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Reduced percolation threshold of conductive adhesive through nonuniform filler localization: Monte Carlo simulation and experimental study

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ABSTRACT

Adhesive nickel based polymer composites were investigated experimentally and by computational modelling with respect to optimization of electrical and mechanical properties. Utilization of polymer blends with an optimized combination of epoxy resin (ER) and polydimethylsiloxane (PDMS) resulted in a reduced electrical percolation threshold (EPT) from 7.9 up to 3.7 vol % of Ni and increased the direct current (DC) conductivity of the composites by 7 orders of magnitude. At the same time, adhesion of the composites was enhanced by 20% and impact strength by 75% due to the PDMS addition. The observed effect of the EPT reduction is determined by the preferred localization of conductive Ni particles near the ER phase, specifically on the ER/PDMS interface. Prior to the composite preparation, the polymer composites were simulated by the Monte Carlo method and were evaluated by two independent methods: i) the growth of the conductive networks was examined by the size of aggregates via aggregation number (script in Python) ii) the conductivity of the polymer composites was calculated via finite element method (FEM, Digimat-FE 6.1.1). The computational simulations correlated well with the experimentally determined EPT and conductivity of the polymer composites.

Keywords: Composite materials Electrical properties Computational modelling Finite element method (FEM)

1. Introduction

Conductive polymer composites (CPCs) have attracted interest from the scientific community as well as industry for their potential applications in various fields of science and technology: electroconductive adhesives (an alternative to soldering), anticorrosion coatings, antistatic materials, marine and space technology, electromagnetic wave shielding (stealth technology), light emitting devices etc. [1]. CPCs consisting of an insulating polymer matrix becomes electrically conductive if a conductive path is created by the addition of a minor phase conductive filler. The conductive path may be a complex multi-scale structure consisting of interconnected particle aggregates forming infinite clusters. Such aggregates stabilize through particle-particles interactions; their size can be visualized by scattering electron microscopy and evaluated by an aggregation number N_{agg} [2]. Percolation theory is relatively successful in predicting the general conductive characteristics of CPCs materials. The distance of conducting particles converge to a percolation distance where the transfer of charge carriers between them is probable. The concentration at which the insulator-conductor transition occurs is called the electrical percolation threshold (EPT) [3]. There have been many attempts to reduce the percolation threshold of CPCs using fillers of different sizes and shapes [4] such as spherical (carbon black (CB) or metal powder [5,6]), fibrous (carbon nanotubes (CNT) [7]), flakes (graphite [8] and asymmetric - arbitrary ellipsoid (nickel [9])). Nickel, in addition to its high conductivity and ferromagnetic properties is also a relatively inert material. According to Scher-Zallen, the percolation limit, calculated for a model system of randomly localized conducting spherical particles in 3D matrix, is around 16 vol % [10]. To effectively reduce the percolation threshold, a novel hierarchical structure of composites, i.e. double percolation threshold (DPT) was developed [5,6, 11]. In the classic double percolation structure, so called percolation-within-percolation [6], the conductive fillers are selectively located in one phase of the co-continuous polymer blend, which means that the fillers only need to form a percolated conductive network throughout their hosting phase. For instance, Gao et al. reported that the percolation threshold of poly(-ether ether ketone)/CB and polyimide/CB composites was reduced from 10 wt% to 5 wt% because of the formation of a double percolation structure in poly(ether ketone)/-polyimide/CB composite [11].

Usually, the particle localization in immiscible polymer blends is heterogeneous, often with the particles preferentially localized only in one phase or at the interphase of the two phases [5]. This preference stems from the different strength of interactions between particles and the immiscible polymer phases, which can be described through the balance of interfacial energies [12]. Generally, polymer chains are losing their conformational entropy if they stretch around solid particles resulting in an increase of entropic over enthalpic interactions. For systems with similar interfacial energies, the particle arrangement can be also be influenced by the melt viscosity of the polymers [13,14].

There have been many attempts to predict the percolation threshold of polymer composites, however, each model has its own limitations and simplified assumptions (i.e. monodisperse particle size distribution [10]). The Monte Carlo (MC) simulation is an effective method to simulate the random dispersion of conductive fillers in a matrix and is often employed to analyze the electrical percolation of composites [8, 15]. Therefore, numerical simulations which are now available by means of Monte Carlo sampling, random sequential addition and computational homogenisation are applied to the study of the percolation threshold concentration of CPCs [16,17], e.g. Dalmas et al. [16] simulated the percolation threshold for fibrous CNT, while, Zhuo-Yue Xiong et al. [17] investigated a hybrid system containing CNT and CB. Musino et al. [2]. used computational modelling to study the rheological induced percolation threshold of spherical silica particles. Moreover, composite materials generated through MC are often used in the calculations of electrical conductivity by finite element method (FEM). The principle of FEM is discretization of the volume continuum (via mesh generation) into finite

smaller segments which are calculated separately [18]. However, for systems exhibiting a double percolation threshold, there are not any appropriate models and thus computer modelling is necessary for predicting the CPCs electrical conductivity, due to the complicated multi-phase morphologies [19]. The computational homogenisation technique assumes the material to be sufficiently homogeneous at the macro-scale but heterogeneous at the micro-scale due to the existence of inclusions [20].

In the current work, the effect of composition on electrical properties of an immiscible polymer blend filled with Ni particles has been investigated experimentally and through computational simulation. The aim of the study is to lower the value of EPT and enhance the mechanical properties of composites including lap shear and Charpy impact strength.

2. Theoretical background

2.1. Electrical percolation threshold

When the conductive fillers reaches a critical value, i.e. the EPT, the first conductive structure starts to form. Thus, the electrical conductivity of epoxy polymer composites depends on the concentration of conductive nickel particles. However, if a second polymer phase is added, part of the sample is inaccessible to the conductive filler, which is more concentrated inside the first polymer phase, leading to a lowering of the EPT. The conductivity of polymer composite material above the EPT can be calculated as:

$$\sigma = \sigma_f (\phi - \phi_c)^n \quad (1)$$

Where σ is the conductivity, σ_f is the conductivity of the filler ϕ_c is the percolation threshold volume concentration, ϕ is the conductive filler volume concentration and n is a scaling parameter.

2.2. Computer modelling

The probability of the formation of a conductive path in the composite was simulated by the three-dimensional continuum Monte Carlo method [18,21]. **Fig. 1a** presents the flowchart of the simulation procedure that was employed. The simulation consists of two steps. Firstly, the generation of a microstructure and the evaluation of aggregates by a Python coded script; and secondly, the simulation of electrical loading in the commercially available software Digimat. The MC model is based on the cubic RVE (relative volume element) with edge length L_{RVE} that is filled with randomly localized spherical conductive particles and nonconductive matrix [18]. Hard Ni particles are set as non-intersecting spheres and hence, particle contact is not probable. Therefore, the contact of the particles is achieved by increasing the radius of all conductive inclusions by the coating with the same thickness t (**Fig. 1c**). A group of particles that are electrically connected are termed an aggregate. The conductive particle is considered to participate in the aggregate if the coating of the particle intersects with the coating of any other particle of this aggregate (the algorithm searches for particle-particle distance $\leq 2t$). One possible evaluation method of the particle configuration produced by the simulation is the aggregation number (N_{agg}) which is the number of particles in an aggregate, as discussed by Musino et al. [2].

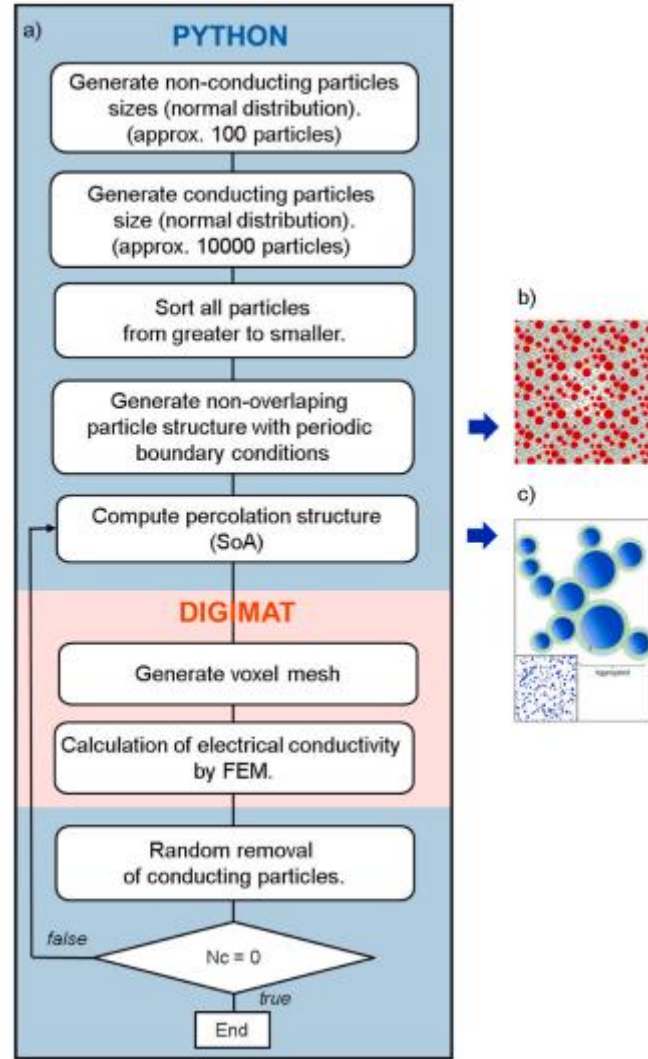


Fig. 1. a) Flowchart of random RVE generation by random filler removal. b) The periodic boundary conditions. The central white background region is a cross section of generated structure. The boundary light grey background regions represent periodic conditions. c) Illustration of Ni particle, aggregate recognition parametrized by t - coating of the particle.

The first moment of the N_{agg} distribution is the average aggregation number, $\langle N_{agg} \rangle$; the second moment, $\langle N_{agg}^2 \rangle$, serves to express the width of the distribution. It is convenient to express the size of aggregates (SoA) in terms of the ratio of these moments:

$$SoA = \frac{\langle N_{agg}^2 \rangle}{\langle N_{agg} \rangle} \quad (2)$$

which is sensitive to the largest aggregates formed at the simulation and neglects isolated particles and small aggregates. The electrical conductivity was calculated by FEM using the Digimat software. FEM is based on a continuum form of Ohm's law, i.e., $\nabla J(x) = 0$, where $J(x)$ is the current density vector, related to the electric field and described by the constitutive law [22]:

$$J(x) = S(x)E(x) \quad (3)$$

where $S(x)$ is the spatially varying matrix conductivity and $E(x)$ is the vector of electric field. The FE analysis provides the solution of effective conductivity σ_{eff} from the equations:

$$\begin{aligned} \langle J \rangle &= \sigma_{eff} \langle E \rangle, \quad \langle J \rangle = \frac{1}{V} \int J(x) dV(x), \\ \langle E \rangle &= \frac{1}{V} \int E(x) dV(x) \end{aligned} \quad (4)$$

where V is the volume of RVE.

2.3. Filler localization

In the double percolation structure, the polymer blend morphology plays an important role for the electrical properties of composites. In our work, the double percolation threshold approach was used, where the thermoset ER is the continuous phase with inclusions of spherical elastomer PDMS particles, the so-called sea island structure. The focus of the previous study [23] was on the technology for the preparation of the polymer blend of ER/PDMS with enhanced mechanical properties, a composite suitable for the preparation of conductive polymer composites.

Several factors determine the localization of solid particles in polymer blends, such as: surface tension [24], polymer crystallinity [25], melt viscosity [26], flexibility of macromolecular chains [27] and processing [28]. However, according to A. Goldel et al. [29] who presented a study on polymer blends polycarbonate/poly (styrene-acrylonitrile) filled with CB and CNT, the localization of particles is primary driven by surface energies because of the system's tendency to minimize its free energy.

When filler particles are mixed with an immiscible matrix consisting of two polymer phases, filler can be dispersed in the first or the second polymer phase or at the interface between polymers. Localization of the filler can be determined by the wetting coefficient (ω) as was proposed by Sumita et al. [12], as defined by the Young's equation [30]:

$$\omega = \frac{(\gamma_{f-A} - \gamma_{f-B})}{\gamma_{A-B}} \quad (5)$$

Localization of filler particles is predicted by the following conditions: if $\omega > 1$, the particles are localized within the polymer phase B, if $\omega < -1$, the particles are localized within the polymer phase A and if $\omega \in (-1;1)$ then the filler is localized at the interface.

3. Experimental

3.1. Materials

The epoxy resin (ER) used was a bisphenol A diglycidyl ether (DGEBA), cured by an aliphatic amine, diethylenetriamine (DETA), while a polydimethylsiloxane (PDMS) was the second phase polymer. Dicumyl peroxide (DCP) was used as a free radical initiator. All chemicals were purchased from Sigma Aldrich (USA) with purity >90%.

Carbonyl nickel (Ni) (Goodfellow, GB) with purity 99.8% was used as a conductive filler with magnetic properties. The particle size distribution was verified by laser diffraction and scanning electron microscopy (SEM).

3.1.1. Filler localization

Considering equation (5) and using data from [31-33], it has been calculated that $\omega = -1.4$ indicating that Ni will be preferentially located in ER phase [12].

3.2. Polymer blend preparation

The compounding of the polymer matrix was investigated in a previous study [23]. The polymer blend was prepared by mechanical stirring (MM-1000, Biosan, Germany) DGEBA, PDMS (10-30 wt %) and DCP (0.5 wt %) at 300 rpm under a nitrogen atmosphere for 2 h at 130 °C. Through this mixing procedure, the cross-linking of PDMS and an improvement of the interphase between ER and PDMS was achieved which lead to spherical particles.

3.3. Fabrication of polymer composites

The magnetic filler - Ni (1.5-13 vol %) was added to the blend after cooling the blend down to room temperature. The mixture was stirred again at 80 °C for 30 min and equimolar amount of DETA was added after cooling the mixture to room temperature. The mixture was precured by stirring at 50 °C for 10 min before casting onto a preheated mold (70 °C). Material was cured at 100 °C for 30 min and after removing from the mold, post-curing (and also cross-linking of PDMS) at 140 °C for 1 h was done.

4. Methodology

4.1. Scanning electron microscopy (SEM)

Phase morphologies of freeze-fracture surfaces of ER/PDMS/Ni polymer composites were investigated by a NovaNanoSEM 450 scanning electron microscope (FEI Company, The Netherlands) at accelerating voltage of 5 kV in topographical SE (Secondary electrons) imaging mode and 15 kV in material contrasting BSE (Backscattered electrons) operating mode.

4.2. Numerical simulation by Monte Carlo method

To simulate EPT and the electrical characteristics of the composite system, multi-scale multi-physics finite element method (FEM), employed by Manta et al. [21], was used via commercially available software (Digimat, © Copyright 2018 e-Xstream engineering, LUX). The principle of simulation consists of the formation of a unit cell and a microcomposite model (Representative Volume Element - RVE) in Digimat-FE 6.1.1 (computational engine Marc).

4.3. DC electrical properties

The I-V characteristics were measured in the two-point setup using electrodes of cylindrical shape ($d = 16 \text{ mm}$) with a programmable electrometer (Keithley 6517 A, USA). Four-point method (developed by Van der Pauw [34]) was used for the measurement of samples with conductivity higher than 10^{-3} S/cm .

4.4. Mechanical properties

The lap shear strength of the cured specimens was investigated with the use of a Universal tensile instrument (Testometric Co. Ltd., Rochdale, UK) according to ISO 4587:2003. The test was performed at a rate of 5 mm/min at room temperature. The substrates used in this method were steel sheets. 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 $80 \times 10 \times 3 \text{ mm}^3$. The mean values over five specimens are presented.

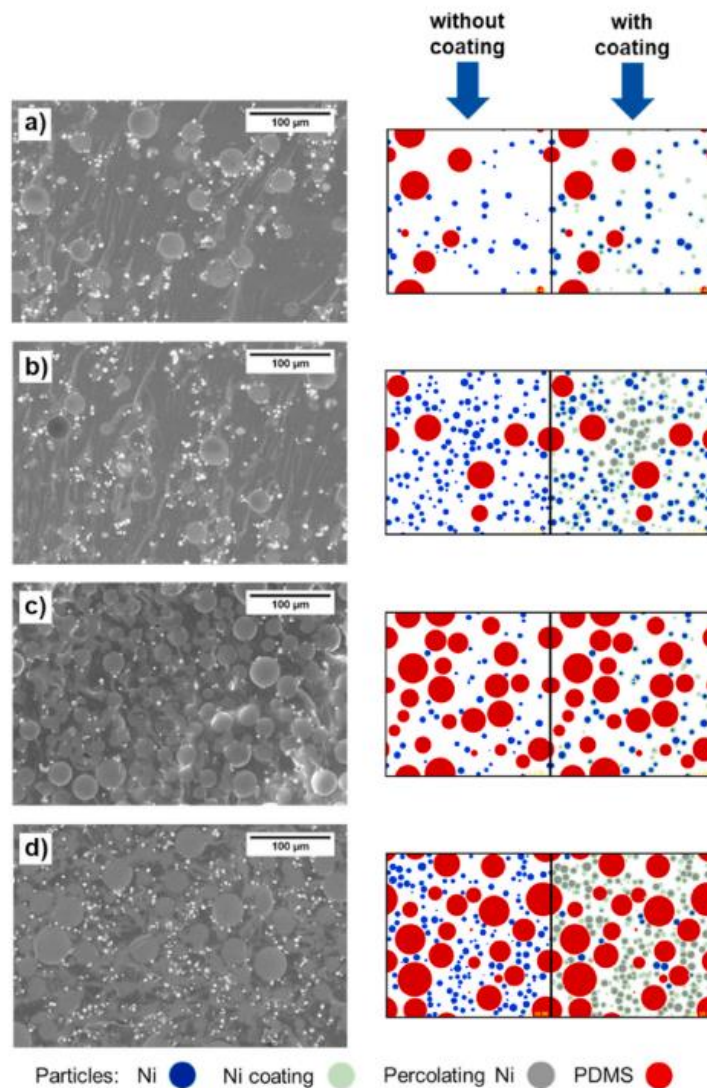


Fig. 2. SEM micrographs (BSE operating mode) of polymer composites (left side) and corresponding results of simulations (right side) in the same scale: a) ER/ PDMS10/Ni3, b) ER/PDMS10/Ni11, c) ER/PDMS30/Ni3, d) ER/PDMS30/Ni11.

5. Results and discussion

5.1. Morphology

In **Fig. 2**, a series of SEM images are presented to show the morphologies of the multiphase ER/PDMS polymer blends filled with Ni particles which are seen as white dots and are compared with crosssections of simulations where Ni and PDMS particles are represented by blue and red circles, respectively. The fractured surface of all modified epoxy based composites showed a three-phase morphology with a rigid continuous phase and a dispersed elastomeric phase of isolated spherical particles of PDMS with the typical sea-island structure of the size 15-55 μm . **Fig. 2a** and **b** presents composites containing 10 vol % of PDMS while **Fig. 2c,d**, contains 30 vol % of PDMS with differering in Ni content. **Fig. 2a,c** and **2 b,d** depict materials below (3 vol % Ni) and above (11 vol % Ni) EPT, respectively.

The resistance against the crack growth in the epoxy composite is due to energy dissipation in the crack tip. The energy of impact causes the dilatational deformation of the matrix initiating crack tip deformation created by local shear yielding. The crack is ceased by PDMS particles leading to energy dissipation improving the impact resistance (or fracture toughness) of polymer composite [23]. This leads to occurrence of stress-whitening regions around PDMS particles which can be observed in micrograph **Fig. 2a**.

In **Fig. 2c** isolated Ni group of particles can be observed which do not penetrate through the whole sample, while in **Fig. 2d**, continuous conductive paths are already created, as is predicted by percolation theory [3].

In **Fig. 3**, epoxy composites ER/Ni and ER/PDMS/Ni are presented in detail. **Fig. 3a** shows the fracture surface of ER/Ni with a Ni concentration above EPT (16 vol %) where conductive paths are created. The "hedgehog-like" structure of Ni particles is visible, where they are well dispersed and randomly localized. On contrary, in multiphase system (ER/PDMS), the nickel particles are preferably located around the PDMS elastomeric phase (**Fig. 3b**). The same effect is noticeable when SEM micrographs are compared with Monte Carlo simulation cross-sections (**Fig. 2**). While the simulation is purely random, Ni particles are preferably located around the PDMS particles in the micrographs of composite materials. This could cause significant lowering of EPT.

5.2. Modelling of particle aggregates

A Monte Carlo simulation with a Python script was used for the simulation of the 3D composite systems in the cubic periodic RVE with an edge length $L_{\text{RVE}} = 200 \mu\text{m}$. Epoxy composites were simulated as a composition of ER (continuous phase) and non-intersecting inclusions defined via parameter adjustments (size distribution, shape, orientation, conductivity). Periodic boundary conditions were chosen to eliminate boundary effects (**Fig. 1b**). To simulate a composite with non-conductive particles (PDMS), initially inclusions with a normal distribution, with a mean diameter $d = 32 \mu\text{m}$ and a standard deviation $\sigma = 8 \mu\text{m}$ were generated. Afterward the conductive Ni particles approximated as spheres with a normal diameter distribution (according to data obtained from laser diffraction) with $d = 5.5 \mu\text{m}$ and $\sigma = 1.8 \mu\text{m}$ were generated (**Fig. 1**). It was assumed, that Ni does not penetrate into the nonconductive inclusions of PDMS (as follows from Young's equation (**Eq.6**) and SEM images (**Fig. 2b**)). The rest of the space was filled by ER which was considered perfectly bonded [18]. The contact of the conductive particles was achieved by increasing the radius of all conductive inclusions by the same

coating (**Fig. 1c scheme**). For various simulations, the thickness of the coating (t) ranged from 1.7 to 2.4 μm .

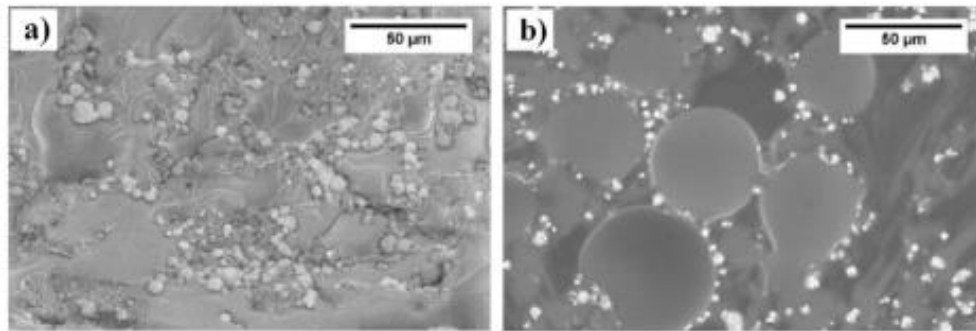


Fig. 3. SEM micrographs of polymer composites: a) ER/Ni16 in SE imaging mode, b) ER/PDMS30/Ni11 in BSE operating mode.

5.3. Modelling of percolative networks

The Digimat-FE 6.1.1 software allows calculations of electrical conductivity of simulated composite material using Ohm's law. **Fig. 4** depicts simulations of polymer composites containing increasing amount of PDMS at percolation concentrations of Ni particles (grey conductive paths). The amount of Ni particles at EPT, effectively the Ni concentration is decreasing with increasing amount of PDMS. In order to calculate the electrical conductivity of simulated composites, a voxel mesh (1 μm side) was generated inside the RVE containing microstructure generated by MC [18]. The electrical conductivity of the Ni particles, the Ni coating and the non-conductive polymer blend ER/PDMS was set to 1 000, 1 and 10^{-12} S/cm, respectively. These systems were tested at a voltage of 1 V and from the I - V characteristic curve the conductivity was calculated (ten times for each concentration). To verify these results, polymer composites were experimentally prepared and measured.

5.4. DC electrical conductivity

The value of EPT depends on filler morphology (shape, size). Although classically an EPT value of about 16 vol % was predicted for spherical particles (e.g. by Scher-Zallen [10]), Krupa et al. [35] mechanically mixed Ni with chain-like structure (formed by individual spherical submicron particles) with polyethylene in a compounder and reached EPT 8 vol %. Different nickel morphology, Ni flakes (diameter 44 μm and thickness 0.4 μm), were utilized by Genetti et al. [36] for achieving an EPT at 5 vol % in LDPE. Both authors [35,36] presented the possibility of reaching lower EPT values by using particles with high aspect ratio, nevertheless Jia et al. [37] studied composites filled with spiked spherical Ni particles (hedgehog-like particles with diameter 1 μm) and found an EPT at 6 vol % in ER. Furthermore, Genetti et al. [36] and Jia et al. [37] studied possible improvements of conductivity of CPCs by: i) employing hybrid composites of Ni with CB [37] which led to improved conductivity below EPT; however, EPT was shifted to 16 vol % of Ni; ii) coating of Ni particles with PPy [36], which improved only the conductivity of polymer composites above EPT.

Fig. 5a shows the dependence of DC specific conductivity with conductive filler content measured at laboratory temperature for ER/ PDMS/Ni composites. Both the ER and ER/PDMS blends are electrical insulators with very low values of conductivity $\sigma_{DC} \sim 10^{-12}$ S/cm. Polymer composites exhibit non-

conductive behaviour with $\sigma_{DC} = (10^{-12}-10^{-9})$ S/cm at low filler concentrations up to the point where the conductivity exponentially increases, signifying the percolation threshold and a simultaneous change of material character to conductorlike behavior with a conductivity of $\sigma_{DC} = (10^{-4}-10^{-2})$ S/cm. It is clearly visible that at a higher content of PDMS leads to a decrease of the critical percolation concentration. The polymer composites containing 0, 10, 20 and 30 vol % of PDMS percolate at 7.9, 7.5, 4.6 and 3.7 vol % of Ni, respectively (**Table 1**). EPT of multiphase polymer composites are in good agreement with SEM images showing that Ni particles are excluded from the PDMS phase (**Fig. 3b**).

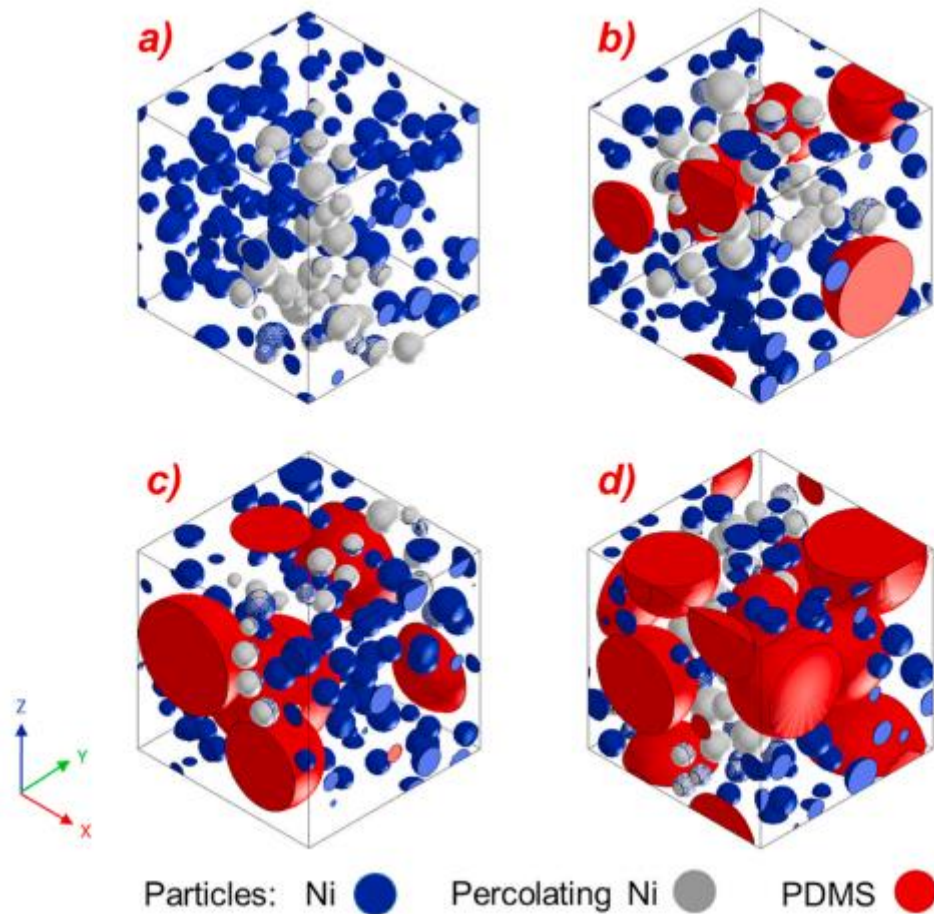


Fig. 4. The simulations reaching percolation threshold: a) ER/Ni, b) ER/PDMS10/Ni, c) ER/PDMS20/Ni, d) ER/PDMS30/Ni.

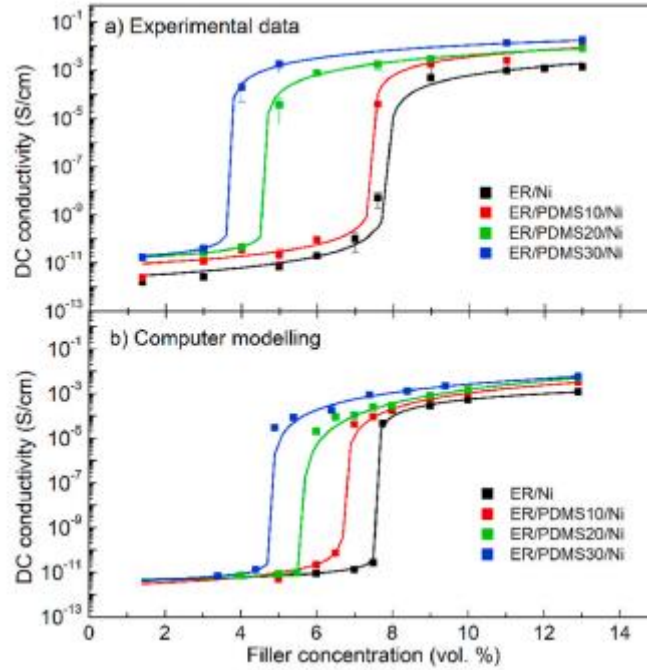


Fig. 5. The concentration dependence of DC conductivities of a) prepared, b) simulated Ni composites.

Table 1 Fitting coefficients obtained from DC conductivity curves.

	ER/Ni	ER/PDMS10/Ni	ER/PDMS20/Ni	ER/PDMS30/Ni
Modelling				
ϕ_c (vol%)	7.9	7.0	5.8	4.9
n	1.7	1.5	1.4	1.6
Experiment				
ϕ_c (vol%)	7.9	7.5	4.6	3.7
n	1.3	1.1	1.4	1.2

The EPT of neat ER when filled by Ni is reached at 7.9 vol % (**Table 1**) at which the first conductive paths through the sample is created, as it can be seen on SEM image (**Fig. 3b**).

Fitting coefficients above percolation threshold were calculated in the range $n \sim 1-2$ (**Table 1**), which is in good agreement with both, theoretical predictions [3,38] and experimental results [39,40]. At Ni particles loading of 5 vol %, the ER/PDMS30/Ni composite exhibits a DC conductivity ($\sim 10^{-3}$ S/cm) which is approximately 8 orders of magnitude higher than the ER/Ni system, at the same level of incorporated Ni particles (**Fig. 5a**). The other option for improvement of electrical conductivity is utilization of the double percolation threshold, which significantly decreases EPT and thus the price of the final product. Additionally, the usage of a polymer blend allows for a substantial improvement of mechanical properties. In our research, EPT of Ni hedgehog particles in ER was 7.9 vol %; however, utilization of ER/PDMS polymer blend reduced EPT by 53% up to 3.7 vol % (**Fig. 5**).

5.5. Size of aggregates

The size of the aggregates is an important feature for the description of composite systems providing additional information about the structure of the system. The value of SoA ranges from 1 implying all particles are isolated to a maximum (= number of particles in the RVE) indicating all particles participate in one aggregate. In terms of percolations, the significant size of the aggregate emerges if the largest aggregate penetrates through the whole sample, thus the diameter of the aggregate is equal to the size of the simulation RVE: $D_{agg} = L_{RVE}$. Fractal model of spheres, as presented by Musino et al. [2], predicts that such a critical aggregate occurs at $SoA \approx 1000$ for our system ($L_{RVE} = 200 \mu m$, $d_{Ni} = 5.5 \mu m$). **Fig. 6** present the dependence of SoA on the volume concentration of nickel for different coating sizes.

Fig. 6a shows that with increasing coating size, the size of the aggregates increases dramatically, approaching a limit of about 10 000 which is the number of particles in the system filled with 10 vol % of Ni particles. The indicated SoA 1000 is the critical size of aggregate which is penetrating through the entire simulated RVE, which roughly corresponds to the percolation concentration. By comparing to the EPT, which was found to be 7.9 vol % (**Fig. 6**), the thickness of the coating was found to be close to 1.95 μm .

The second simulation (**Fig. 6b**) was performed for a system with 30 vol % of PDMS. **Fig. 6** depicts the concentration of Ni in the ER on the x-axis (volume of PDMS is subtracted for comparability with **Fig. 6a**). For the coating with 1.95 μm , EPT is reached again at 7.9 vol % Ni in ER, i.e. 5.5 vol % Ni in the composite system ER/PDMS30/Ni. This means that the percolation behaviour of the model does not depend on the addition of PDMS, which is in an agreement with expectations because the model does not incorporate any irregularities in the localization of the filler like the concentration of conductive particles near the ER/PDMS interphase. However, the actual percolation of the ER/PDMS30/Ni system is 3.7 vol % of Ni, which corresponds to 5.3 vol % Ni in the ER (after deducting volume of PDMS). This difference is due to the difference between the simulation, which contains a random independent localization of particles in RVE, and the experiment with the preferential position of Ni particles near the PDMS surface was observed, which significantly affects the final EPT.

Computational simulation demonstrated that the addition of nonconductive particles enables the decrease of EPT while maintaining the same concentration of Ni inside the ER phase. It is in good agreement with experimental data (**Fig. 5**) at low concentrations of PDMS (up to 10 vol %) in ER. However, it is not valid in the case for higher concentrations of PDMS (more than 20 vol %), where the computer simulation underestimates the true situation.

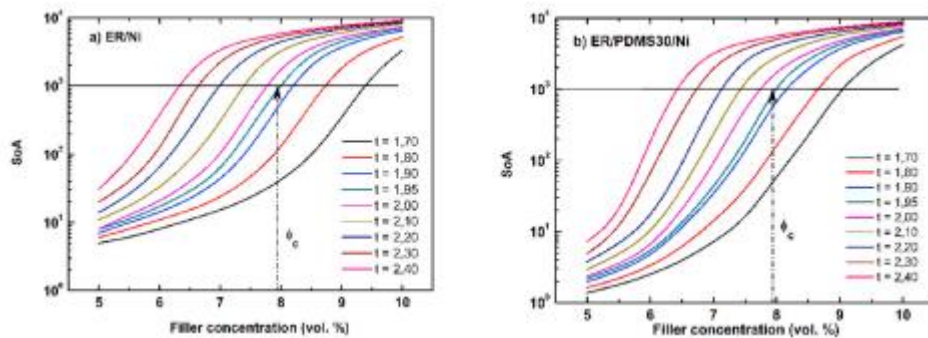


Fig. 6. SoA determined from aggregation number (N_{agg} distribution obtained by Monte Carlo simulation for a) ER/Ni particles systems and b) ER/PDMS30/Ni particles systems. Coating thickness (t) is in pm. The horizontal line shows the onset of percolation.

The values of the EPT are shifted to lower Ni concentrations. The reason for this is that modelling simulations are based on random generation of Ni particles in ER while in manufacturing of composites, the Ni particles are preferentially situated near/on the interphase of ER/PDMS due to enthalpic reasons - the value of wetting coefficient ($\omega = -1.4$) is close to -1 . This preference is clearly visible on micrograph **Fig. 3b**. The decrease of Ni content at processing leads to a low cost production of a lighter final product, due to the lowered density of composite.

5.6. Mechanical properties

Conductive composites based on the matrixes containing neat epoxy resin and polymer blend ER/PDMS30 and polymer samples based on these matrixes were selected for mechanical testing. To evaluate mechanical properties, specimens containing ER, ER/PDMS and conductive composites from these matrixes were prepared. Results of mechanical testing are presented in **Table 2**. The impact strength of materials was evaluated using the Charpy method. It was found, that the presence of Ni does not affect impact strength; however, addition of 30% of PDMS leads to increase of impact strength by 60%.

6. Conclusion

The electric properties of two-phase polymer blends (ER and PDMS) filled with conductive Ni particles with hedgehog-like structure were investigated experimentally and by computational modelling. The multi-phase composites exhibited reduced percolation thresholds and enhanced conductivities above that of the individually Ni filled ER.

It is crucial that conductive Ni particles are selectively located not only in the continuous ER phase but preferentially on the interphase of ER/PDMS as was observed on SEM micrographs. The percolation threshold of the ER/PDMS/Ni composites was reached at 3.7 vol % Ni particles, where the DC conductivity rose by 7 orders of magnitude. This EPT of the polymer blend was reached at a significantly lower nickel content and thereby weight than the individually filled ER (7.9 vol %). It leads to decrease not only in the density from 1.7 g/cm^3 to 1.4 g/cm^3 but also in the cost of the final composite product.

Table 2 Mechanical properties of selected polymer composites.

	ER	ER/PDMS30	ER/Ni8	ER/PDMS30/Ni4
Failure mode [41]	adhesive	cohesive in the material	adhesive	adhesive and cohesive in the material
Lap shear strength (kgf)	370 ± 40	430 ± 50	460 ± 40	430 ± 50
Charpy impact strength (kJ/m ²)	10 ± 1	16 ± 2	11 ± 3	16 ± 3

Prior to actual preparation of polymer composites, the system was simulated using a three-dimensional Monte Carlo model. It was found, that at low PDMS concentrations, the simulations were quite precise in comparison with measured data of DC conductivity. However, the results of the simulations at higher concentration of PDMS underestimated the value of the percolation threshold,

which in the ER/PDMS30/Ni system was found to be 3.7 vol %, instead of 4.9 vol % reached in simulation due to different filler localization.

The mechanical properties of conductive nickel based composite adhesives were tested by lap shear test. The composites containing 30 vol % of PDMS exhibit better adhesion (by 20%) to the metal plates than neat epoxy resin. Impact strength of composite materials was tested by Charpy impact test. Inclusion of PDMS in ER enhanced impact strength by 75%.

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