts in matrixes

Matrixes [%]	LN0	LN 25	LN50	LN75	LN 100
CB wt. [%]	3	1	1	1	0,375
	5	2	3	2	0,5
	7	3	5	3	1
	8	5	6	5	2
	9	6	8	6	2,5
	10	7	10	10	3
	15	8	12	12	5
	20	10	15	15	8
	25	15	20	20	11
	30	20	25	25	12
	-	25	-	-	13
	-	-	-	-	14
	-	-	-	-	20

Note: LN0 = pure epoxy resin, LN 25 = Lukopren 25%: epoxy 75%, LN50 = LN 50%: epoxy 50%, LN75 = LN 75%: epoxy 25%, LN100 = pure LN.

3.4 Conditions of measurements

Preparation of polymer mixtures was made in humidity 31-33%, and the room temperature 25°C. CB was dried in drying device at 90°C for 30 minutes.

Epoxy resin must stay opened as little as possible, because it can absorb humidity.

All of the specimens were sealed in air free polyethylene bags prior to testing in order to avoid atmospheric and humidity effects that can induce some changes of the surface conductivity of the samples. Measurements of conductivity were taken at room temperature.

The fracture surfaces of the composites for SEM were prepared by using of cryogenic fracturing in liquid nitrogen followed with gold coating in an SPI sputter coater.

The morphology was determined using an accelerating voltage of 10 kV.

The hardness of the samples was determined at 25°C.

3.5 Proportions of samples

For soft samples sheets of 12.9 x 12.9 mm² in size were made with the thickness of 3 mm.

Hard samples were cast moulded right off to forms of proportions; 13 mm in diameter and thickness of 3 mm. For measurements of composite hardness sheets of 30 x 30 mm² and thickness of 6mm were made.

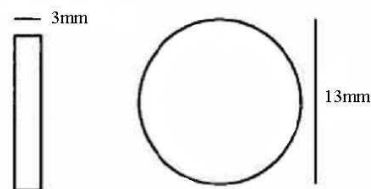


Fig. 23 Sample dimensions for conductivity measurements.

3.6 Measurements

3.6.1 Conductivity

Generally, the major problems with measurements of conductivity are the following:

- The conductivity can vary over a large range, either from sample to sample, or within the sample, if the temperature, the pressure, or the doping level is changed.
- The contacts can influence the measurements.
- Homogeneity of the sample. [9]

The four-point probe technique is the most common method for measuring of semiconductor resistivity. Two-point probe methods would appear to be easier to implement, because only two probes need to be manipulated. But the interpretation of the measured data is more difficult. [9]

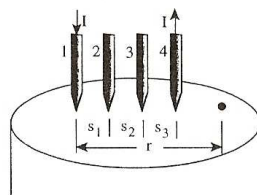


Fig. 24 A collinear four-point probe [9]

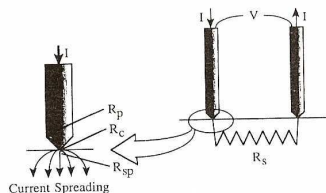


Fig. 25 Two – point probe arrangement showing the probe resistance R_p , the contact resistance R_c , the spreading resistance R_{sp} , and the semiconductor resistance R_s . [9]

The square arrangement is more commonly used, not as an array of four mechanical probes, but rather as contacts to square semiconductor samples. Occasionally it is difficult to provide, sample in a square format. In fact sometimes the sample is irregularly shaped. The theoretical foundation of measurements on irregularly shaped samples is based on conformal mapping developed by van der Pauw.

He showed how the specific resistivity of a fiat sample of arbitrary shape can be measured without knowing the current pattern, if the following conditions are met:

- the contacts are at the circumference of the sample,
- the contacts are sufficiently small,
- the sample is uniformly thick, and
- the surface of the sample is singly connected, i.e., the sample does not contain any isolated holes . [9]

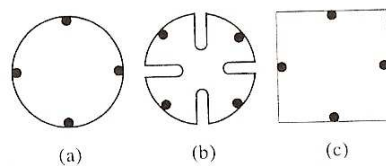


Fig. 26 Typical symmetrical circular and square sample geometries [9]

The van der Pauw equations are used on the assumption of negligibly, small contacts located on the sample periphery. Real contacts have finite dimensions and may not be exactly on the periphery of the sample. The error introduced by nonideal contacts can be eliminated by the use of the cloverleaf configuration of Fig. 26 (b). Such configurations make sample preparation more complicated and are undesirable, so square samples are generally used. One of the advantages of the van der Pauw structure is the small sample size compared with the area required for four-point probe measurements. Van der Pauw structures are, therefore, preferred for integrated circuit technology. For simple processing it is preferable to use the circular or square sample geometries shown in Fig. 26. For such structures it is not always possible to align the contacts exactly. The placement of contacts for square samples is better at the midpoint of the sides as in Fig. 26 (c), than at the corners. [9]

Volume resistivity of epoxy resin and silicone rubber composites containing carbon blacks was measured with the standard two-point or four-point, van der Pauw methods. All values of resistivity reported in this work are values of DC resistivity.

Three specimens of each composition were tested, and measured three times. From this, the medium value of the nine measurements was determined. For ensuring

a good electrical contact the surfaces of samples were polished with soft sandpaper and gold electrodes were sputtered on it. [12]

The current and potential comes through the samples which are measured by van der Pauw method. Low conductive composites are measured by the two-point method.

The data are obtained in ohm units and they are re-counted on volume resistance according to this formula [9]:

$$\rho = \frac{0.785}{l} \cdot R \quad (4)$$

where ρ is volume resistivity, l is length of electrodes and R is resistance [9]. The resistance of the samples was measured.

3.6.2 Scanning electron microscope (SEM)

The morphology of blended composites and the distribution of carbon black in the epoxy/silicone rubber blend were observed using a SEM.

The specimens were fractured under cryogenic conditions with liquid nitrogen

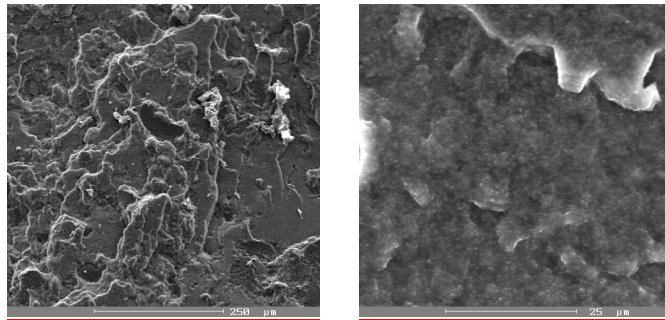


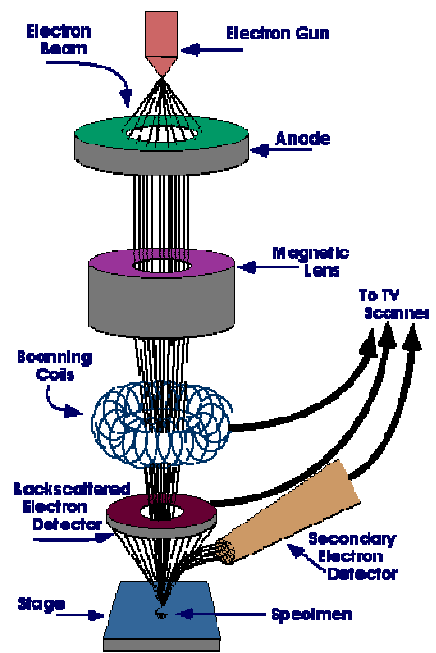
Fig. 27 presents SEM micrographs of cryogenically fractured surfaces of the blends LN75 with 0 wt.% CB and LN75 with 22 wt.% CB.

The SEM is designed (as shown in Fig. 27) for the direct study of surfaces of solid objects. It takes advantage of the wave nature of rapidly moving electrons. Where visible light has wavelengths from 400 nm to 700 nm, electrons have a wavelength of 0.012 nm. [60]

By scanning with an electron beam that has been generated and focused by the operation of the microscope, an image is formed in much the same way as a TV. The SEM allows

a greater depth of focus than the optical microscope. For this reason the SEM can produce an image that is a good representation of the three-dimensional sample. [60]

General principle of SEM:



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Fig. 28 The structure of SEM. The electron gun produces a stream of monochromatic electrons. [60]

A vacuum coating unit is essential in almost every laboratory concerned with electron microscope. The equipment is needed for metal coating materials. Non-conductive or low conductive composites were coated with Au. [61]

3.6.3 Hardness

The tests of hardness are based upon measuring of resistance against sinking of steel point by various shapes. Shore A is used for soft materials in scale 0-100 units. The hard composites are measured by hardness tester Shore D. [62, 63]

Hardness tester HHP-2001 (Bareis) was used for hardness measurements. For accurate testing, composite samples at least 6 mm thick with even surfaces were prepared. [62, 63]

Five data points were taken on each sample, and no difference was found between hardness

measurements on both sides of each specimen.

|

|

Two types of hardness tester were used:

- Shore A – for elastomer matrix and their blend (LN 100, LN 75)
- Shore D – for thermoset matrix and their blends (LN 0, LN 25, LN 50) [62, 63]

4 DISCUSSION

In this work, we demonstrate that the electrical conductivity of polymer composites can be changed by addition of conducting carbon black particles. We focus on the possibility of lowering the percolation threshold of these systems by using immiscible blends as a matrix. Two main ways of improving the conductivity at a given filler concentration have been followed in some previous studies: the double percolated networks induced by immiscible blends, as well as multicomponent fillers in a single polymer matrix. We choose the first one. Thermosets, which can be easily cross-linked at room temperature by addition of crosslinking agents, were chosen as blend matrix. One of the materials has hard but brittle mechanical properties and the other is elastomer. CB was chosen as conductive filler, which is the most often used as conducting filler in practice and many previous studies.

Preparation of polymer matrices with CB is described in section 3.3 and these problems occurred:

Air bubbles in samples must have been removed in a vacuum oven for 10 minutes. This problem was eliminated in CB-containing composites.

CB can absorb humidity and consequently be worse mixed with polymers. So, it was dried before blending.

Ultrasonic homogeniser was used for mixing, but it turned out that materials with high concentrations of CB are very viscous. These samples were not mixed properly so after they were longer mixed by hand.

The dc electric conductivity of composites was measured by the four-point van der Pauw method with a Keithley 237 and multimeter Keithley 2010 with a 2000 SCAN 10-channel scanner card.

Two opposite sides of sample surfaces were vacuum evaporated with thin gold layers as the electrodes. These layers are used to reduce the contact resistance and to provide intimate electrical contact between the samples and the electrical contacts. These low-conducting samples were measured by two-points method. The resistance of data was measured in ohm units and they were re-counted to volume resistivity according to formula (4). The volume conductivity is used in calculation of Kirkpatrick model. [16] Volume conductivity is the inverse value of volume resistivity. The measured data of conductivity were inscribed in these diagrams.

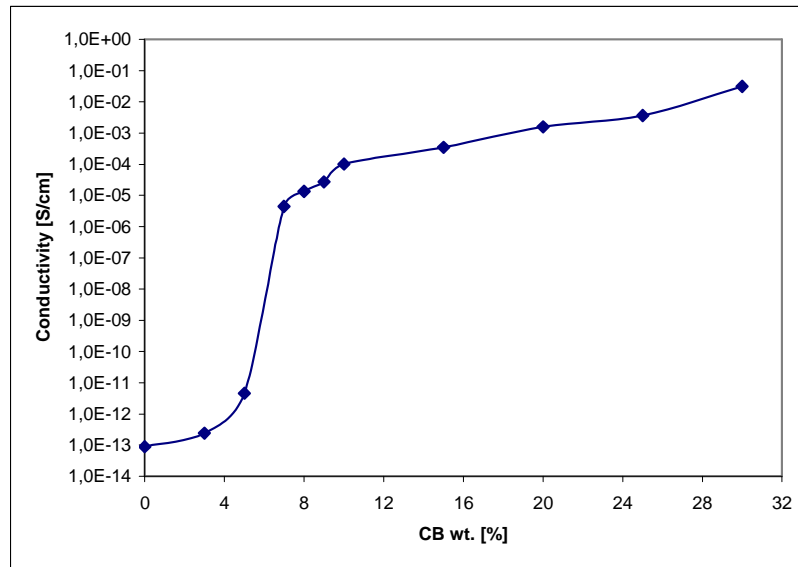


Fig. 29 The measured data dependence of conductivity on wt. % of CB for composite LN 0

In Fig. 29, the critical volume fraction (v_c) at PT was found in point 5.9 wt. % of CB. The values about 4 wt. % and below have low volume fraction of filler. It is localized under the PT. On the other side, the values about 17 wt. % and more have high volume fraction of filler. It is localized above the PT and reaches the conductivity 10^{-2} S/cm and more.

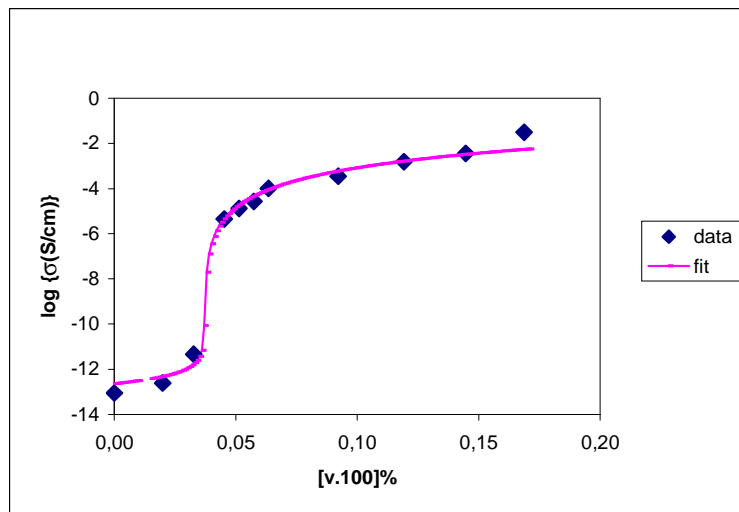


Fig. 30 Comparison between experimental and theoretical values of conductivity vs. the concentration CB according to Kirkpatrick model for composite LN0

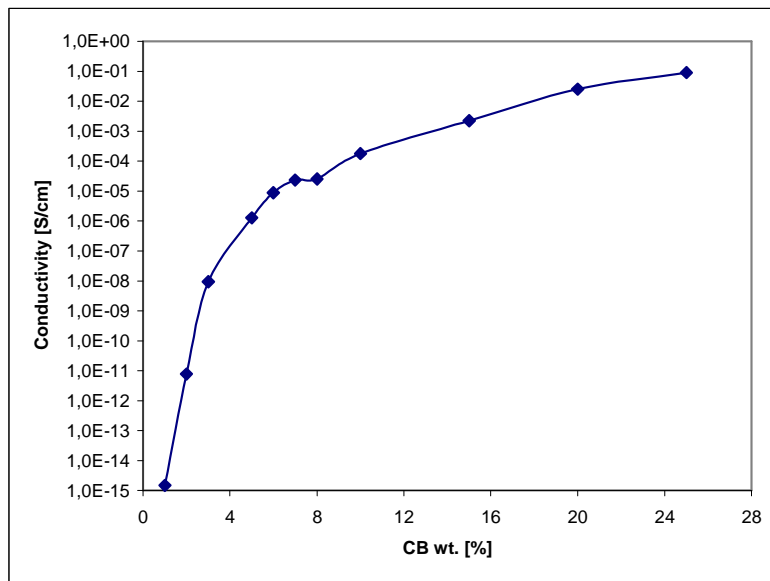


Fig. 31 The measured data dependence of conductivity on wt. % of CB for composite LN25

In Fig. 31, the critical volume fraction (v_c) at PT was found in point 2.1 wt. % of CB. The values about 1 wt. % and below were localized under the PT. On the other side, the values about 12 wt. % and more were localized above the PT and their conductivity growths from 10^{-4} to 10^{-1} S/cm at 25 wt% of CB.

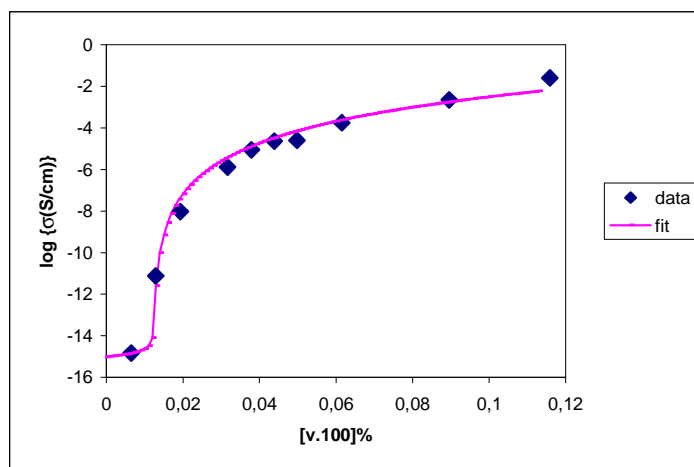


Fig. 32 Comparison between experimental and theoretical values of conductivity vs. the concentration CB according to Kirkpatrick model for composite LN25

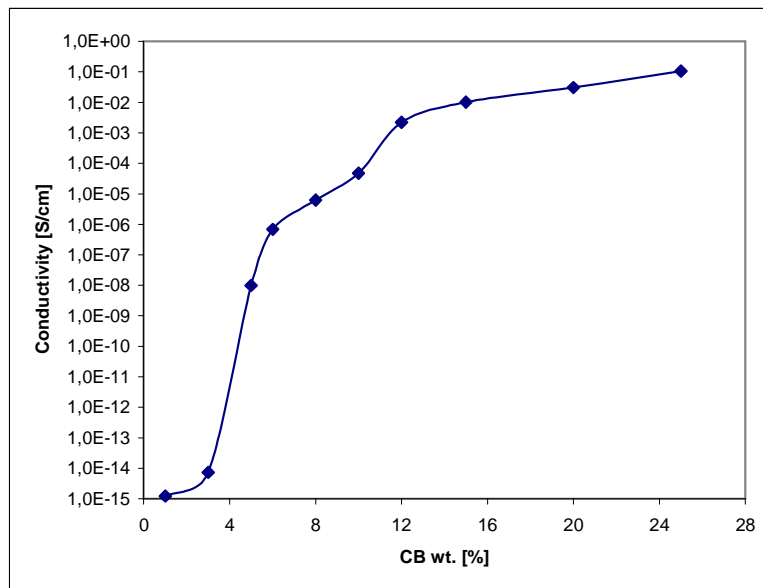


Fig.33 The measured data dependence of conductivity on wt. % of CB for composite LN 50

In Fig. 33, the critical volume fraction (v_c) at PT was found in point 4.7 wt. % of CB. The values about 3 wt. % and below were localized under the PT. On the other side, the values about 16 wt. % and more were localized above the PT. Against the conductivity above the PT reaches almost 10-1 S/cm at the highest measured content of filler.

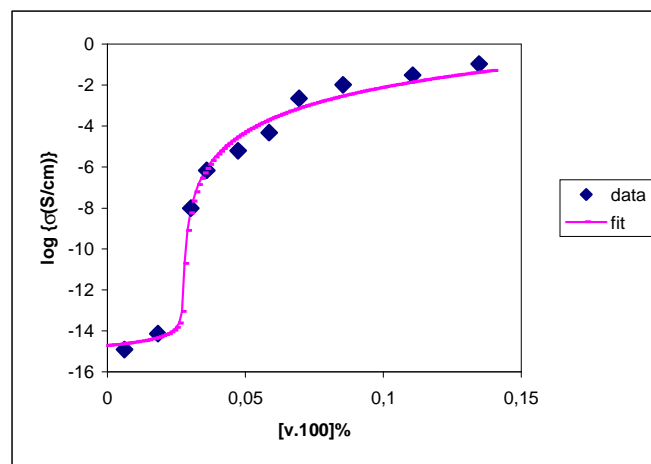


Fig. 34 Comparison between experimental and theoretical values of conductivity vs. the concentration CB according to Kirkpatrick model for composite LN 50

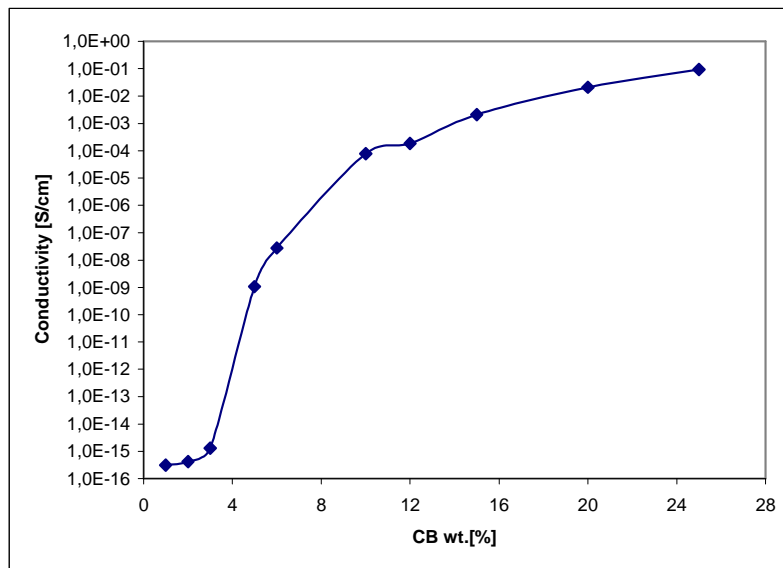


Fig. 35 The measured data dependence of conductivity on wt. % of CB for composite LN75

In Fig. 35, the critical volume fraction (v_c) at PT was found in point 4.1 wt. % of CB. The values about 3 wt. % and below were localized under the PT. On the other side, the values about 16 wt. % and more were localized above the PT. The conductivity above the PT varies from 10^{-4} to 10^{-1} S/cm.

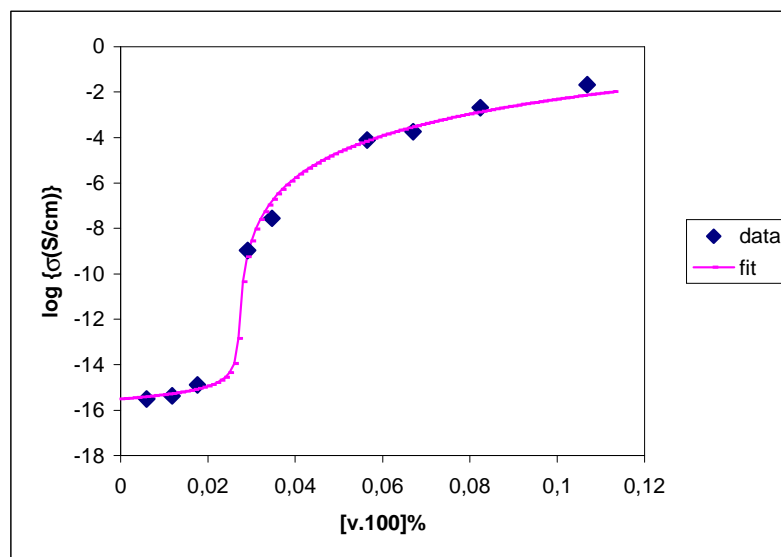


Fig. 36 Comparison between experimental and theoretical values of conductivity vs. the concentration CB according to Kirkpatrick model for composite LN75

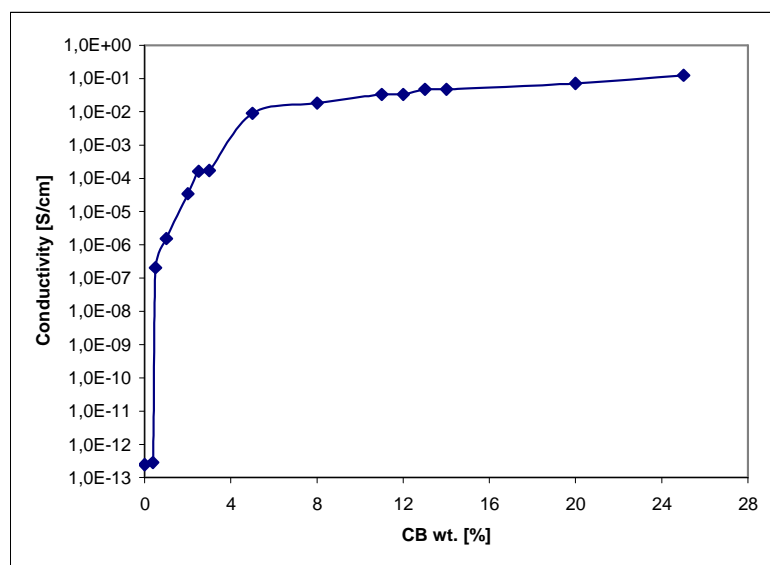


Fig. 37 The measured data dependence of conductivity on wt. % of CB for composite LN 100

In Fig. 37, the critical volume fraction (v_c) at PT was found in point 0.5 wt. % of CB. The values about 0.3 wt. % and below were localized under the PT. On the other side, the values about 11 wt. % and more were localized above the PT. The conductivity above the PT rises from 10^{-2} to 10^{-1} S/cm. The percolation is the most sharp for this type of composite.

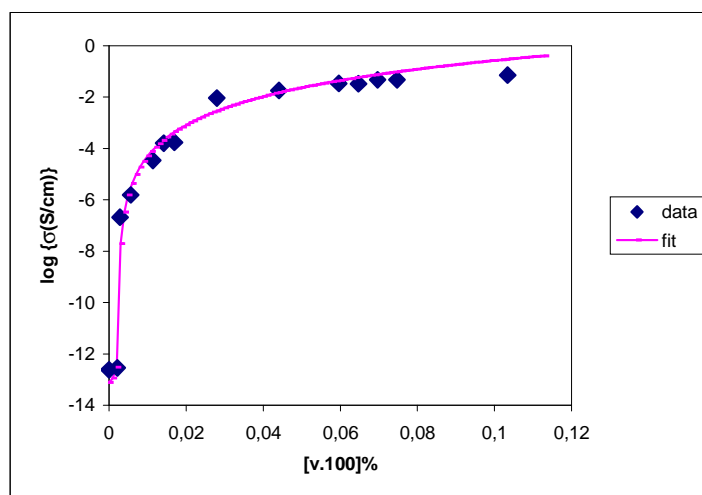


Fig. 38 Comparison between experimental and theoretical values of conductivity vs. the concentration CB according to Kirkpatrick model for composite LN 100

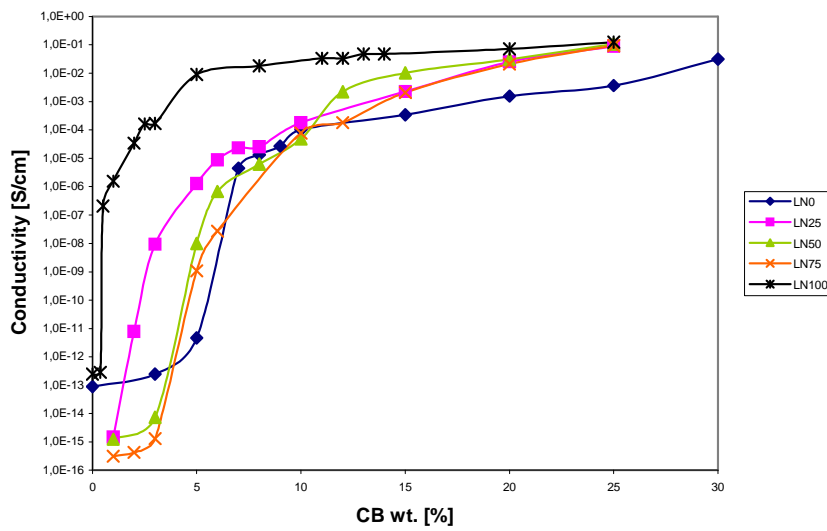


Fig. 39 The measured data dependence of conductivity on wt. % of CB for all composites

Values of the v_c at PT were compared with each other. The conductivity measurements showed that the composites of pure silicon rubber reach the lowest PT and the highest values of conductivity above the percolation threshold concentration of CB.

In opposite the composites of pure epoxy resin were found to have the PT at the highest concentration of CB in comparison with other four types of composites and the lowest conductivity above the PT concentration.

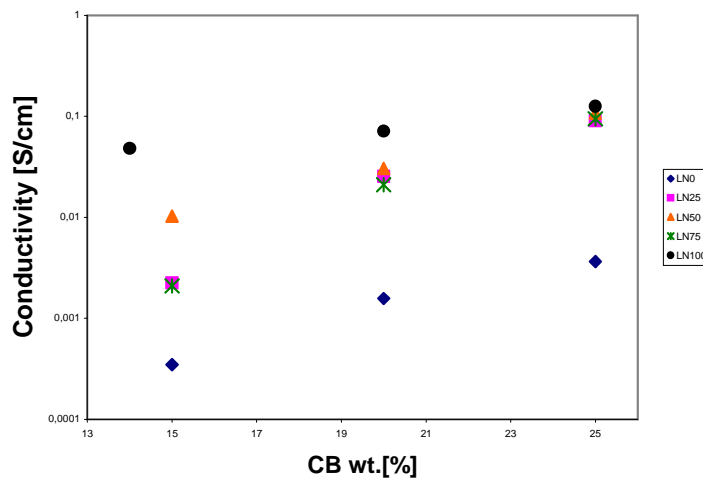


Fig. 40 Influence of CB concentration on conductivity of four tested types of composites above the PT.

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Fig. 40 presents a comparison between all composites with 14, 15, 20, and 25 wt. % of CB.

Further, it becomes obvious from the measurements that the conductivity of epoxy composites filled with carbon black, the conductivity of composite is increased to the value of pure silicone rubber/CB composite. It means the conductivity enhancement about two or three orders of magnitude as you can clearly see in Fig. 40 by addition of silicone rubber into epoxy/CB composite. The percolation threshold concentration was also lowered in comparison to pure epoxy/CB composites.

The second material testing was the investigation of material heterogeneity by scanning electron microscope. The SEM micrographs of the fractured surface of the cured blends (LN 25) containing 10 wt. % CB [Fig. 42] show characteristics of phase heterogeneity of the system. The SEM micrograph of the blend (LN50) containing 0 wt % CB [Fig. 41] displays morphology of connected globules but with some characteristics of bi-continuous phase structure.

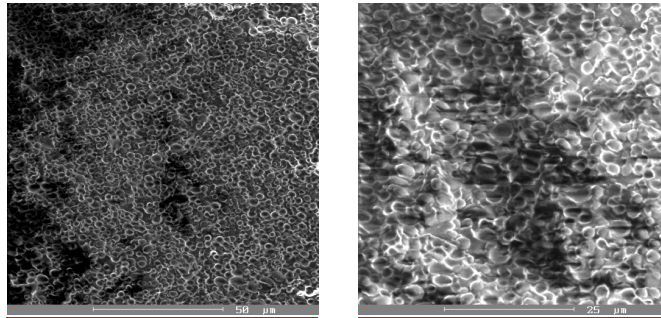


Fig. 41 Composite LN 50:epoxy 50 with 0 and 0 wt. % of CB
Note that second picture is 2x zoom.

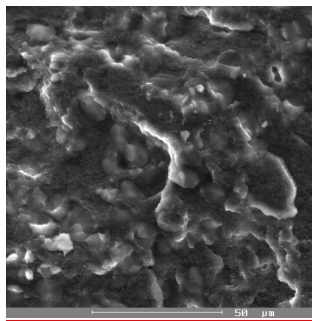


Fig. 42 Composite LN 25:epoxy 75 with 10 wt. % of CB

The white graphics in Fig. 42 indicates the presence of CB in the interfacial regions between the matrix particles, forming a network of CB conductive channels/paths. In Fig. 42 is shown regularly distribution of CB in matrixes. There are seen inclusions of one matrix in the other one.

Phase heterogeneity is also more obvious in the blends with 15 to 25 wt. % of CB [Fig. 43], because in these composites critical filling of filler arises. Material has poor structural integrity.

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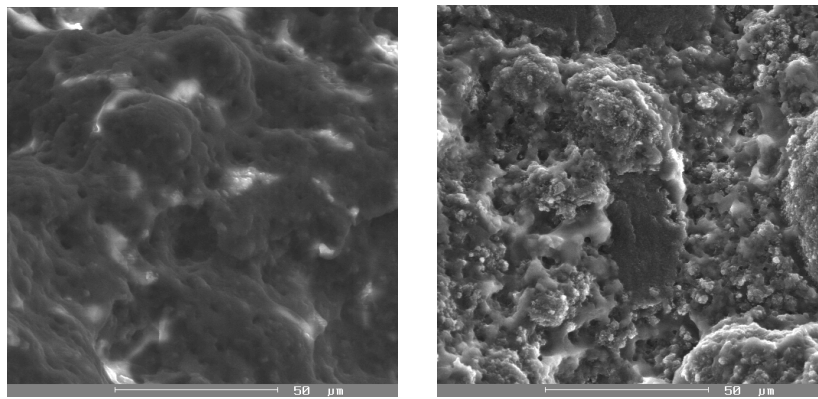


Fig. 43 Composite LN 50:epoxy 50 with 10 and 25 wt. % of CB

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Epoxy resin is a stiff material with excellent temperature performance and solvent resistance. These desirable properties come from the high cross-link density that develops during curing.

However, the fully cross-linked resin cannot absorb energy under stress and hence is of a brittle structure. Thus it is desirable to improve the toughness of epoxy resin. The most well established method of toughness increase is incorporation of a second phase of dispersed rubber into the cross-linked polymers. Addition of rubber to epoxy resins has been shown to enhance their fracture toughness, while lowering their glass transition temperature and thermal and solvent resistivity. [62]

Due to the lack of time only hardness of studied composites was measured from mechanical properties.

The hardness Shore D of samples differs with filler concentration, within the range from 61 to 68 unities for LN 0 and 48 to 60 unities for LN 25 (as shown Fig. 46). Hardness of LN 25 in comparison with LN 0 is decrease about 10 units.

Variations of the mean error for LN 25 and LN 0 were higher than for LN 100, especially matrix LN 0 with 20% CB. Their values were from 6 to 17 unities for LN 25 and from 9 to 37 unities for LN 25.

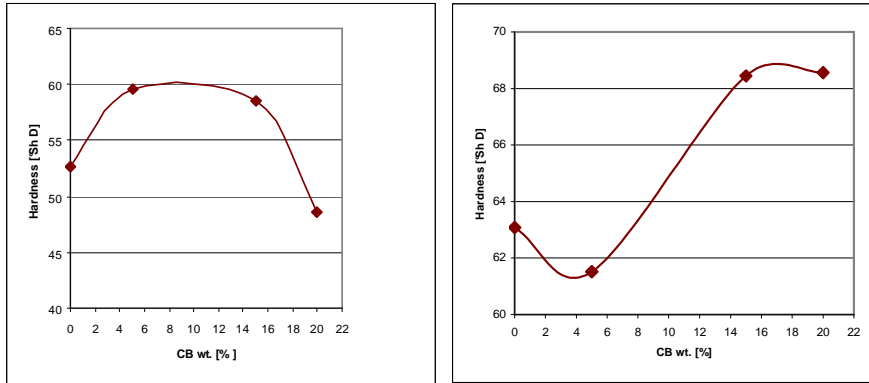


Fig. 44 Hardness of LN 0 and LN 25 composites with various amounts of CB

Figure 46 illustrates the Shore D hardness of pure epoxy resin (LN 0) composites. LN 0 is very hard material but a brittle, too. It should have better mechanical properties after silicone rubber supplement. The hardness of epoxy was found to decrease with only 25% of silicone rubber addition which is understable. The hardness was also found to arise with the CB content growth until the critical filler concentration. It is also clear as CB is commonly used to improve mechanical properties of polymers, among others.

The Shore A hardness was used for soft material as pure silicone rubber is (LN 100).

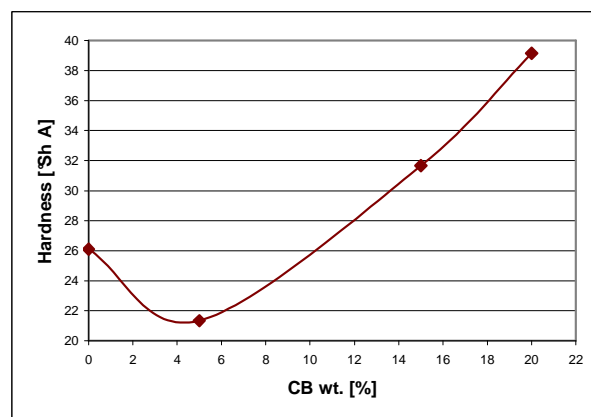


Fig. 45 Hardness of LN 100 with various amounts of CB

The investigation of composites of LN 100 samples revealed an initial decrease in hardness BC content increase and then continuous growth for higher concentrations [Fig. 47].

Variations of the mean error for LN 100 were very low < 1 unites. Consequently, that measuring data are quite well accurate.

CONCLUSION

Nowadays the utility of conducting polymer composites is well established and many efforts were involved to their investigation. Recently conducting polymers filled with multi-wall carbon nanotubes or fullerenes are considerable studied or new generation of efficient CPCs possessing a low percolation threshold concentration and high conductivity continues to be sought. Lowering the percolation threshold of a composite system appears to be an effective way to reduce the amount of filler required to produce adequate conductivity and thereby, among others, minimize problems with mechanical performance.

In this work the method of percolation threshold reduction by use of immiscible blend matrix was followed. We studied blends of epoxy resin with silicone rubber filled with carbon black. Four types of composites differing in the amount of silicone rubber were filled with concentration spectra of carbon black and their direct current conductivity was measured. It was found that by the addition of only 25 % of silicone rubber into epoxy resin the percolation threshold was lowered by the lowering was not as significant as we expected. But with the same amount of silicone rubber we increased the conductivity of epoxy resin composites about two to three orders of magnitude above the percolation threshold.

By the addition of silicon rubber the improvement of mechanical properties of brittle epoxy resin are expected too. In this diploma work only hardness of some composites was measured, which understandably showed lowering with the increasing amount of silicone rubber in epoxy resin and simultaneously increasing with concentration of carbon black growth until the critical filling.

The SEM exhibits the heterogenous structure of immiscible blend of composites without fillers as well as the presence of carbon black particles arranged mostly at the interfaces.

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Odstraněno: ¶

LIST OF SYMBOLS

IPN	Interpenetrating polymer networks
PT	Percolation threshold
PTC	Positive temperature coefficient
NTC	Negative temperature coefficient
L-PTC	Low positive temperature coefficient
H-PTC	High positive temperature coefficient
TiB ₂ /HDPE	Titanium Diboride/ High density polyethylene
S/m	Siemens per metre - electrical conductivity units
σ	Sigma - symbol for electrical conductivity
γ	Gamma - symbol for electrical conductivity
ϵ	Relative dielectric constant of insulating materials
Ω .cm	Ohm per centimetre – units of resistivity
d	Width of potential barrier
V ₀	Height of potential barrier
σ_c	Composite conductivity
σ_f	Conductivity of the filler
v_f	Volume fraction of filler at the percolation threshold
t	Critical exponent - describes the rate of conductivity change
q	Critical exponent for pure matrix
v_c	Critical volume fraction
T _g	Glass transition temperature
CTBN	Carboxyl-terminated butadiene-acrylonitrile
μm	micrometre
vol. %	Volume percent
K	Kelvin
EMI shielding	Electromagnetic interference shielding
RT	Room temperature
wt.%	Weight percent
g	Gramme
min	Minute
kV	Kilovolt

mm	Millimetre
ρ	Volume resistivity [Ω .cm]
R	Resistance [Ω]
SEM	Scanning electron microscope
κ	Kappa - symbol for electrical conductivity
s	Characteristic exponent of PT
σ_m	Conductivity of the matrix
W/Km	Watt/Kelvin.meter
l	Length of electrodes
BaTiO ₃	Barium Titanate
v	Volume fraction

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