

# **Epoxy-silicone matrix filled nanocomposites: Study of mechanical and electrical properties**

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Doctoral Thesis Summary

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**Epoxy-silicone matrix filled nanocomposites:  
Study of mechanical and electrical properties.**

**Nanokompozity na bázi plněného epoxid-silikonu:  
Studium mechanických a elektrických vlastností.**

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## ABSTRACT

The work is focused on the modification of the brittle epoxy matrix by silicone elastomer with a view to improve the toughness characteristics without significant reduction of modulus, glass transition temperature and interfacial adhesion, and, to obtain conductive nanocomposites. The emphasis has been put on the preparation technology of epoxy-silicone polymer system with controlled morphology and mechanical properties. To this end, epoxy resins based on diglycidyl ether bisphenol A and different types and content of polydimethylsiloxanes were mixed. Curing was carried out using diethylentriamine hardener and dicumyl peroxides as compatibilizator. These blends were subsequently filled with carbon black or carbon nanotubes to obtain electroconductive systems. It has been established that mechanical properties of such nanocomposites are influenced by the microstructure of the multiphase system, which in turn is determined by the presence or absence of interphase compatibility between two polymer phases. The electrical properties of nanocomposites heavily depend on filler aspect ratio, filler content, and, to some extent, on polymer matrix composition. Aforementioned types of conductive materials can be used as conductive adhesives, electromagnetic interference (EMI) isolation materials, antistatic coatings, etc.

## SHRNUTÍ

Práce je zaměřena na modifikaci křehké epoxidové matrice silikonovým elastomerem s cílem zlepšit houževnatost bez významného snížení modulu, teploty skelného přechodu a mezifázové adheze a získání vodivých nanokompozitů. Důraz byl kladen na technologii přípravy epoxid-silikonového polymerního systému s řízenou morfologií a fyzikálně-mechanickými vlastnostmi. Za tímto účelem byla smíchána epoxidová pryskyřice na bázi diglycidyl ether bisphenol A s různým podílem a typy polydimethylsiloxanů. Síťování bylo provedeno za použití diethylentriaminu a dikumyl peroxidu jako kompatibilizátoru. Tyto směsi byly následně naplněny sazemí nebo uhlíkovými nanotrúbkami, aby se získaly vodivé systémy. Bylo zjištěno, že mechanické vlastnosti takových nanokompozitů jsou ovlivňovány mikrostrukturou vícefázového systému, který je zase určován přítomností nebo nepřítomností mezifázové kompatibility mezi dvěma polymer. Elektrické vlastnosti nanokompozitů velmi závisí na štíhlostním poměru plniva, koncentraci plniva a na složení polymerní matrice. Tyto materiály mohou být použity jako vodivá lepidla, materiály pro elektromagnetic. interferenci (EMI), antistatický povlak.

# CONTENTS

ABSTRACT.....	3
SHRNUTÍ.....	3
CONTENTS .....	4
INTRODUCTION.....	5
1 STATE OF ART.....	6
1.1 Conductive polymer composites .....	6
1.2 Polymer blends .....	9
1.3 Factors influencing the electrical properties of composites .....	12
1.4 Morphology and the electrical properties relationship.....	12
AIMS AND OBJECTIVES OF WORK.....	14
2 METODOLOGY .....	14
2.1 Epoxy polydimethylsiloxane blends – materials and preparation	14
2.2 Epoxy polydimethylsiloxane composites filled with conductive filler - materials and preparation .....	15
2.3 Characterization of materials.....	17
3 RESULTS AND DISCUSSION.....	18
3.1 Effect of peroxide on the compatibilization of epoxy resin with polysiloxanes .....	18
3.1.2 SEM morphology .....	19
3.1.3 Dielectric properties .....	21
3.1.4 Rheological properties.....	22
3.1.5 Mechanical properties .....	24
Dynamic mechanical properties .....	24
Impact strength .....	26
3.2 Polysiloxane composites filled with CB and CNT .....	27
3.2.1. A solvents dispersion method for modification of CNT .....	27
3.2.2. PDMS/CNT-NMP composite - Sonication.....	27
3.2.3. DC electrical conductivity.....	27
3.3 Effect of epoxy-polysiloxane blends microstructure on mechanical and electrical properties of nanocomposites. ....	29
3.3.1. CNT nanocomposites .....	29
3.3.2. CB nanocomposites .....	32

CONCLUSIONS.....	34
FUTURE PROSPECTS .....	34
CURRICULUM VITAE .....	35
ABBREVIATIONS AND SYMBOLS .....	36
LIST OF FIGURES .....	38
LIST OF TABLES .....	39
REFERENCES .....	39

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## INTRODUCTION

Multiphase polymers systems (MPS) such as polymer blends and polymer composites are of particular interest from both the fundamental point of the view and that of applications. Different properties of the particular components can be combined in such systems. Moreover, new properties not inherent to the components may emerge because of synergy. High resistance to crack growth [1,2,3,] characterizes rubber-modified epoxy resin. To this end, epoxy resin generally can be modified by rubber: natural liquid [4], hydroxyl terminated polybutadiene [5, 6], carboxyl-terminated copolymer of acrylonitrile liquid rubber etc. [7, 8]. When elastomer is added to the uncured epoxy resins and after the cross-linking reactions, the elastomer modified epoxy resins exhibited a two-phase microstructure consisting of relatively small rubber particles dispersed in a matrix of epoxy. This microstructure resulted in the material possessing a higher toughness than the unmodified one with only a minimal reduction in other important properties, such as modulus. As the content of the minor component increases to a critical value, the morphology of multicomponent,

mixture changes into a co-continuous structure [9]. Multiphase systems exploit the structural percolation of one of the phases in the other with percolated phase filled with conductive filler. This due to morphological reasons consequently lowers the required amount of filler, i.e. percolation threshold in the multiphase systems compared to a standard filler/matrix composite. Therefore, the formation of conductive network is affected not only by the filler volume fraction, but also by the processing technology and different affinity of filler to each polymer in the system; thus, it is selectively dispersed in one of the two phases [10-11]. For example, the percolation value in such multicomponent system is governed by the percolation of the carbon black (CB) rich phase and the continuity of this phase in the system [10].

In current work we introduce methodology that can significantly reduce the percolation threshold and enhance the total conductivity of polymer composites and simultaneously to modify the brittle behaviour of epoxy resin by elastomers.

## 1 STATE OF ART

### 1.1 Conductive polymer composites

Polymer composite is defined as a multicomponent material comprising multiple different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase. Conductive polymer matrix composite (CPC) [12] consists from a nonconductive polymer matrix (with electrical conductivity,  $\sigma < 10^{-11} \text{ S cm}^{-1}$ ) and conductive fillers. Total electrical conductivity of CPC is affected by: 1) volume fraction of filler, 2) interface between matrix and filler, at which these are chemically and mechanically combined and 3) processing conditions. The matrix is a continuous phase in CPC and plays several important roles: it holds the filler in place, acts as a path for stress transfer between fillers, and protects the reinforcements from an adverse environment.

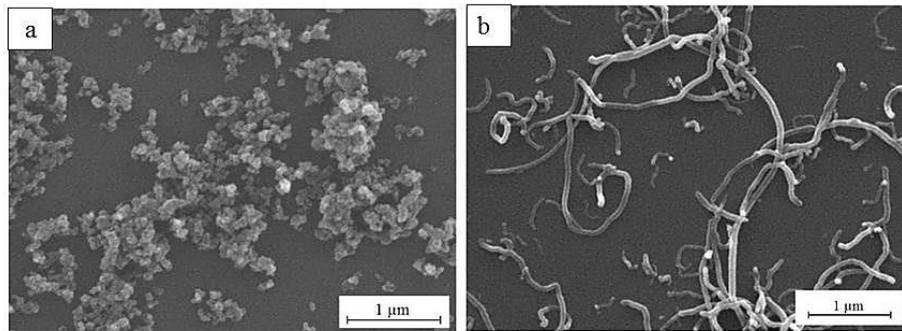
*The polymer matrix* has a major influence on composite processing characteristics. Generally, polymer matrixes are classified as thermoplastic or thermosetting polymers and their blends. *Epoxy resins (ER)* are a class of polymers with molecules containing an epoxide group (oxirane) consisting of an oxygen atom attached to two connected carbon atoms. Epoxy resin can be divided into 2 groups: a) glycidyl (2,3 – epoxy propyl) which is used extensively in the technologies as filament winding, pultrusion or some adhesives and b) glycidylamine, where the typical representant of group is tetraglycidyl methylene dianiline (TGMDA), also known as tetraglycidyl- 4,4"-

diaminodiphenylmethane (TGDDM), which is used for a large number of the commercial and high-tech composite matrix systems in aircraft. In my study I concentrated on ER of glycidyl group - diglycidyl ether of bisphenol - A (DGEBA). The major classes of epoxy curing agents are aliphatic amines [13], acid [14], anhydrides [15], and amines [16]. The most widely used aliphatic curing agents are diethylenetriamine (DETA), triethylenetetramine (TETA) and diethylaminopropylamine (DEAPA). Diglycidyl ether bisphenol A and amines are normally used for preparation of composites and cycloaliphatics are used extensively in electrical applications or as a minor epoxy in composite matrix systems. In my study DETA was used as curing agent for epoxy resin composite for its low viscosity, easy mixing, and relatively fast curing at room temperature. Its disadvantages comprise high volatility, toxicity, short pot life and temperature limit of 80°C. The isothermal curing reaction of an epoxy resin is complex as a consequence of the interaction of the chemical curing with other physical processes, such as gelation and vitrification, causing important changes in the physical properties of the reacting system [17].

*Silicones* are mixed inorganic-organic polymers with the chemical formula  $[R_2SiO]_n$ , where R is an organic group such as methyl, ethyl, or phenyl, which are also known as polymerized siloxanes or polysiloxanes. Silicone consists of an inorganic silicon-oxygen backbone chain (...-Si-O-Si-O-Si-O-...) with organic side groups attached to the silicon atoms, which are tetravalent. The (-Si O-) repeat unit is called as the “siloxane” bond. High demand of these materials is due to the interesting combination of properties offered, which include extremely high backbone flexibility and very low glass transition temperatures ( $T_g$ ), around -120 °C, good thermal and oxidative stability, high gas permeability, excellent dielectric properties and physiological inertness or biocompatibility [18-20]. Silicone polymers display an unusual combination of physical and chemical properties when compared with homologous carbon-based polymers [21]. Although low molecular weight silicones (< 500 g/mole) are miscible, high molecular weight, PDMS is quite immiscible with the epoxy resins [22, 23].

*Filler* is a crucial component of the composite material not only improving composite stiffness but in the case of electric filler rendering it electroconductive. Electrically conductive filler, such as metal powder [24], fibers [25], carbon black [26-29] and carbon nanotubes [30] are used to prevent heat loss and achieve high electrical conductivity of the composite. Filler type and shape, aspect ratio, and dispersion degree of filler in polymer matrix influence the total electrical conductivity significantly. In my work I focused on

the following types of filler: carbon black, carbon nanotubes. *Carbon black (CB)* is an amorphous form of carbon with a structure similar to disordered graphite. CB is a form of paracrystalline carbon that has a high surface area to volume ratio. Domain structures of CB are particle ( $\sim 50 \mu\text{m}$ ), aggregate ( $\sim 1 \mu\text{m}$ ) and agglomerate ( $\sim 10 \mu\text{m}$ ). Crystallites then form primary particles, which further fuse into primary aggregates. Van der Waals forces cause these aggregates to join in more loosely assembled agglomerates. There are five types of CB manufactured in the CB industry: furnace black, thermal black, lamp black, channel black, and acetylene black (Fig.1 a). Electrical conductivity of dry compressed CB is of the order  $10^4 \text{ S/cm}$  [31] with density in the range ( $1.7\text{-}1.9 \text{ g/cm}^3$ ). CB have great potential in the application sphere as: electromagnetic interference shielding, electrostatic and heat dissipation [32].



*Fig. 1. SEM photographs of the of fillers: a) CB (acetylene blacks, Cabot, USA),  
b) CNTs (MWCNT–2040, Conyuan Biochemical Technology, Taipei, Taiwan*

*Carbon nanotubes (CNT)* represent the youngest allotropic form of carbon having a high degree of constitutional organization. They exist in two fundamental forms, single-wall (SWNT) and multi-wall (MWNT) Fig. 1 b. SWNT consist of a single tube of graphene, whereas MWNT are composed of several concentric tubes of graphene fitted one inside the other. CNT has very high aspect ratios  $p$  ( $p=L/D$ , where  $L$ = length,  $1\text{-}50 \mu\text{m}$  and  $d$ -diameter,  $1\text{-}50 \text{ nm}$ ) of the CNT, which was discovered in 1991 by Iijima [33]. They have electrical conductivity of  $10^6\text{-}10^7 \text{ S.cm}^{-1}$ , low apparent density, high surface area, porosity, gas permeability and excellent mechanical properties: the high tensile strength ( $13\text{-}53 \text{ GPa}$ ) and Young's modulus ( $1000\text{-}5000 \text{ GPa}$ ). However, the effective utilization of the properties of nanotube composites depends on the quality of their dispersion and the level of interfacial bonding of nanocomposites [34]. There are two distinct approaches for dispersing carbon nanotubes: the mechanical method and methods that are designed to alter the surface energy of the solids, either physically (non-covalent treatment) or chemically (covalent treatment). Mechanical dispersion methods, such as ultrasonication and high

shear mixing, separate nanotubes from each other, but can also fragments the nanotubes, decreasing their aspect ratio [35]. Generally, there are two groups of surfactants—non-ionic, with no charge in its head, and ionic: cationic, anionic and zwitterionic. Ionic surfactants can be used with water soluble polymers such as polyvinyl alcohol (PVA) [36-38]. Surfactant can also cause the non-covalent modification of the CNT surface, which is helpful for dispersion of this kind of filler in polymeric matrix. However, pristine carbon nanotubes cannot be homogeneously dispersed in most solvents. CNT are poorly soluble in nearly all classical solvents, with the exception of amide solvents such as N, N dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP).

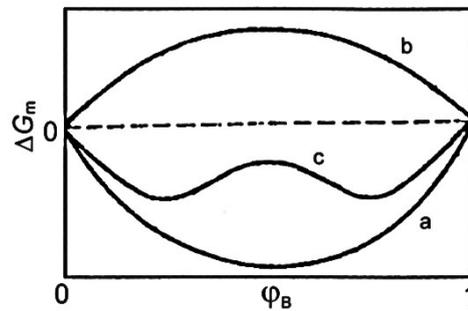
## 1.2 Polymer blends

Polymer blends can be divided into three categories: miscible, partially miscible and immiscible. An immiscible polymer blend represents a multiphase system. The reasons for incompatibility are high interfacial tension and poor interfacial adhesion [39]. Generally, one polymer is dispersed in another, and the multicomponent mixture forms a sea-island microstructure. As the content of the minor component increases to a critical value the morphology of multicomponent mixture changes into a co-continuous structure. Utracki [40] defines the polymer blend as a mixture of at least two polymers or copolymers comprising more than 2 wt. % of each macromolecular component. Depending on the sign of the free energy of mixing, the components of the blends are miscible and immiscible. An immiscible polymer blend is associated with positive value of the Gibbs free energy of mixing (eq.1), upper curve. Complete miscibility in a mixture of two polymers requires that the following condition was fulfilled [40]

$$G_m = \Delta H_m - T\Delta S_m < 0 \quad [1]$$

where  $\Delta G_m$ ,  $\Delta H_m$  and  $\Delta S_m$  are Gibbs free energy, the enthalpy and entropy of mixing at temperature T [K<sup>-1</sup>]. Miscible polymer blend is homogenous down to the molecular level associated with negative value of the free energy of mixing and the domain size is comparable to the dimensions of the macromolecular statistical segment. The value of  $T\Delta S_m$  is positive since there is increase in the entropy on mixing. Therefore, the sign of  $\Delta G_m$  depends on the value of the enthalpy of mixing  $\Delta H_m$ . The polymer pairs mix to form a single phase only if the entropic contribution to free energy exceeds the enthalpic contribution and is valid ( $\Delta H_m < T\Delta S_m$ ). Blends can be classified as either *homogeneous* or *heterogeneous* systems. The homogeneous system can be depicted as a solution

with a single phase or single glass-transition temperature ( $T_g$ ). A heterogeneous blend has both continuous and dispersed phases, each retaining its own distinctive  $T_g$ . Until recently, blending was either restricted to polymers that had an inherent physical affinity for each other or else a third component, called a compatibilizer, was employed. The incompatible polymers produce a heterogeneous blend with poor physical properties. In details, a system is thermodynamically stable if its formation is accompanied by a decrease  $\Delta G_m$ , in morphological terms of homogenous domains size is presented. The  $\Delta G_m$  decreases to a definite equilibrium value, which does not change subsequently with time. The mixing of polymers at elevated temperatures and of amorphous polymers can be considered a mixing of two liquids [41]. The polymer blends opens up the possibility of effectively producing advanced multicomponent polymeric matrices with new properties.



*Fig. 2 Plots of Gibbs free energy of mixing ( $\Delta G_m$ ) for a) miscible b) immiscible c) partly miscible blends [42].*

### 1.2.1. Physical compatibilization methods of multiphase polymer composites

Compatibilized blends are characterized by the presence of a finely dispersed phase, good adhesion between phases, strong resistance to phase coalescence, and technologically desirable properties [45]. Physical compatibilization includes the addition of different kinds of copolymers into the immiscible blend [46-49]. The main disadvantage of the physical compatibilization is the tendency of the added copolymers to form micelles, which reduces the compatibilizing efficiency, increases the blend viscosity and may worsen the mechanical properties [46]. Another method is to use of peroxide-initiated functionalization leading to grafting or crosslinking reactions thus initiate compatibilization of two components [47]. Peroxides are commonly used as the sources of radicals and upon decomposition; they generate free radicals in linear silicones. Peroxides are classified in two classes: (i) vinyl group specific catalyst, (ii) vinyl group non-specific catalysts. The dialkyl ones that are unable to crosslink polydimethylsiloxane (PDMS) if they do not contain any vinyl groups on the

chain mainly constitute the first class of peroxides. The second group corresponds to the family of diaroyl peroxides because they can be used to crosslink PDMS with vinyl group. Use of dicumyl peroxide (DCP) as modifier to optimize the properties of epoxy resin modified by silicone elastomer is proposed to be investigated in this work.

### **1.2.2. Toughness improvement of epoxy resin by rubber**

Epoxy resin was toughened by using reactive liquid rubber synthesized by company BF Goodrig Co., USA in 1965. For improvement of epoxy resin properties was used carboxyl terminated butadiene acrylonitrile copolymers (CTBN), amine terminated butadiene acrylonitrile copolymers (ATBN) and hydroxyl terminated butadiene acrylonitrile copolymers (HTBN). Garina Tripathi et al. [48] have reported the toughening effect of CTBN in ER increases initially very rapidly with increasing CTBN concentration. Raju Thomas [48] mentioned the critical concentration of CTBN in ER was 15 wt. %. When the CTBN phase attains a level between 20 to 25 wt. %, a state of cocontinuity is attained and further increase in the concentration leads to phase inversion. Horiuchi [49] mentioned that addition of rubbery materials to epoxy resins enhance their fracture toughness while lowering glass transition temperature ( $T_g$ ) and thermal and solvent stability. The toughening of epoxy resin is an important subject in epoxy technology, where polydimethylsiloxane (PDMS) is used as a perspective elastomer. The mechanical properties of modified epoxy resins by PDMS depend on the method of modification [52]. ER and PDMS blends are initially immiscible; however, chemically bonding of epoxy to the PDMS chain by the reaction between their reactive groups such as hydroxyl, oxirane and amine lead to partial compatibilization. An alternative to this approach is to use of peroxide-initiated functionalization leading to grafting or crosslinking reactions. Procedures that have been used for introducing such active sites include treatment of polymer backbone with an organic compound that is capable of generating radicals. These radicals form the active grafting sites on the polymer and then initiate polymerization of monomer as was presented in [50,51]. The optimum performance was observed at the 10 wt. % of PDMS, the fracture toughness of modified epoxy resins increases dramatically with only slight reduction in the glass transition temperature and the modulus. Miwa [53] introduced that volume fraction of silicone rubber particles (5-10 wt. %) and temperature appears to be the most suitable for obtaining a blend with epoxy resin in which the decrease in Young's modulus and tensile strength is relatively low. Sobhani et al. [30] presented that epoxy modified by hydroxyl – terminated

PDMS by 10 % showed the highest value of elongation at break (i.e. 3, 55) and the highest fracture energy (i.e. 150 J) belonged to the sample containing 5 wt. % PDMS. The aim was to prepare of polymer composites, and one of the important methods to form carrier path in an insulating blends, is the incorporation of conductive fillers.

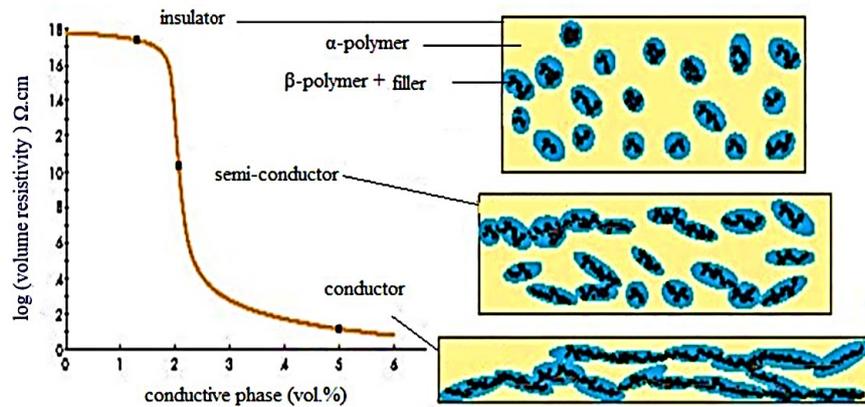
### **1.3 Factors influencing the electrical properties of composites**

The main feature of the CPC is a drastic difference between electrical conductivity of polymer matrix and the filler reaching a factor of  $10^{22}$  in terms of conductivity. This is due to the important specific feature – direct current (DC) can flow along such materials only through continuous chains of filler (if the possibility of quantum-mechanical tunnelling is not taken into account). Probability of forming such a structure depends on a variety of factors, namely: volume fraction, type and shape of filler, aspect ratio, distribution of lengths and orientation, degree of dispersion and processing. The electrical conductivity of CPC can be described by using abstract model of percolation theory. The majority of polymers are typical insulators, the probability of transfer of current carriers between two conductive points isolated from each other by an interlayer of the polymer decreases exponentially with the growth of gap  $i_{\text{tunnelling}}$  (the tunnel effect) and is other than zero only for  $i_{\text{tunnelling}} < 10 \text{ nm}$  [54]. For this reason, the transfer of current through macroscopic distance can be affected via the contacting particles chains. Calculation of the probability of the formation of such chains is the subject of the percolation theory. The main notion of the percolation theory is the so-called percolation threshold  $p_c$  – minimal concentration of conducting filler  $c$  in that a continuous conducting chain of macroscopic length appears in the system [55]. Sherman [56] described percolation threshold as the point at that a macroscopic – length continuous chain first appears. Percolation theories are frequently applied to describe the insulator-to-conductor transitions in composites made of conductive filler and an insulating matrix. It has been shown both experimentally and theoretically, that percolation threshold strongly depends on the aspect (length-to diameter) ration of the filler [57].

### **1.4 Morphology and the electrical properties relationship**

Figure 3 presents the percolation curve of typical CPC material. The infinitely steep change in conductivity of the composites with a minor change in conductive phase at the percolation threshold is evident. The percolation threshold, as well as, varies considerably with the shape and agglomeration of the conductive component [58]. If the conductive component is in the form of

particles and are spatially correlated in three dimensions, the observed percolation threshold can be reduced and critical exponent elevated, both valuable traits for achieving highly sensitive stimuli sensitive materials. A reduction in the conductive element content required for percolation in CPC materials can be accomplished with a “percolation-within-percolation” approach and has been termed multiple percolation (Fig 3). It is possible to demonstrate the systematic reduction in conductive filler required for bulk conductivity resulting from this approach with an example of a ternary blend. We can identify two immiscible polymers, the  $\alpha$ -polymer which is selectively filled with a conductive filler and the  $\beta$ -polymer which is to be filled with the conductive  $\alpha$ -polymer blend.



*Fig. 3. Schematic of the variation in volume resistivity ( $\rho$ ) of a multiple percolation composite and corresponding morphology*

Denoting the critical fraction of the conductive filler required to insure conductivity in the  $\alpha$ -polymer as  $p_\alpha$  and the critical fraction of the  $\alpha$ -phase required to insure connectivity of  $\alpha$  in  $\beta$  as  $p_\beta$ , the critical fraction of the conductive filler in the total ternary blend [59] is

$$p_c = p_\alpha \cdot p_\beta [2]$$

Extending the approach to higher levels of percolation

$$p_c = p_\alpha \cdot p_\beta \cdot p_n [3]$$

where  $p_n$  is the threshold of co-continuity of the  $(n-1)$ -polymer blend in the  $n$ -polymer. A multiple percolation approach allows, at least theoretically, for the feasibility to obtain a CPC material with as low a level of conductive material as desired. In accordance with Eq. (2), for example the CB will be selectively blended into the polyolefin and this binary blend, which is designated the minor phase  $\alpha$ -polymer, will be incorporated into the polar polymer and is designated

the major phase  $\beta$ -polymer. The two polymers in the system under investigation will have a structural similarity in the sense that the former will be a completely nonpolar polyolefin while the latter will differ only by the random insertion of the polar group (e.g., ethylene vinyl acetate) in the chain backbone [60] This phenomenon was described by Sumita [60] For instance, Gubbles et al. [3] Showed the localization of filler influenced electrical percolation of the blend system polyethylene/polystyrene/carbon black and electrical conductivity passes through a maximum when the particles are localized at the interface. Stabilization of domain size by addition of nanoparticles has been extensively reported [61].

## **AIMS AND OBJECTIVES OF WORK**

The aim of the work is to modify the brittle behaviour of epoxy resin by silicone elastomers and to develop on their base nanocomposites with high total conductivity.

The work that has been carried out within doctoral thesis entitled “Epoxy-silicone filled nanocomposites” can be summarized into following parts:

1. Development of technology for preparation of epoxy-silicone polymer system with improvement of mechanical properties.
2. Development of homogenous nanocomposites based on epoxy-silicone matrix filled with carbon black and carbon nanotubes.
3. Characterization of morphostructural, mechanical and electrical properties of polymer systems and nanocomposites.
4. Optimization of nanocomposites technology with a view to improve their toughness and electrical properties.

## **2 METODOLOGY**

### **2.1 Epoxy polydimethylsiloxane blends – materials and preparation**

The epoxy resin (ER) used was a bisphenol A diglycidyl ether (DGEBA), D-3415, epoxide equivalent weight = 172–176 g, liquid, Sigma Aldrich, USA) with purity > 90%. The curing agent was an aliphatic amine, diethylenetriamine (DETA-D93856, Sigma Aldrich, USA) with purity > 90%. Liquid silicone-epoxy resin, Silikopon EF (SEF, Tego, Evonik, GE) was used as a comparison

sample. N-methyl-2-pyrrolidone (NMP) with purity  $\geq 99\%$  was used to modify CNTs (Sigma Aldrich, Saint Luis, MO, USA). Dicumyl peroxide (DCP, Sigma Aldrich, USA) with purity  $>90\%$  was used as a free radical initiator. Two kinds of PDMS were studied: vinyl-terminated PDMS (VT-PDMS, Sigma Aldrich, USA) with purity  $>90\%$  supplied in the liquid form and PDMS (PDMS – base A, Dow Corning, USA).

#### **ER and ER /DCP**

The first set of *ER* samples was prepared without DCP, whereas the second set *ER/DCP* consisted of ER with DCP in concentration varying from 1 to 3 wt. %. DGEBA was mixed in a 50-mL beaker using a mechanical stirrer (MM-1000, Biosan, Germany) for 30 min. The appropriate amount of DETA was added, and the mixture was stirred for further 10 min at 80°C. All polymer blends were prepared from a stoichiometric mixture of DGEBA and DETA with molar ratio of 100:12. Rectangle-shaped samples with 3-mm thickness were produced by cast moulding into vacuum desiccators, where air bubbles were removed. Then, the form was closed and placed into a drying oven, where the material was cured for 2 h at 100 °C. The post curing process was carried for 4 h at 80 °C.

#### **ER/VT-PDMS and ER/PDMS**

The second set of *ER/VT-PDMS* and the fourth set of *ER/PDMS* polymer blends with varying concentrations of polysiloxane PDMS (5, 10, 15 wt. %) were prepared as follows: DGEBA was solved in acetone and mixed with PDMS and VT-PDMS at 80°C in vacuum at 300 rpm for 1 h. The reaction mixture was cooled to room temperature, and amino curing agent DETA was added and stirred for 10 minutes. The curing process was carried out in the same manner as in Section *ER and ER /DCP*.

#### **ER/VT-PDMS/DCP and ER/PDMS/DCP blends**

The fifth *ER/VT-PDMS/DCP* and sixth *ER/PDMS/DCP* sets of samples were prepared in a 50-mL beaker using DGEBA and a varying amount of DCP (1-3 wt. %). Both components were stirred at 300 rpm for 1 h under reduced pressure at 80°C. Subsequently, PDMS (VT-PDMS or PDMS) was added in an amount in the range of 5-15 wt.%, and the mixture was stirred for 2 h at 80°C. After cooling to 25°C, the stoichiometric amount of DETA was added. The curing process was carried out in the same manner as described in Section *ER and ER /DCP*.

## **2.2 Epoxy polydimethylsiloxane composites filled with conductive filler - materials and preparation**

For preparation of conductive polymer composite were used polymer

matrixes presented in Chapter 2.1. As conductive filler, were used carbon black (CB, Vulcan, CABOT XC-72R, USA) and multiwall CNTs (MWNT-2040, purity  $\geq 95$  %, diameter of 20–40 nm, length 5–15 $\mu\text{m}$ , specific area of 40–300  $\text{m}^2 \text{g}^{-1}$ , and density of 1.8  $\text{g cm}^{-3}$ ) were purchased from Conyuan Biochemical Technology (Taipei, Taiwan). NMP with purity  $\geq 99$  % was used to modify CNTs (Sigma Aldrich, Saint Luis, MO, USA). Acetone (Sigma Aldrich, Saint Luis, MO, USA) and distilled water were used without further purification.

#### **PDMS/CNT and PDMS/CB composite - Mechanical mixing**

The first PDMS/CNT set of composites consisted of several samples with CNTs concentration varying from 0 to 5 wt. % (0 – 3.4 vol. %) and the second PDMS/CB composite sets with CB concentration varying from 0 to 14 wt. % (0 – 12 vol. %) were prepared. The certain amounts of CNTs or CB and PDMS were placed into a beaker and stirred using mechanical mixer (IKA Labortechnik, Staufen, Germany) at 100 rpm for 1hr. Then a curing agent was added and subsequently stirred at 100 rpm for 5 min. After that, the mixture was filled into the mold and placed into the vacuum desiccators where air bubbles were removed. Finally, the mold was closed and placed into drying oven where material cured at 70 °C for 12 hrs.

#### **PDMS/CNT-acetone composite – Sonication**

The third *PDMS/CNT-acetone* sets of nanocomposites filled by CNT with polymer matrix PDMS were prepared. CNTs were sonicated in acetone by using ultrasonic treatment (1 hr, at frequency 24 kHz and power 400 W). PDMS was mixed in a 50-mL beaker using a mechanical stirrer (MM-1000, Biosan, Germany) for 30 min then CNT mixture was added and ultrasonic bath was applied for 20 min. In order to remove acetone the mixture was dried at 60 °C for 2 days. After that, the mixture was filled into the mold and placed into the vacuum desiccators where air bubbles were removed. Finally, the mold was closed and placed into drying oven where material cured at 70°C for 12 hrs.

#### **ER/CNT and SEF/CNT**

The fourth and fifth sets of nanocomposites samples based on polymer matrix (ER and SEF) filled with CNT were prepared. CNTs were sonicated in acetone by using ultrasonic treatment (1 hr, at frequency 24 kHz and power 400 W). ER or SEF was mixed in a 50-mL beaker using a mechanical stirrer (MM-1000, Biosan, Germany) for 30 min, then CNT mixture was added and ultrasonic bath was applied for 20 min. In order to remove acetone the mixture was dried at 60 °C for 2 days. The curing process was carried out in the same manner as in Section *ER and ER/DCP*.

### **ER/VT-PDMS/CNT and ER/SEF/CNT**

The sixth ER/VT-PDMS and seventh ER/SEF sets of multicomponent polymer composite with varying concentration of VT- PDMS and SEF from 5 to 40 vol. % were prepared. ER was solved in acetone and mechanically mixed with VT-PDMS or SEF at temperature of 80°C, in vacuum at 300 rpm for 2 hrs. The dispergation of CNTs and curing process were carried out in the same manner as in Section *ER/CNT and SEF/CNT*.

### **ER/VT-PDMS/CB and ER/VT-PDMS/DCP2/CB**

Polymer matrix ER/VT-PDMS was used for preparation with different concentration of CB from 0 to 15 wt. % (0 – 12 vol.%) was used as a conductive filler. Samles were prepared without and with DCP (2 wt.%). The certain amount of CB and ER/VT-PDMS or ER/VT-PDMS/DCP2 polymer blend as a matrix were placed into a beaker and stirred mechanically (IKA Labortechnik, Staufen, Germany) at 100 rpm for 1hr. The curing process was carried out in the same manner as described in Chapter 2.1.

## **2.3 Characterization of materials**

Phase *morphologies* of cured epoxy-polysiloxane polymer blends were investigated by a VEGA//LMU scanning electron microscope (Tescan) operated at accelerating voltage of 25 kV in SE imaging mode. Prior to examination, freeze-fracture surfaces of the samples were coated with a thin layer of Au/Pd because of the high sensitivity of the material to an electron beam. The *current-voltage (I-V) characteristics* were measured using programmable electrometer Keithley 6517A (USA). DC conductivity of the samples was determined from the measured I-V characteristics, area of electrodes and thickness of the sample. Measured data were fitted by percolation theory. *Dielectric measurements* were performed for a frequency sweep from 0.1 Hz to 10 MHz in the temperature range from –150°C to 80 °C with a measuring voltage amplitude of 1 V using a Concept 50 impedance analyser (Novocontrol, Germany) on disc samples (with a diameter of 13 mm and thickness less than 1 mm), which were cut out from the prepared sets of samples. The *rheological properties* were measured using a rotational rheometer (Bohlin Gemini, Malvern Instruments, UK) with disposable parallel plate geometry (25 mm diameter) in the oscillatory mode. Two different tests have been performed to determine the gelation time. The first one was performed at a constant frequency of 1 Hz under a strain of 0.05 and is henceforth referred to as a “single frequency test”. The evolution of rheological parameters such as complex viscosity,  $\eta^*$ , storage,  $G'$ , loss,  $G''$ , and viscoelastic moduli was recorded in time until the crossover of  $G'/G''$  occurred. All the

experiments were performed isothermally at 60 °C, 80 °C, and 100 °C. *Dynamic mechanical analysis* (DMA) was carried out with dual cantilever geometry in the dynamic (frequency/strain experiments) mode using a Q800 DMA instrument (TA Instruments, USA). The tested samples had a dimension of 35×10×3 mm. The analysis was carried out from –120 °C to 190 °C at a heating rate of 3°C/min at a fixed frequency of 1 Hz and at amplitude of 20 μm. *Charpy impact tests* were performed according to ISO 179 on unnotched izod specimens using an impact tester (Zwick/Roell, Germany). The dimensions of samples were 80×10×3 mm. The fracture mechanism of polymer systems was studied on the surface of fractured area via SEM. The mean values over five specimens are presented. The *lap shear strength* of the cured specimens was investigated with the use of a Universal tensile instrument (Instron 5567, UK) according to ISO 4587:2003. The test was performed at a rate of 5 mm/min at room temperature. All adhesion values were averaged over five samples. The substrates used in this method were steel sheets.

### **3 RESULTS AND DISCUSSION**

In the current work, the effect of siloxanes compatibilized with ERs by DCP on the mechanical properties of ER was investigated. The aim of the work is to determine the optimum composition of the epoxy-polydimethylsiloxane blend that results in improved toughness of the final composite.

#### **3.1 Effect of peroxide on the compatibilization of epoxy resin with polysiloxanes**

In this study, glycidyl epoxy for which the best performance and the highest crosslinking degree is achieved when they are cured via an addition reaction with amines is studied. Epoxies can undergo ring opening reactions towards nucleophiles [62]. For the compatibilization between ER and, it is necessary to introduce peroxide in the compound (Fig. 4).

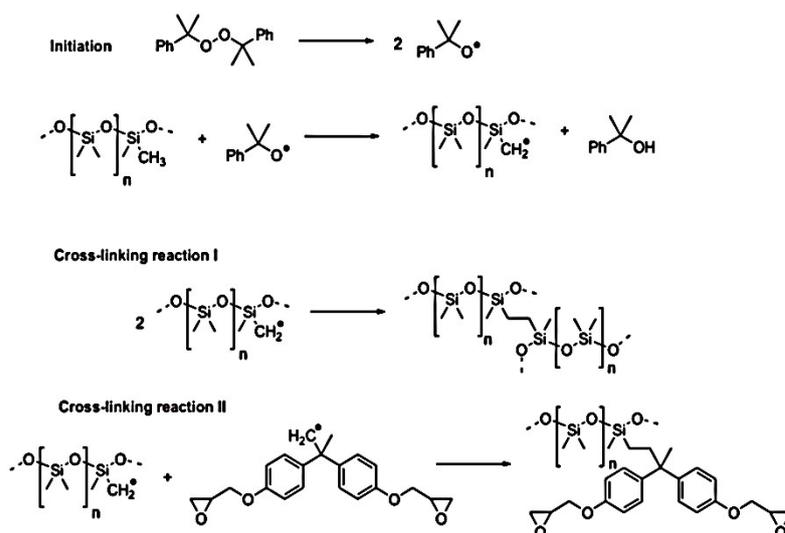


Fig. 4. Peroxides initiations and two possible chain scissions reactions. For the sake of transparency only middle parts of polysiloxane chains are depicted.

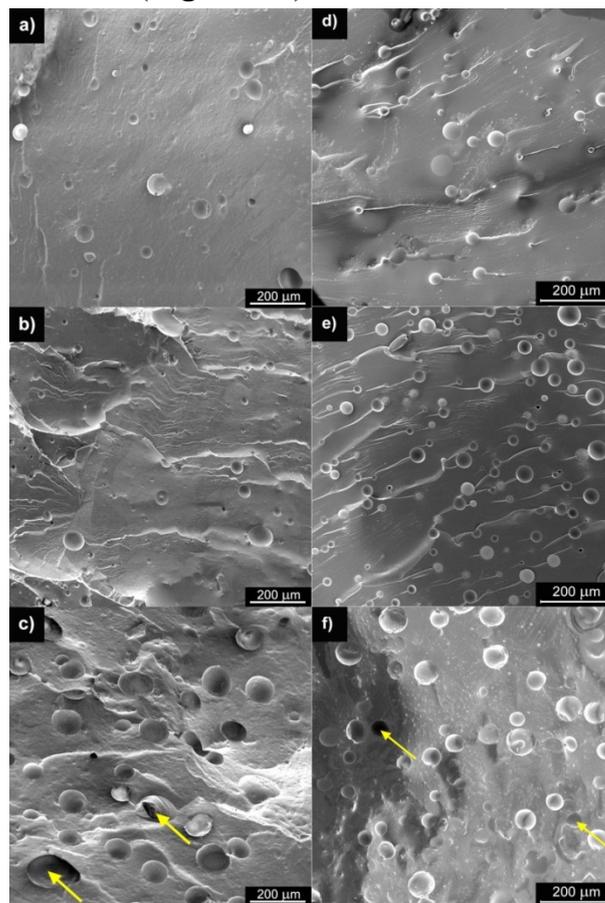
It is known that peroxides decompose to form free radicals, which abstract hydrogen atoms from polysiloxane. Hydrogen atom in macromolecules (ER or polysiloxane) is transferred to a reactive free radical (initiation stage). There are two possible essential models of crosslinking reactions: I) recombination reaction between two radicals of PDMS (curing of polysiloxane), and II) reaction between radicals of polysiloxane and DGEBA. There are approximately 800 of  $\text{CH}_3$  groups [400 mers] and only 2 vinyl groups per one polysiloxane macromolecule [ $M_n$  27.000]. Therefore, the probability of a reaction of radical with vinyl is very low compared to  $\text{CH}_3$ . Therefore, we do not consider that this reaction has any important role and we do not include it in the Fig. 4.

### 3.1.2 SEM morphology

Polysiloxane was added to uncured ERs, and, after cross-linking reactions, Elastomer modified ERs exhibited a two-phase microstructure consisting of relatively small (15-80  $\mu\text{m}$ ) elastomer particles dispersed in ERs due to its immiscible nature with the ER, which results in phase separation from the dominant epoxy component throughout the curing reaction (Fig. 5). Toughening of glassy polymers (such as thermosetting epoxy resin) with a soft low-modulus polymers occur when elastomer is introduced into the plastic [63-65].

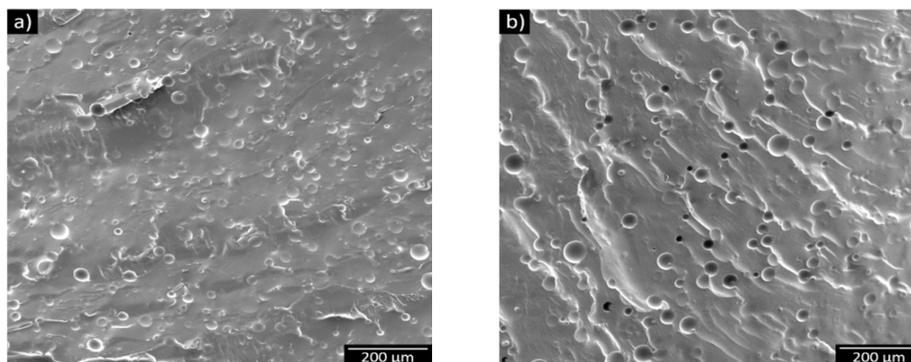
The soft dispersed phase of elastomer, however, provides not only an increase in the toughness (due to the ability to dissipate impact energy), but also an increase in strength under uniaxial tension and with other types of deformation, which is especially effective when thermosetting polymers are filled with elastomer [66-74]. It is true that in highly cross-linked epoxy polymers, plastic shear deformation is considered the main energy absorbing process, as can be seen in

our case for 5 and 10 % in both studied systems, where we can observe cracks propagating from rubber inclusions as these act as stress concentrators (Fig. 5a, b, d, e). However, increase of the elastomer concentration up to 15 wt. % leads to a different mechanism of energy absorption as can be seen by absence of cracks but appearance of damage zone around elastomer particles (Fig. 5 f). Damage zone presence is manifested by stress whitening region around elastomer particle comprising small holes. The presence of such holes (see yellow arrows) is interpreted as caused by the dilatational deformation of the particles and the matrix [71, 72] that nucleates local shear yielding of the epoxy matrix causing a significant crack tip deformation. The synergic effects of localized cavitation at the elastomer/matrix interface and plastic shear yielding in the epoxy matrix are supposed to be responsible for deformation that results in energy dissipation process, which ultimately improves the impact strength values of the elastomer-modified epoxies. Increase in elastomer concentration in the epoxy also leads to higher particle concentration per unit volume (e.g. Fig. 5 d, e) as well as the shift of particle size distribution towards slightly higher values such as in VT-PDMS (Fig. 5 e, f).



*Fig. 5 SEM micrographs for epoxy modified PDMS: a) ER/PDMS5, b) ER/PDMS10, c) ER/PDMS15, d) ER/VT-PDMS5, e) ER/VT-PDMS10, and f) ER/VT-PDMS15.*

Figure 6 shows a morphological comparison between modified ER/PDMS and ER/VT-PDMS by DCP. One can observe that DCP modification results in a more regular and homogenous distribution of the individual component in the blend.

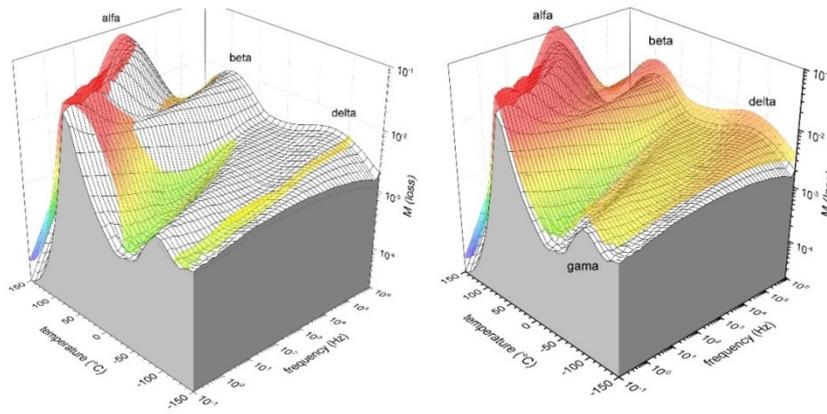


*Fig. 6. SEM micrographs for ER modified by polysiloxane and DCP (2 wt. %):  
a) ER/PDMS 10/DCP2 and b) ER/VT-PDMS10/DCP2.*

Upon addition of DCP, emulsification of ER and silicone elastomer take place, leading to a much finer dispersion and improved interfacial adhesion. The beneficial effect of DCP on the dispersion and interfacial adhesion of ER/PDMS and ER/VT-PDMS blends was examined by the investigation of the dynamic mechanical properties of the blends.

### **3.1.3 Dielectric properties**

Epoxy resin exhibits four relaxations processes – alpha, beta, gamma and delta (Figure 7). While the beta, gamma and delta relaxations follow the Arrhenius equation rather well with linear dependence of  $\ln f_{\max}$  on  $1/T$ , the alpha relaxation shows considerable bending in agreement with the Vogel–Fulcher–Tamman (VFT) model. Fitting experimental data to the Arrhenius model allows one to determine the activation energy of the observed relaxation process, which are following  $\beta = 326.0 \text{ kJ mol}^{-1}$ ,  $\gamma = 55.5 \text{ kJ mol}^{-1}$ , and  $\delta = 21.5 \text{ kJ mol}^{-1}$ .



*Fig. 7 Dielectric spectra comparison of ER/PDMS10 (a) and ER/VT-PDMS10/DCP2 (b); white surface in both figures shows pure ER spectrum for easier comparison.*

The VFT model does not explicitly contain activation energy as a parameter for alfa relaxation process. On the contrary, an ER/PDMS blend (Fig. 7 a) exhibits significant differences from ER spectrum which means there is no chemical bonding between PDMS and ER as in the previous case, which is mainly down to non-presence of compatibilizator.

### **3.1.4 Rheological properties**

Rheological measurements were carried out at different isothermal temperatures to characterize physical transformations such as gelation that take place during curing. Figure 8 depicts the typical rheological behaviour at 80°C through polymerization of neat ER and ER with DCP (ER/DCP2) with the time evolution of  $G'$  and  $G''$  of the developing gel. Initially, the system is in the liquid state with low stiffness and with  $G''$  dominating over  $G'$ , both almost constant in time. This zone represents the state of the system before the start of the curing process. However, as the curing and the resulting cross-linking progress, both viscoelastic moduli increase until a crossover of  $G'/G''$  occurs. This point shows that the gelation of the system is approximately 913 s for neat ER, while, for ER with DCP, it is only 638 s.

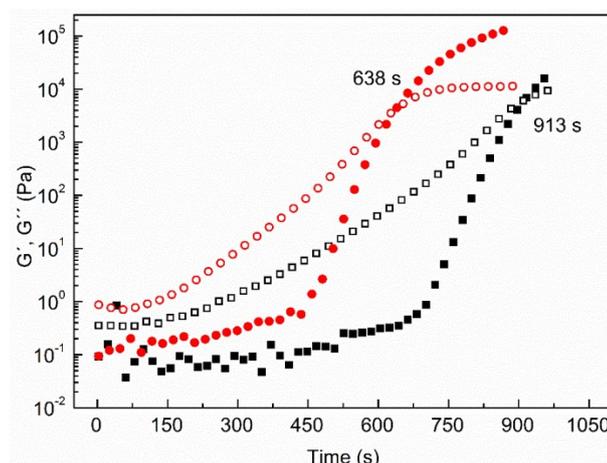


Fig. 8 Storage,  $G'$ , (solid) and loss,  $G''$ , (open) moduli as a function of time for: ER(■, □), ER /DCP2 (●, ○) at 80°C.

The results obtained show that DCP speeds up the curing of ER as far as it plays the role of a compatibilizing agent in polymer systems at all temperatures investigated (60-100) °C as indicated in Table 1. The compositions with DCP have also significantly lower curing time compared with the corresponding compositions without DCP for the systems ER modified by polysiloxane. It should also be noted that the curing time of resin generally modified by polysiloxane decreases with increasing polysiloxane content. The curing time variation is determined by the dissimilarity between the crosslinking density and the size of rubber domains [75]. As can be also seen in Table 1, a slight difference in  $G'/G''$  at the crossover point was observed in samples ER/VT-PDMS10/DCP2 (612 s) and ER /VT-PDMS10 (632 s), while samples ER /PDMS10/DCP2 (690 s) and ER /PDMS10 (815 s) exhibited a significant difference at this crossover point. Both of these shifts confirm that the addition of DCP speeds up the curing process and more significantly for ER systems modified by PDMS compared with its analogue modified by VT-PDMS. Furthermore, an increase in the curing temperature leads to a decrease in the curing time, which indicates that the curing process is thermally activated.

The results of a single-frequency test represent only an approximate gelation point since, as the transient gel network structure forms, stress relaxation also takes place. So, unless measurements on the gelling system are made extremely rapidly, the exact time of gelation is obscured by changes due to stress relaxation [76]. That is why the stress relaxation is precisely captured in a multiwave test. Apart from the discussion related to the single-frequency test, Table 1 summarizes also rheological gelation times for systems under investigation obtained via multiwave tests. Evidently, a variation in the gelation time

measured by two methods shows the same tendency, namely, the curing time decreases with DCP presence within the system as well as with incorporation of polysiloxane into the system. So, unless measurements on the gelling system are made extremely rapidly, the exact time of gelation is obscured by changes due to stress relaxation [77].

**Tab. 1 Rheological gelation times at  $T_{\text{cure}}$  of 60, 80, and 100 C for given polymers.**

<b>Samples</b>	<b>T(°C)</b>	<b>Single Frequency test</b>	<b>Multiwaves test</b>
ER	60	2642	2047
ER	80	913	782
ER	100	279	210
ER/DCP2	60	2292	2002
ER/DCP2	80	638	447
ER/DCP2	100	212	167
ER/VT-PDMS5	80	660	570
ER/VT-PDMS10	80	632	420
ER/VT-PDMS15	80	695	700
ER/VT-PDMS10/DCP2	80	612	449
ER/PDMS5	80	850	500
ER/PDMS10	80	815	453
ER/PDMS15	80	665	367
ER/PDMS10/DCP2	80	690	500

### **3.1.5 Mechanical properties**

#### **Dynamic mechanical properties**

Dynamic mechanical analysis is a powerful technique for the investigation of viscoelastic properties of polymer blends and composites as a function of the temperature and modified interfacial compatibility between different phases as well as for the determination of the glass transition temperatures ( $T_g$ ).

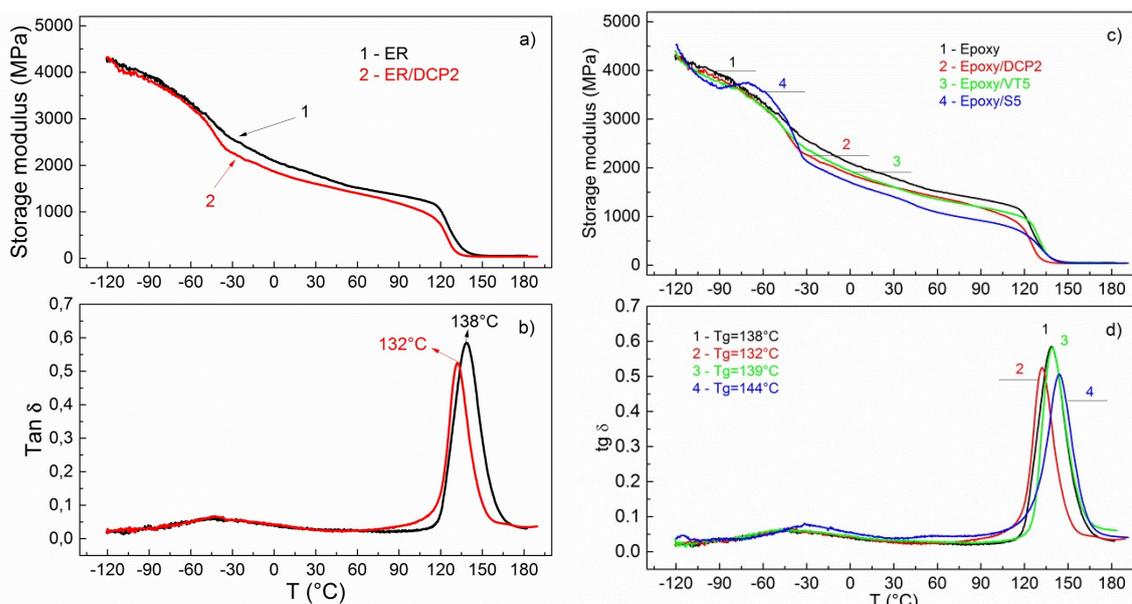


Fig. 9. Storage modulus (a) and loss factor (b) as a function of temperature for 1- ER, 2 - ER/DCP2 and storage modulus (c) and loss factor (d) as a function of temperature for 1- ER /VT-PDMS10, 2 - ER /PDMS10, 3 - ER /VT-PDMS10/DCP2 and 4 - ER/PDMS10/DCP2.

Storage moduli  $E'$  and loss factors  $\tan \delta$  of neat epoxy, epoxy with DCP and ER/polysiloxane blends with or without DCP are shown in Figures 9 a, b. As seen in Figure 9 a, the neat ER at -120 C exhibits a storage modulus of 4300 MPa; however, around -40°C, there is a first decrease in the storage modulus (2600 MPa), which corresponds to the movement of the side groups of the polymer chain (gamma-relaxation). A significant temperature drop of  $E'$  at 140°C can be related to the segmental motion of polymer chains (alpha-relaxation) in epoxy resins, which is in good agreement with the dielectric spectroscopy data (Figure 7). Typically, as the temperature approaches the  $T_g$ , the storage modulus markedly drops. The  $T_g$  was determined from as the maximum value of the  $\tan \delta$  peak. The neat epoxy resins showed  $T_g$  at 138°C. DCP (2 wt. %) was added to ER to improve the curing process. The addition of DCP decreased the storage modulus of the epoxy sample about 20% and shifted its  $T_g$  to lower temperatures about 6°C, which indicates changes upon the molecular structure. Figure 9 c, d shows storage moduli and  $\tan \delta$  curves of epoxy resins blended with 10 wt. % of VT-PDMS and PDMS. The addition of VT-PDMS and PDMS influenced viscoelastic properties of epoxy resins differently. Both polysiloxanes admixed with epoxy resins caused a formation of two phase systems. VT-PDMS decreased  $T_g$  of epoxy resins about 3°C and PDMS increased  $T_g$  of epoxy resins about 10°C. These differences may correspond with different end-functional groups of polysiloxanes, which control

their dispersion in epoxy resins as well as viscoelastic properties. The addition of DCP into epoxy resins/polysiloxane blends slightly increased stiffness, which can indicate the improvement in the compatibility between epoxy resins and polysiloxane due to the new chemical interactions. Moreover, the lower values of  $T_g$  indicate that DCP could reduce a crosslinking density of epoxy resins/polysiloxane.

### Impact strength

The highest impact strength was recorded in ER/VT-PDMS10/DCP2 with value of  $17 \pm 2 \text{ kJ/m}^2$ , which equals a 70 % improvement. The enhancement of impact strength in the DCP modified blends is due to the higher density of the network and inter-chain bonds in ER. The formation of inter-chain bonds is supposed to take place during the melt blending (Fig. 10). The improvement in the toughness of the polysiloxane systems stems from the reduction in the crosslinking density and, to a lesser extent, from flexibilization. The increase in the impact strength, toughness behaviour of ER/VT-PDMS samples showed a better energy-transfer mechanism because of the excellent interfacial adhesion and bonding with the matrix.

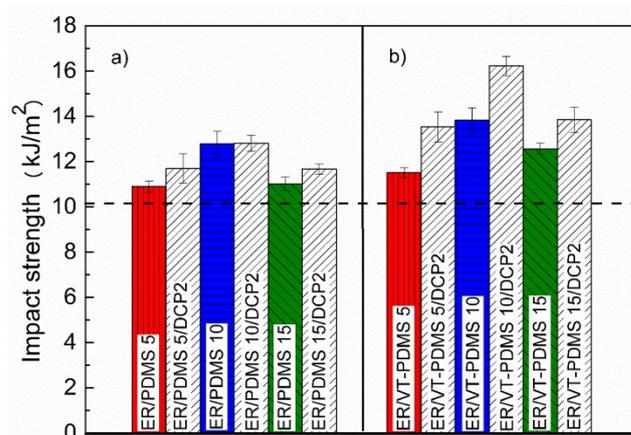


Fig. 10 Impact strength of epoxy polymer blends with (a) PDMS and (b) VT-PDMS polymer. Dashed line is for neat epoxy.

### Lap shear strength

Adhesive bonding properties of ER and its polymer blends with polysiloxane and DCP were investigated on metal plates. Samples with polysiloxane without DCP show lower values ( $379 \pm 22 \text{ kgf}$ ) than the neat resin ( $417 \pm 31 \text{ kgf}$ ). The maximum value of lap shear strength was observed for 10 wt% of VT-PDMS in the presence of 2 wt.% of DCP ( $431 \pm 27 \text{ kgf}$ ). This result shows that peroxide improves the interfacial adhesion between ER and polysiloxane.

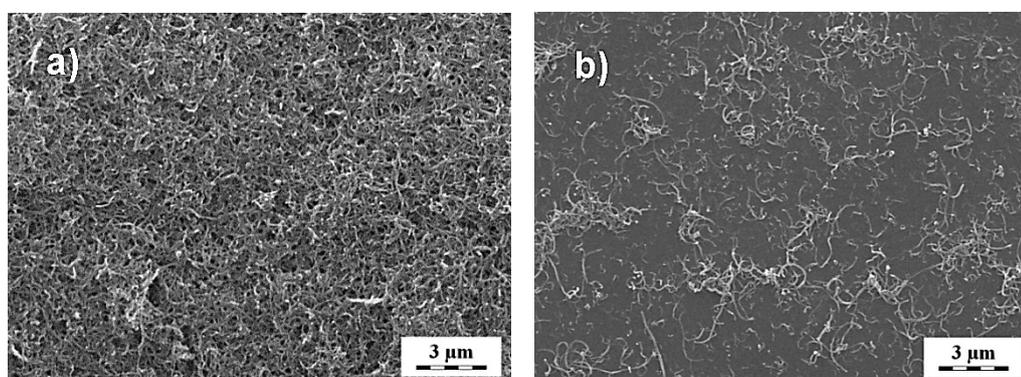
## 3.2 Polysiloxane composites filled with CB and CNT

### 3.2.1. A solvents dispersion method for modification of CNT

The CNTs (1 g) were dispersed in 40 ml of neat NMP by ultrasonic treatment. The ultrasonic treatment has been carried out at 40 % amplitude and 0.4 cycles for 1 hr. After sonication, the visual inspection confirmed the absence of aggregates in all dispersions. The dispersion was immediately vacuum-filtered through binder-free glass fiber filters with 125  $\mu\text{m}$  porosity. After filtration, the CNT-NMP was dried in drying oven (Binder, ED, USA) at 200 °C from 2 hrs. to 1 day. As can be seen from Fig. 11b modified CNTs are dispersed better than raw CNTs (Fig. 11 a).

### 3.2.2. PDMS/CNT-NMP composite - Sonication

Several composites of different filler concentrations (0, 1, 2.2, 2.8, 4 and 4.5 vol. %) were prepared. The certain amount of CNT-NMP, 15 ml of acetone and PDMS were placed into 50 ml beaker and sonicated by an UP 400s ultraprobe. The sonication frequency, power and time were 24 kHz, 400 W and 5 minutes, respectively. Then the beaker with the mixture was placed into the dish with hot oil (60°C) and mixed using magnetic stirrer until evaporation of whole acetone. Prepared mixture was subsequently filled into the mold and placed into the vacuum desiccators for the removal of air bubbles. Finally, the mold was closed and placed into drying oven where material cured at 70°C for 12 hrs.



*Fig.11 SEM image of raw CNTs a) before surface modification and b) after modification by NMP.*

### 3.2.3. DC electrical conductivity

We presume that once the volume fraction of CNT reaches a critical value, i.e. the percolation threshold, the new conductive structure starts to form. This indicates a phase transition from insulator to conductor state. Fig. 12 shows the dependence of DC specific conductivity against conductive filler content in composites. As regarding the pure polysiloxane matrix, it is an electrical

insulator with very low value of conductivity.

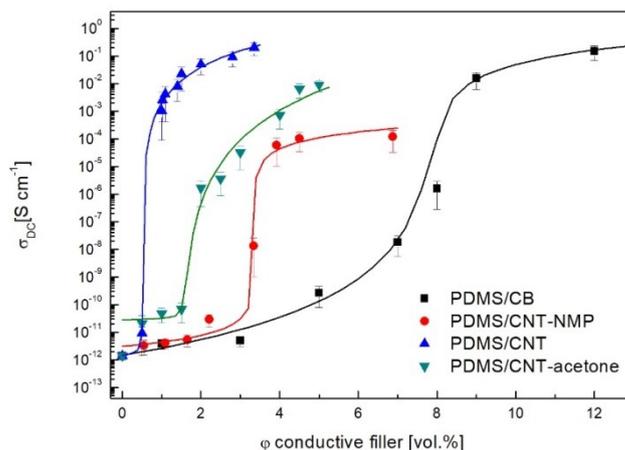


Fig. 12 The dependence of electrical conductivity  $\sigma_{DC}$  on the conductive filler content in the composite.

The values of electrical conductivity of the PDMS/CNT increased by more than nine orders of magnitude, i.e. from  $10^{-12}$  to  $10^{-3}$  S cm<sup>-1</sup> compared with PDMS matrix ( $\sigma_{DC} = 5 \cdot 10^{-12}$  S cm<sup>-1</sup>). The value of percolation threshold of PDMS/CNT was reached at low content of conductive filler ( $\phi_c \sim 1$  vol. %), which is caused by poor dispersion and big bundles (agglomeration) where charge carriers are transported through conductive bundles of CNTs. A different behaviour is noted for the CNT modified by NMP and acetone, which caused insulation and separation of CNTs and exerted influence on the shift of percolation threshold to higher value ( $\phi_c \sim 4$  vol. %, 2,5 vol. %). This value of percolation threshold for CNT-NMP and CNT-acetone composite indicates good dispersion of CNTs in the PDMS. The separation of CNTs decreases the probability of percolation cluster formation but increases the area of the CNT-polymer matrix interface. As can be seen, the good dispersion of CNTs shifts  $\phi_c$  to the higher value. The percolation threshold of polymer composites with CB amounts to 9 vol. %. Such a high value of percolation threshold is caused by low aspect ratio of filler. Generally, it is known that with an increase in the aspect ratio of filler the percolation threshold shifts to higher values. Aspect ratio can significantly influence behaviour of polymer composites in AC electric field. The particular filler (CB) has  $L/D \approx 1$ , on other hand, fibrous filler (CNT) has  $L/D \approx 10^2 - 10^3$ , which can significantly influence the concentration of charge carriers at the end of fibrous filler and change values of  $\epsilon'$ .

### 3.3 Effect of epoxy-polysiloxane blends microstructure on mechanical and electrical properties of nanocomposites.

#### 3.3.1. CNT nanocomposites

Blending immiscible polymers is one of the most cost-effective methods to develop new materials with enhanced properties and performance than existing polymeric materials. It is well known that electrical conductivity of polymer blends filled with electrically conductive fillers depends on the percolation of the polymer phases and the percolation of the filler particles.

In the Fig. 13a, we can see comparison electrical properties of three types of nanocomposites with polymer matrix (VT-PDMS, ER and SEF) and dispersive (CNT-aceton) carbon nanotubes (experimental data fitted by percolation model). CNT are strongly entangled forming aggregates due to Van der Waal's forces and to create polymer nanocomposites they have to be uniformly dispersed throughout the polymer matrix. CNTs were sonicated in solvent in order to achieve regular, homogenous distribution. It can be seen that the percolation threshold has significantly shifted to lower concentration for SEF/CNT composite (0.6 vol. %) compared to 1.3 vol. % in the case of ER/CNT and VT-PDMS/CNT. However, CB exhibited substantial difference in percolation threshold depending on the used polymer matrix (Fig. 13 b).

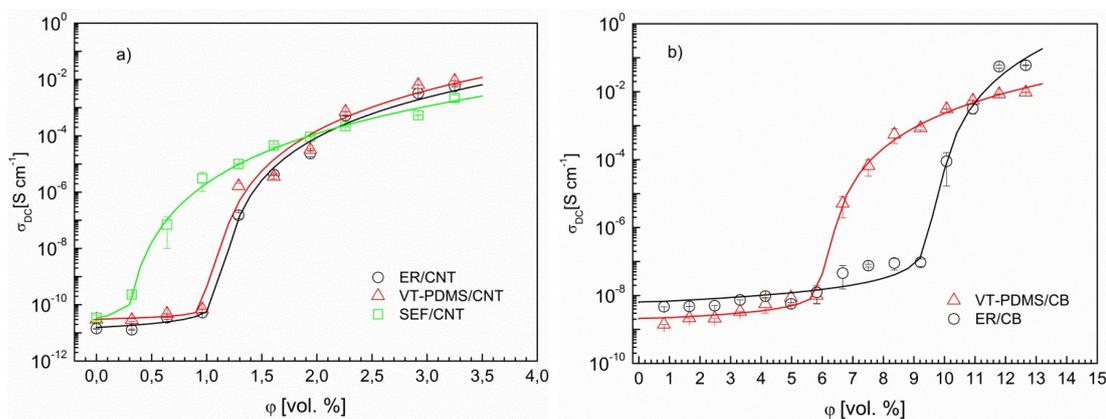


Fig.13. The dependence of DC electrical conductivity on conductive filler  
a) CNT b) CB, content for polymer nanocomposites.

While ER/CB has a critical concentration of about 10 vol. %, CB mixed in VT-PDMS/CB shows decrease in percolation to 7 vol. %. This is probably due to different crystallinity of these two matrixes. Comparing CNT and CB, it can be seen that CNT based composites have much lower percolation threshold (~1 vol.%) compared to CB (7 and 10 vol. % respectively; depending on matrix).

This is a result of different aspect ratio of each filler, where CNT clearly dominate. Another way to even further decrease the value of electrical percolation threshold is to utilize so-called *double percolation*. The idea of double percolation introduces two polymers resulting in a polymer blend, which is subsequently filled with filler (Fig. 14). Such polymer blend must have co-continuous morphology so that both phases are said to be percolated. Finally, conductive filler has to be selectively dispersed in a continuous phase, which is ideally a minor component in order to get low percolation threshold.

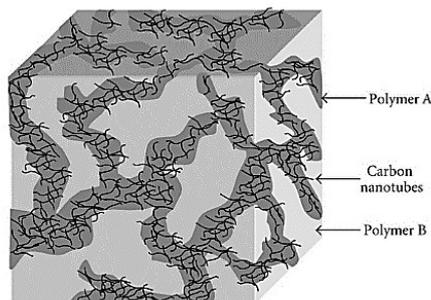


Fig. 14. Schematic illustration of the double percolation phenomenon.

In the case of our blend only one of the phases is continuous (ER) while the other (polysiloxane) is present in the form of isolated inclusions creating so called “sea island” structure. Filler (CNT, CB) is then dispersed in the continuous phase. Based on so obtained results of electrical percolation threshold, multicomponent systems (immiscible and partially miscible) with constant CNT content  $\sim 2$  wt. % (1.3 vol. %) were prepared. The dependence of DC electrical conductivity on increasing volume ratio between polysiloxane (VT-PDMS and SEF) and ER (Fig. 15). The dramatic increase is registered at 5 wt. % PDMS and 20 wt. % SEF near the percolation threshold. The percolation threshold is reached at ER/VT-PDMS/CNT2 and ER/SEF/CNT2.

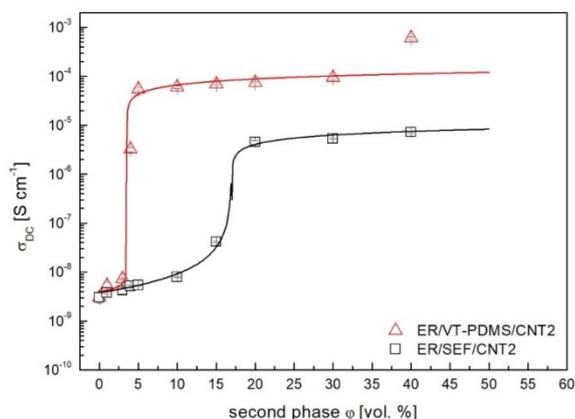
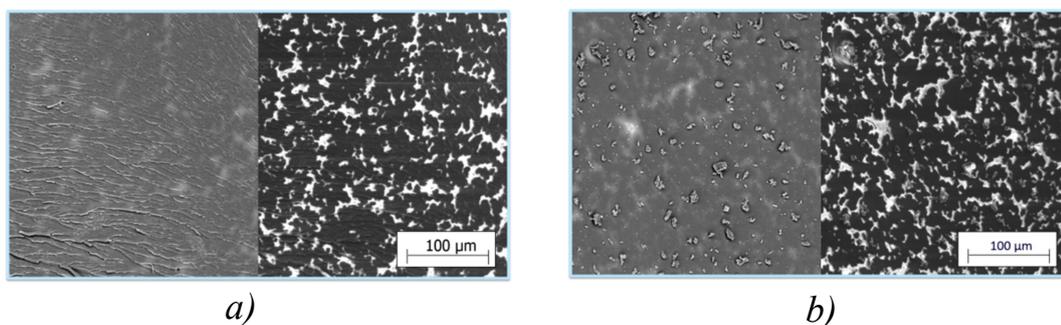


Fig. 15 The dependence of DC electrical conductivity on increasing content of PDMS and SEF in nanocomposites containing 2 wt. % of CNT. Experimental data is fitted by a percolation model vyhodit fitting (volume %).

It is established that the electrical properties of nanocomposites are influenced not only by the content of the CNT but also by the microstructure of the polysiloxane – epoxy resin system. Morphology was studied by scanning electron microscopy, in Fig. 16 a, we can see phase structure of nanocomposite ER/VT-PDMS/CNT2, for which jump change of electric conductivity (from  $10^{-9}$  to  $10^{-5}$  S cm<sup>-1</sup>) was observed.



*Fig. 16 SEM micrographs of multicomponent polymer nanocomposites a) ER/VT – PDMS5/CNT2 and b) ER/SEF20/CNT2.*

CNT are homogeneously dispersed in ER because its surface energy ( $50$  mJ/m<sup>2</sup>) is close to CNT value ( $54$  mJ/m<sup>2</sup>) while VT-PDMS exhibit values predominantly around  $30$  mJ/m<sup>2</sup>, thus confirming our initial assumption of low affinity of CNT towards VT-PDMS. On the other hand, multicomponent polymer nanocomposite ER/SEF20/CNT2 percolated only at 20 wt.% with conductivity of one order lower. The microstructure of this composite is shown in Fig. 16 b. For ER/VT-PDMS5/CNT2 we can observe a brittle structure of ER with VT-PDMS dispersed therein. ER/SEF20/CNT2 exhibits different structure with “sea islands” i.e. polysiloxane create integrated homogeneously dispersed particles of ER; thus, we can see miscibility between ER and SEF, however there is also a partial separation of polysiloxane component in the shape of anisometric droplets. Both systems created irregular droplets. This demonstrates that the systems are partially miscible. Both systems comprise homogeneously dispersed droplets of polysiloxane – a proof of an appropriate choice of preparation method. As can be seen, the change in morphology is small at low mixing ratios of components which results in big distance between individual nanotubes.

### 3.3.2. CB nanocomposites

CB particles are mixed with an immiscible matrix consisting of epoxy and polysiloxane, CB can be dispersed in epoxy or polysiloxane or at the interface between. Sumita et al [84] exposed that the localization of the CB is determined by the wetting coefficient ( $\omega$ ) that is defined by the following equation:

$$\omega = \frac{(\gamma_{CB-PDMS} - \gamma_{CB-ER})}{\gamma_{ER-PDMS}} [4]$$

Where  $\gamma_{CB-ER}$  is the interfacial tension between epoxy and carbon black,  $\gamma_{CB-PDMS}$  is the interfacial tension between silicone and carbon black,  $\gamma_{ER-PDMS}$  it the interfacial tension between epoxy and polysiloxane. The localization of CB particles is predicted by the following conditions:  $\omega > 1$  CB particles are localized in ER;  $-1 < \omega < 1$  CB are localized at the interface (where  $\omega=0.85$ );  $\omega < -1$  CB particles are localized in VT- PDMS. Surface tension of uncured DGEBA is  $50.6 \text{ dyn cm}^{-1}$ [78], CB has  $34.4 \text{ dyn cm}^{-1}$  [78] and surface tension of VT-PDMS is  $21.6 \text{ dyn cm}^{-1}$  [79].

The location of conductive filler and the phase morphology of the composites could considerably affect the electrical properties of the polymer blends, and it is clear that the phase morphology can be changed by adjusting the CB concentration and the ER/VT-PDMS ratio. Fig. 17a, shows the electrical conductivity of ER/VT-PDMS/CB composites with and without DCP as a function of CB content. In both systems recorded percolation threshold (0.5 and 1.5 vol. % for with and without DCP respectively) is approximately ten times lower than for ER/CB (see Fig. 17 b). This dramatic shift of percolation is most probably due to double percolation effect and the fact filler is dominantly located at phase interface ( $= 0.85$ ). However even incorporated DCP affects blends percolation threshold and shifts it from 1.5 to 0.5 vol. %.

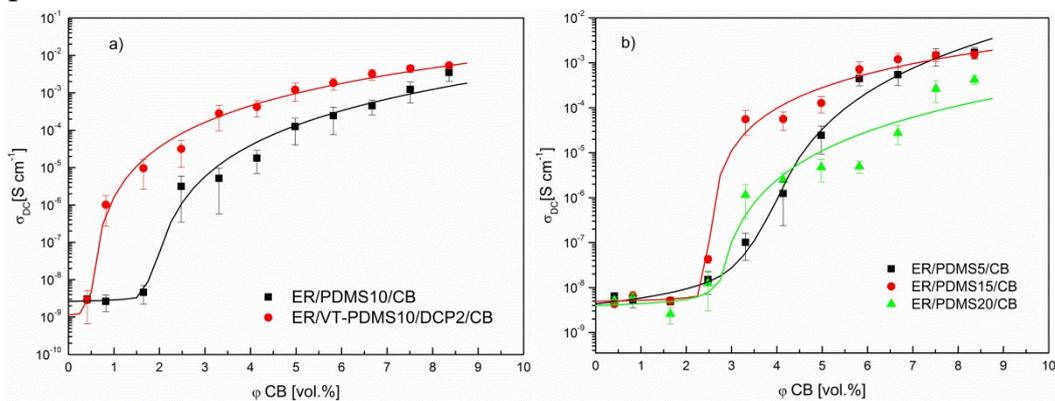


Fig.17 a) The influence of DCP on percolation threshold of CB filled polymer blends and b) Influence of elastomer phase on the percolation threshold.

The percolation threshold in polymer blends was also studied in relation to the polysiloxane content (Fig. 16 b). As can be seen there is no clear influence of polysiloxane on percolation threshold however the shape of the curve namely around the percolation threshold is altered for systems with polysiloxane content above 5 vol. %. Fig. 18 shows the morphology of the ER/VT-PDMS/CB and ER/VTPDMS/DCP2/CB. The ER/VT-PDMS/CB composite without DCP shows typical sea-island morphology, in which VT-PDMS irregular droplets several micrometers (5-10  $\mu\text{m}$ ) large are dispersed in the ER phase (Fig. 18 a). On the other hand, 2 vol. % of DCP in composites leads to the more regular spherical droplets however their size distribution is wider (Fig. 18 b). The regularity of polysiloxane spheres is due to the compatibilization efficiency of the DCP.

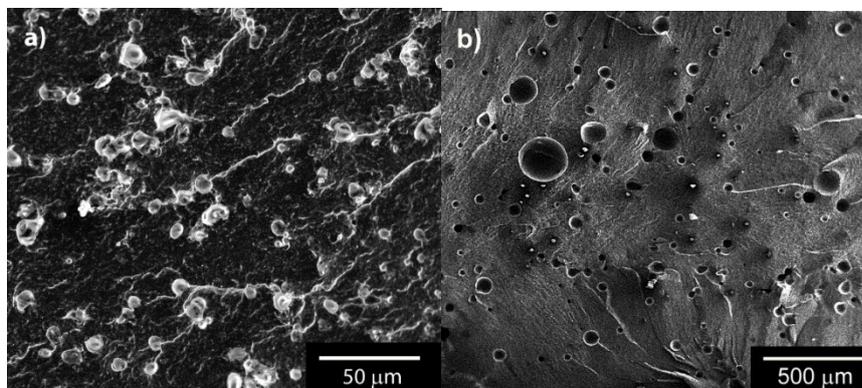


Fig.18. SEM images of a) ER/VT-PDMS10 and b) PDMS10/DCP2/CB at 7 vol% CB.

To investigate the impact strength of the epoxy-silicone blends with carbon black we have conducted Charpy impact tests. The results are plotted in Fig. 19.

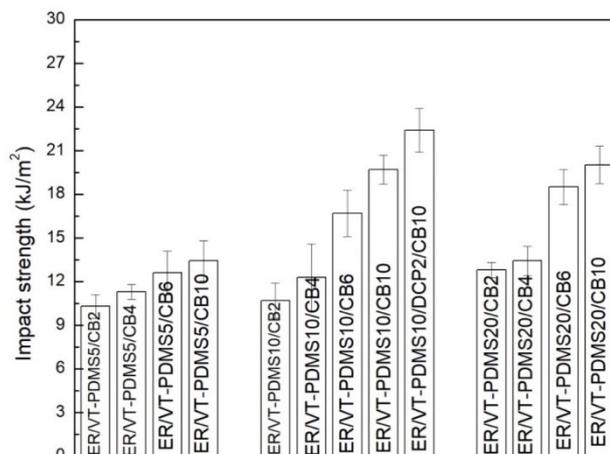


Fig. 19 Impact strength of epoxy-polysiloxane blends with CB.

It is verified that the increasing of CB content improves the impact strength. Although the error bars do overlap to some degree, the general trend is that the impact strength increases with VT-PDMS and CB content. Even though increasing concentration (2–10 wt.% equal to 1–7 vol. %) of CB enhances blend's toughness for all investigated systems, steepest dependence was recorded with ER/VT-PDMS10/DCP2 blend. In this case nanocomposite containing 7 vol. % of CB exhibited a remarkable improvement of the impact toughness by more than 23 % (from 17 to 22 kJ/ m<sup>2</sup>) confirming the synergic effect of DCP (2 vol. %) and CB.

## CONCLUSIONS

- It is established that microstructure of epoxy-polysiloxane immiscible blends has great influence on the mechanical properties, namely whether or not there is compatibility between polymer phases. Therefore, the morphology of the blends was controlled through selection of elastomeric phase (PDMS, VT-PDMS) and its content together with the use of certain concentration of compatibilizator (DCP).
- Optimal composition leading to 70% enhancement of ER toughness (17 kJ/m<sup>2</sup>) without significant reduction of polymer system modulus (2 GPa), glass transition temperature (138 °C) and interfacial adhesion (lap shear strength of 430 kgf) was found for ER filled with 10 wt. % of VT-PDMS and 2 % of DCP. This stemmed from transition from brittle to ductile fracture mechanism registered by SEM morphology and DMA investigations.
- In order to obtain electrically conductive systems, binary polymer matrix was filled with conductive filler (CNT, CB). Especially for CNT-based composites, special attention was paid to CNT surface modification and its distribution within polymer matrix. Value of percolation threshold was found to heavily depend on aspect ratio of filler and to some extent on used polymer matrix. Thus, depending on the matrix CNT percolated at about 0.5–1 vol. %, while CB only at 7–10 vol. %.

## FUTURE PROSPECTS

We intend to apply our processing technology and experience with various ER-polysiloxane blends to create new materials with improved mechanical properties that would be achieved by the compatibilising effect of components in

blends. In addition, we plan to use our technology for the design of efficient composite materials with controlled electrical properties for shielding of electromagnetic radiation that is required for many applications. For example, use of composite material such as antistatic coating, electromagnetic shielding material, electroconductive glue.

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## **ABBREVIATIONS AND SYMBOLS**

CNT	Carbon nanotubes
PVA	Polyvinylalcohol
DGEBA	Diglycidyl ether bisphenol A
DBSA	Dodecylbenzensulfonic acid
PDMS	Polydimethylsiloxane
DETA	Diethylenetriamine

MPS	Multiphase Polymer Systems
p	Aspect ratios
DMA	Dynamic Mechanical Analyze
DSC	Differential Scanning Calorimetry
SWNT	Single-wall carbon nanotubes
CB	Carbon black
MWNT	Multi-wall carbon nanotubes
$\sigma$	Electrical conductivity
DCP	Dicumyl peroxide
ER	Epoxy resin
T	Temperature
TGMDA	Tetraglycidyl methylene dianiline
TTT	Triethylenetriamine
TGDDM	Tetraglycidyl- 4,4"-diaminodiphenylmethane
DEAPA	Diethylaminopropylamine
$T_g$	Glass transition temperature
$\Delta G_m$	Gibbs free energy of mixing
$T_{cure}$	Curing temperature
$\Delta G_m$	Gibbs free energy of mixing
$\Delta G_m$	Gibbs free energy of mixing
$\Delta H_m$	Enthalpy of mixing
$\Delta S_m$	Entropy of mixing
CTBN	Carboxyl terminated butadiene acrylonitrile copolymers
R	Universal gas constant
ATBN	Amine terminated butadiene acrylonitrile copolymers
CTAB	Cetyltrimethylammonium bromide
HTBN	Hydroxyl terminated butadiene acrylonitrile copolymers
DMF	N,N-dimethylformamide
NMP	N-methyl-2-pyrrolidone
$T_{curie}$	Curie temperature
CPC	Conductive polymer composites
DC	Direct current
AC	Alternating current
$\phi_c$	Volume fraction of filler at PC
PC	Percolation threshold
SEM	Scanning Electron Microscopy
VT-PDMS	Polydimehtyl siloxane vinyl terminated
ER	Epoxy resin
MEK	Methyl ethyl ketone peroxide
BP	Benzoyl peroxide
VFT	Vogel–Fulcher–Tamman
SEF	Silikopon EF

## LIST OF FIGURES

Fig. 1 SEM photographs of the of fillers: a) CB (acethylene blacks, Cabot, USA), b) CNTs (MWNT-2040, Conyuan Biochemical Technology, Taipei, Taiwan),	p. 8
Fig. 2 Plots of Gibbs free energy of mixing ( $\Delta G_m$ ) for a) miscible b) immiscible c) partly miscible blends [31].	p. 10
Fig. 3 Schematic of the variation in volume resistivity ( $\rho$ ) of a multiple percolation composite and corresponding morphology	p. 13
Fig.4 Peroxides initiations and two possible chain scissions reactions. For the sake of transparency only middle parts of polysiloxane chains are depicted.	p. 19
Fig. 5 SEM micrographs for epoxy modified PDMS: a) ER/PDMS5, b) ER/PDMS10, c) ER/PDMS15, d) ER/VT-PDMS5, e) ER/VT-PDMS10, and f) ER/VT-PDMS15.	p. 20
Fig.6 SEM micrographs for ER modified by polysiloxane and DCP (2 wt. %): a) ER/PDMS 10/DCP2 and b) ER/VT-PDMS10/DCP2	p. 21
Fig. 7 Dielectric spectra comparison of ER/PDMS10 (a) and ER/VT-PDMS10/DCP2 (b); white surface in both figures shows pure ER spectrum for easier comparison.	p. 22
Fig. 8 Storage, $G'$ , (solid) and loss, $G''$ , (open) moduli as a function of time for: ER(■, □), ER /DCP2 (●, ○) at 80°C.	p. 23
Fig. 9. Storage modulus (a) and loss factor (b) as a function of temperature for ER, 2 - ER/DCP2 and storage modulus (c) and loss factor (d) as a function of temperature for 1- ER /VT-PDMS10, 2 - ER /PDMS10, 3 - ER /VT-PDMS10/DCP2 and 4 - ER/PDMS10/DCP2.	p. 25
Fig. 10 Impact strength of epoxy polymer blends with (a) PDMS and (b) VT-PDMS polymer. Dashed line is for neat epoxy.	p. 26
Fig. 11 SEM image of raw CNTs a) before surface modification and b) after modification by NMP	p. 27
Fig. 12 The dependence of electrical conductivity $\sigma_{DC}$ on the conductive filler content in the composite	p. 28
Fig.13 The dependence of DC electrical conductivity on conductive filler a) CNT b) CB, content for polymer nanocomposites.	p. 29
Fig. 14 Schematic illustration of the double percolation phenomenon.	p. 30
Fig. 15 The dependence of DC electrical conductivity on increasing content of PDMS and SEF in nanocomposites containing 2 wt.% of CNT. Experimental data is fitted by a percolation model vyhodit fitting (volume %)	p. 30
Fig. 16 SEM micrographs of multicomponent polymer nanocomposites	p. 31

a) ER/VT – PDMS5/CNT2 and b) ER/SEF20/CNT2.	
Fig. 17 a) The influence of DCP on percolation threshold of CB filled polymer blends and b) Influence of elastomer phase on the percolation threshold.	p. 32
Fig. 18 SEM images of a) ER/VT-PDMS and ER/VT-PDMS/DCP2/CB at 7 vol. % CB	p. 33
Fig. 19 Impact strength of epoxy-polysiloxane blends with CB	p. 33

## LIST OF TABLES

Tab. 1 Rheological gelation times at $T_{\text{cure}}$ of 60, 80, and 100 C for given polymers.	p. 24
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