Electrical Conductivity and Mechanical Strength of Composites Consisting of Phenolic Resin, Carbon Fibers, and Metal Particles

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ABSTRACT: Composites of phenolic resin of novolac type as matrix, with metal particles of Zn as conducting filler, without or with 15% v/v carbon fibers were manufactured by hot pressing. The porosity ratio, the hardness, the flexural and shear strength, and the electrical conductivity of the composites were determined. The percolation threshold was determined based on two models of electrical conductivity versus the content of metal particles of Zn, namely, an analogous to polymer gelation model and the other based on the power law. The composites of carbon fibers combined with Zn particles have higher electrical conductivity than the corresponding without carbon fibers and high strength, lower than that of the composite reinforced with carbon fibers without Zn particles, but still acceptable. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1890–1900, 2011

Key words: composites; conducting filler; phenolic resin; carbon fibers; percolation threshold; mechanical strength; electrical conductivity

INTRODUCTION

Electrically conducting plastics can be generally divided into two categories: filled conductive plastics, in which conductive fillers, such as metal particles,[1–4] carbon black,[5–8] and carbon fibers,[8–10] is added to a thermoplastic or thermosetting resin, and intrinsically conductive polymers, which have obtained electrical conductivity after proper doping by oxidation or reduction reactions.[11,12] The extrinsic conductive composites of the first category have been applied in numerous technological areas including electromagnetic/radio frequency interference shielding for electronic devices (e.g., computers and cellular housings), shelf-regulating heaters, overcurrent protection devices, photothermal optical recording, direction-finding antennas, and chemical-detecting sensors that are used in electronic noses.[13]

Probably, the simplest conducting composite consists of fine metal powder dispersed uniformly throughout an insulating plastic matrix. The metal particles remain isolated from each other, and therefore they do not contribute to the conductivity of the composite, unless they are present in very high concentration. However, such high concentrations cause the deterioration of the mechanical properties of the composite. Furthermore, high conductivity of a composite due to high concentration of metal particles is practically not required or even desirable.[11] Experiment shows that the conductivity of composites with conducting fillers increases abruptly as the conducting particle concentration is increased beyond a certain critical value (percolation threshold), where effectively active paths of particles are formed in the system. For example, for bakelite, the critical content of silver powder is 35% v/v.[11,14]

Short carbon fibers are used as conductive filler in a polymer matrix, especially in epoxy resin, to give electrical conductivity to the composites.[9,10] On the other hand, continuous carbon fibers are used almost exclusively as reinforcing fibers in composites for unidirectional or multidirectional reinforcement and not as electrically conducting medium. Furthermore, tin–lead alloy particles (20–25 μm in size) are effective as a second filler in polymer–matrix composites containing short carbon fibers for increasing the electrical conductivity of the composite.[1] However, such systems are not extensively studied, probably because the mechanical properties of the composites deteriorate.

The aim of this work is the manufacture of new multifunctional polymer–matrix composite materials combining proper mechanical properties with increased electrical conductivity. The methodology to achieve this target is the use of continuous carbon

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fibers in low volume percentage to improve significantly the mechanical properties of the composite and simultaneously to retain as low as possible the cost of the composite material by avoiding a high content of the expensive carbon fibers. It is expected that such low-carbon fiber content (15% v/v) will not be able to increase the electrical conductivity transversely to the fiber axis. Therefore, metal particles will be used to improve this conductivity. A high-conductivity metal will be used as filler, namely, zinc particles (Zn, $\sigma = 1.69 \times 10^5$ S/cm). A common thermosetting resin, such as phenolic resin of novolac type, has been chosen as the matrix.

EXPERIMENTAL

The novolac resin was laboratory synthesized by polycondensation of phenol (p.a., Merck) with formaldehyde (p.a., Fluka), using acetic acid (p.a., Fluka) as catalyst.[15,16] Hexamethylenetetramine (Hexa, p.a., Merck) was used as the curing agent. Novolac and Hexa were grounded and sieved before their use (the particle size for both of them was below of 300 μm). The continuous carbon fibers used were of type Tenax HTS 800 (1600 tex, density: 1.77 g/cm^3, R and G Faserverbundwerkstoffe GmbH). The short carbon fibers were of the type CS 3MM (Faserverbundwerkstoffe GmbH) with average fiber length of 3 mm. Zinc in the form of fine powder (Zn, density: 7.14 g/cm^3, <60 μm, Merck) was used as received.

The manufacture of the composites consisting of novolac/Hexa—carbon fibers—metal particle includes the following steps[15]:

- The continuous carbon fibers were preimpregnated with novolac resin by immersing them in a solution of water/methanol (in ratio of 4/1 v/v) containing a mixture of solids of novolac/Hexa (in ratio of 14/1 w/w) in a proportion of 25/100, weight of solids in grams to volume of solvents in milliliters. After preimpregnation, the solvent was removed by drying at 60°C for 30 min, the resin was partially cured at 130°C for 2 h, and then the preimpregnated carbon fibers were cut into laminates (prepregs). The amount of the continuous carbon fibers used in the composite (in the form of prepreg) was $P_f = 15\%$ v/v and calculated as follows. The whole molding consists of four parallel individual moldings, two of them having width, $W_n = 1$ cm and the other $W_w = 1.7$ cm. The length of a molding, and therefore the length of each specimen, was $L = 21$ cm. The thickness of the specimens depends mainly on the number of the laminates of the prepreg used. We wanted to manufacture specimens with thickness, $T = 0.3$ cm. The density of the carbon fibers used was $\rho_c = 1.77$ g/cm^3. A carbon fiber of length, $L = 21$ cm weighs $M = 0.3408$ g. Consequently,

Volume of a specimen:

a. narrow specimen: $V_n = L \times W_n \times T = 6.30$ cm^3
b. wide specimen: $V_w = L \times W_w \times T = 10.71$ cm^3.

Mass of carbon fibers demanded for a composite specimen of $P_f = 15\%$ v/v:

a. narrow specimen: $M_n = V_n \times P_f \times \rho_c = 1.673$ g.
b. wide specimen: $M_w = V_w \times P_f \times \rho_c = 2.844$ g.

Number of carbon fibers demanded for a composite specimen of $P_f = 15\%$ v/v:

a. narrow specimen: $M_n/M = 4.91 \approx 5$ carbon fibers.
b. wide specimen: $M_w/M = 8.35 \approx 8$ carbon fibers.

According to the define apparatus for the manufacture of the laminates, three and four carbon fibers correspond to the narrow and the wide specimen, respectively. Thus, two laminates were used for the manufacture of the narrow specimen (consisting of three and two carbon fibers) and two laminates for the wide specimen (consisting of twice of four carbon fibers).

- The novolac powder was mixed with Hexa powder in the ratio of 7 : 2 w/w, the certain amount of metal Zn powder was added, and all of them were mixed to produce a macroscopically homogenous powder.
- The carbon fiber laminates were placed unidirectionally in a proper mold by the addition of the mixture of novolac/Hexa–metal particles between the laminates and then the mold was heated up to 150°C in a time interval of 20 min without applying pressure to cause the gelation of the novolac matrix. Then, the temperature was raised to 175°C and kept constant for 40 min by applying a pressure of 13 MPa. The cured composite remained under pressure until slowly cooling to room temperature.

The composites consisting of novolac/Hexa–metal particles were manufactured by mixing them as previously described, putting the mixture in a proper mold, and hot pressing them under the above-described thermal program. For comparison reasons, composites consisting of novolac/Hexa–short carbon fibers were also manufactured by mixing them, putting the mixture in a proper mold, and hot pressing them under the above-described thermal program.

The morphology of zinc powder and that of the composites were examined with a FEI Quanta 200 Scanning Electron Microscope (SEM) equipped with element dispersive X-ray analysis (EDAX). The experimental density (d_e) of the composites was determined as the ratio of m/V by cutting rectangular parallelepiped (narrow and wide) specimens, weighting them (m), and measuring their dimensions (length, width, and thickness), and then calculating their volume (V). It is known that this is a proper method to determine the experimental density when the specimen has a defined geometrical shape. The standard error of the measurement of the experimental density was ±2%. The flexural and the shear strength of the composites were determined according to the three-point method by ASTM D790-71 and D2344-65T using the narrow specimens, respectively, using specimens with dimensions: 21 × 1.0 × 0.3 cm (narrow specimens) for flexural strength and 21 × 1.7 × 0.3 cm (wide specimens) for shear strength.[15] The standard error of the measurement for the determination of flexural and shear strength was ±5%. The shore hardness of the composites was measured according to the ASTM D2240 using a Shore *D* durometer, and the standard error of the measurement was ±2%. The electrical conductivity of the composites transversely to the carbon fiber axis was measured using the two-probe technique,[11] and the standard error of the measurement was ±5%. It should be noted that the longitude electrical conductivity of the continuous carbon fiber composites is that of the carbon fibers, because, in that direction, the continuous fibers create active paths.

RESULTS AND DISCUSSION

The SEM images of the Zn powder and the transverse section of composites are presented in Figure 1. Zinc consists of small particles with a mean diameter of 2.3 μm [Fig. 1(a)]. The elemental analysis of the powder according to EDAX showed that it consists of 100% of zinc. The particles show the characteristic metallic brightness. The latter is also observed in the composite of phenolic resin with Zn [Fig. 1(b)]. There are observed individual particles, and some of them are in contact, consisting small island and not metallic paths. The transverse sections of carbon fibers embedded in the phenolic resin are observed in circlelike forms [Fig. 1(c)]. Some short parts of the carbon fibers, which are cut during the transversely cutting of the composite, are observed as longitudinal parts. There is not a metallic brightness. Although the carbon fibers content in the composite is only 15% v/v, the distances between them are short. This indicates that small spaces should be covered with a conductive medium (such as particles) to be formed conductive paths in the composite. This state seams to take place for the composite of phenolic resin with Zn and carbon fibers [Fig.1(d)].

Various composites have been manufactured consisting of novolac resin, carbon fibers, continuous or short, and metal particles of Zn. The composites with the defined compositions are presented in Table I. The main groups are that of N-Zn and N-Zn-CF consisting of novolac and zinc in different proportions, without or with carbon fibers (15% v/v), respectively. The materials are presented separately: N, N-CF15, and N-SCF5, that is, the matrix alone, matrix with 15% v/v continuous carbon fibers, and matrix with 5% v/v short carbon fibers for comparison reasons.

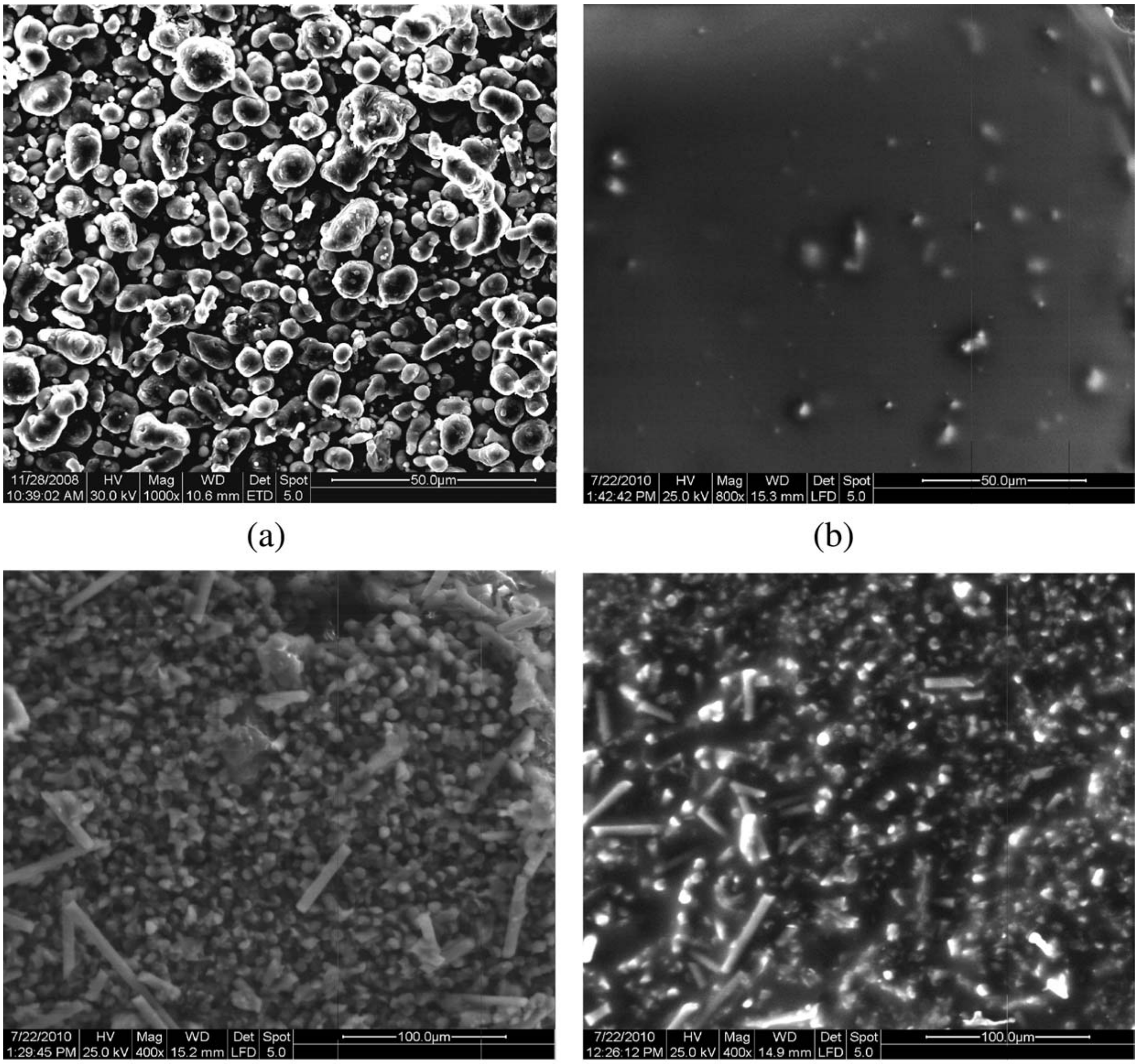
The theoretical density of the composite (d_t) consisting of novolac/Hexa-Zn, as matrix (subscript: m) and metal particles (subscript: p), respectively, was calculated from the Eq. (1):

$$d_t = (1 - V_p)d_m + V_p \cdot d_p \tag{1}$$

where *V* is the volume fraction and d is the density. Then, the composites' porosity (τ) was determined according to the Eq. (2)[13]:

$$\tau = \left(\frac{d_t - d_e}{d_t}\right) \times 100 \tag{2}$$

where d_e is the experimental density of the composite. Figure 2 shows the porosity ratio versus volume ratio of Zn particles (% v/v) of composites of group N-Zn and from Ref. [13] concerning composites of urea-formaldehyde embedded in cellulose with zinc particles. The quality of the latter composites has been characterized as good based on an upper value around 11.5% and an average value of 6.9%. The corresponding values of the composites of group N-Zn are 12.4% and 7.3%, indicating also a good quality of them. It should be noted that the composites based on phenolic matrix show practically always some porosity. This is attributed to their curing mechanism, which is a step-polymerization and especially polycondensation in opposite to the curing mechanism of other resins, such as epoxy (step-polymerization and case of polyaddition) and unsaturated polyesters (chain-polymerization). During the curing of phenolic resins, small molecules are created, which are evolved as gases causing voids in the composite formed. The use of additives to absorb partially the gases and to reduce or "vanish" the porosity of the composite was out of the scope of this work. The introduction of new interfaces or the increase of porosity on the other hand leads to the deterioration of the mechanical strength and the electrical conductivity of the composites. The percentage of Zn particles, expressed as w/w or v/v, is not influenced by



(a) (b) (c) (d)

Figure 1 SEM images of the Zn powder and the transverse section of composites. (a) Zn powder, in magnification of ×1000. (b) Composite of phenolic resin with 30% w/w Zn (N-Zn30, in Table I), in magnification of ×800. (c) Composite of phenolic resin with 15% v/v carbon fibers (N-CF15, in Table I), in magnification of ×400. (d) Composite of phenolic resin with 30% w/w Zn and 15% v/v carbon fibers (N-Zn30-CF15), in magnification of ×400.

the porosity, which is expressed only at the charge of the matrix content.

Table II presents the mechanical strength and the electrical conductivity of the composites. The composites without carbon fibers (N-Zn) and the cured matrix alone (N) were very brittle, and their mechanical strength could not be measured, with some exceptions. On the other hand, the novolac with 15% v/v carbon fibers (N-CF15) was strongly reinforced showing the maximal values of flexural and shear strength between all the composites. The mechanical strength of the composites (N-Zn-CF) decreases by increasing the Zn content. The hardness of N was 35 shore *D*, whereas that of the composites with Zn particles was 50 and was independent of Zn content. The composites with carbon fibers (i.e., N-CF15 and N-SCF5) had hardness around 60, higher than that of N and N-Zn composites. The combination of carbon fibers and Zn particles (i.e., group of composites N-Zn-CF) leads to the further increase of the hardness at around 75 shore *D* values, which was only slightly affected by the Zn content.

The electrical conductivity of the cured matrix alone is very low, because novolac is a typical thermosetting polymer, and it belongs to the insulating materials. The electrical conductivity of the composites without carbon fibers (N-Zn) increases by increasing the Zn content. The electrical conductivity of N-CF15 is almost two orders of magnitude higher than that of novolac (N). This improvement is

TABLE I
Composites Consisting of Phenolic Resin, Carbon Fibers, Continuous or Short, and Metal Particles of Zn

			Metal particles of Zn		Carbon fibers	
Code of group	Code of composite	Matrix Novolac/ Hexa mixture (% w/w)	(% w/w)	(% v/v)	Continuous (% v/v)[a]	Short (% v/v)[b]
	N (matrix alone)	100	–	–	–	–
N-Zn	N-Zn2.5	97.5	2.5	0.45	–	–
	N-Zn5	95	5	0.92	–	–
	N-Zn10	90	10	1.91	–	–
	N-Zn15	85	15	3.00	–	–
	N-Zn20	80	20	4.19	–	–
	N-Zn30	70	30	6.98	–	–
	N-Zn40	60	40	10.45	–	–
	N-CF15	100	–	–	15	–
	N-SCF5	100	–	–	–	5
N-Zn-CF	N-Zn2.5-CF15	97.5	2.5		15	–
	N-Zn5-CF15	95	5		15	–
	N-Zn10-CF15	90	10		15	–
	N-Zn15-CF15	85	15		15	–
	N-Zn20-CF15	80	20		15	–
	N-Zn30-CF15	70	30		15	–
	N-Zn40-CF15	60	40		15	–

[a] The volume fraction of matrix with or without metal particles of Zn is 85 % v/v.
[b] The volume fraction of matrix is 95 % v/v.

attributed to the high conductivity of carbon fibers (which was measured with the four probe technique as 21 S/cm). However, this small increase indicates that in such low-carbon fibers content, there are not many active paths formed. On the other hand, due to the high cost of carbon fibers, high-carbon fiber content could lead to high electrical conductivity, but it would also increase the total cost of the composite.

To investigate the possibility of high electrical conductivity and adequate mechanical strength, a composite consisting of novolac resin with short carbon fibers was manufactured (N-SCF5). Indeed, the electrical conductivity of this composite is more than two and a half orders of magnitude higher than N-CF15, indicating the presence of active paths due to random distribution of the short fibers, opposite to the axial orientation of the continuous carbon fibers. Generally, the percolation threshold in composites of short carbon fibers is very low, and it strongly depends on the pretreatment of the short carbon fibers

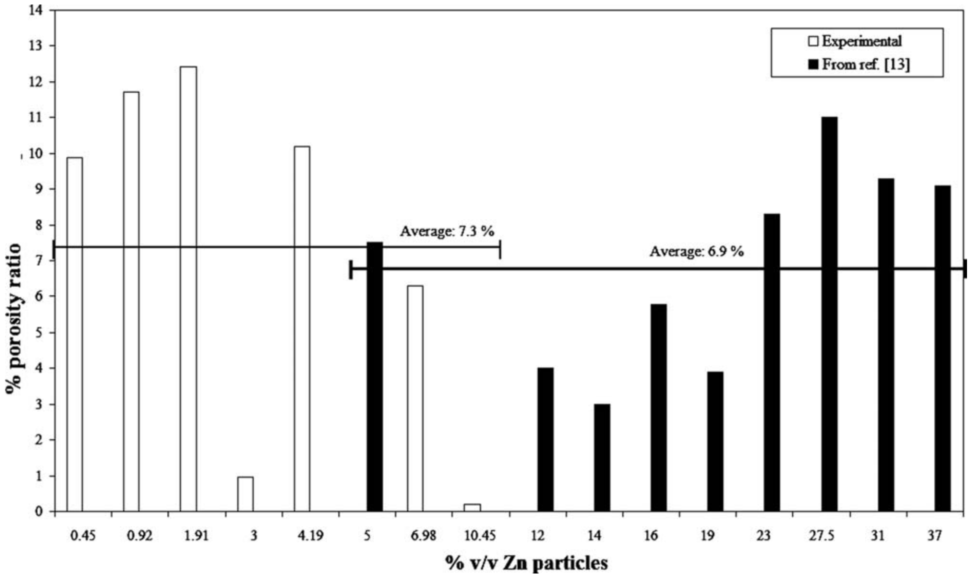


Figure 2 Porosity ratio of composites of group N-Zn and from Ref. [13] versus volume ratio of Zn particles (% v/v). The average values of each group are also presented.

TABLE II
Mechanical Strength, Hardness, and Electrical Conductivity of Composites Consisting of Phenolic Resin, Carbon Fibers, Continuous or Short, and Metal Particles of Zn

		Mechanical strength			
Code of group	Code of composite	Flexural strength (MPa)	Shear strength (MPa)	Hardness (shore *D*)	Electrical conductivity (S/cm)
	N	–	0.65	35	2.90E-11
N-Zn	N-Zn2.5	–	0.38	50	8.50E-10
	N-Zn5	–	–	50	3.30E-9
	N-Zn10	–	–	50	7.20E-9
	N-Zn15	–	–	50	8.10E-9
	N-Zn20	–	–	50	9.10E-9
	N-Zn30	–	–	50	1.60E-8
	N-Zn40	–	–	50	8.50E-5
	N-CF15	540	10.94	60	1.48E-9
	N-SCF5	36	1.61	55	7.50E-7
N-Zn-CF	N-Zn2.5-CF15	306	10.92	70	8.00E-7
	N-Zn5-CF15	289	10.91	70	2.30E-5
	N-Zn10-CF15	268	10.38	75	2.38E-5
	N-Zn15-CF15	271	10.69	75	5.99E-5
	N-Zn20-CF15	260	10.30	75	1.88E-4
	N-Zn30-CF15	193	9.39	75	1.98E-4
	N-Zn40-CF15	170	8.60	75	5.90E-3

to decrease their length. Thus, according to Ref. [17], short carbon fibers of average diameter 7 μm and length 3 mm, density 1.76 g/cm^3, were mixed with NaCl crystals and crushed in a mixer at room temperature and after proper separation process the length of the final fibers was 100–150 μm, and the threshold of the corresponding composites with polyester resin was ~ 0.7 vol %. By using short carbon fibers with average length of 1.7 mm in polyester or epoxy composites, the percolation threshold is reached at 1 vol %.[9] The value of 36 MPa for the flexural strength of N-SCF5 is indeed higher than that described in the literature for the corresponding short carbon fibers/phenolic resin composites, varying between 12 (untreated) and 25 MPa (surface-treated fibers).[10] However, these values of mechanical strength (flexural and shear) are very low compared to those of N-CF15. Therefore, the use of short carbon fibers will be not studied any further.

For a more quantitative correlation, the influence of the metal particle of Zn content on the flexural strength, the shear strength, and the electrical conductivity of the composite materials are presented in Figures 3–5, respectively. The flexural strength of the composite N-Zn2.5-CF15 abruptly decreases compared to that of N-CF15. The flexural strength of the composites of group N-Zn-CF slightly decreases by increasing the Zn particles content following a linear relationship (Fig. 3). Shear strength decreases slightly, following a linear relationship (Fig. 4). The addition of Zn particles in the system of novolac-carbon fibers 15% to produce composites introduces additional defects. These defects, which are not only in macroscopic level (e.g., defects due to voids/porosity) but also in molecular level, depend on the length of the specimen. According to a general characteristic of the composites, the longer the length of the specimen, the lower is its strength, which is interpreted from the higher possibility of defect positions in the longer specimen. The abrupt decrease of the flexural strength of the composite Zn2.5-CF15 compared to the slight decrease of the shear strength is due to the higher possibility of defect positions in the longer length of the flexural test specimen compared to that of shear test.

The linear fittings of the experimental data for the flexural and the shear strength versus the % w/w metal particles of Zn (Figs. 3 and 4) are

$$\text{For the flexural strength}: y = 3.5969x + 314, R^2 = 0.9487$$

$$\text{For the shear strength}: y = 0.0579x + 11.153, R^2 = 0.9191$$

According to Figure 5, the curve of the electrical conductivity of the composites without carbon fibers versus the metal particles of Zn (% w/w) can be distinguished in three parts. The electrical conductivity increases two orders of magnitude in the initial part (0–5% w/w Zn), then remains constant (5–30% w/w Zn), and finally it increases abruptly almost four orders of magnitude (30–40% w/w Zn). Similarly, the curve of the electrical conductivity of the composites with carbon fibers versus the metal particles of Zn (% w/w) also includes three parts; however, it differs from the former. In the initial part, the

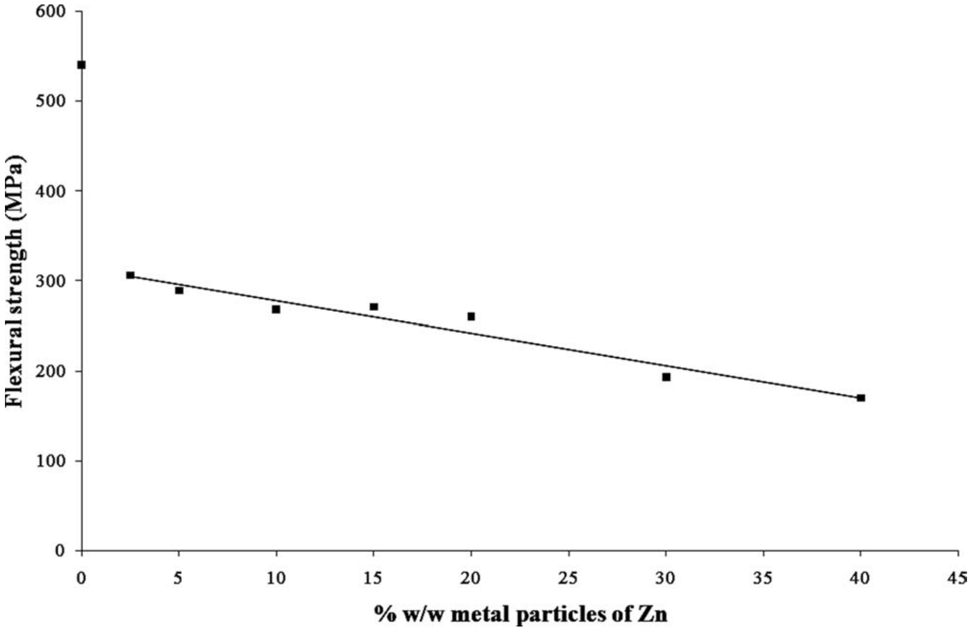


Figure 3 Flexural strength of the composites of the group N-Zn-CF (with 15% v/v carbon fibers) versus % w/w metal particles of Zn. Fitting of the experimental data, excepting the composite without particles of Zn.

electrical conductivity increases abruptly four orders of magnitude (0–5% w/w Zn), then increases slightly (5–30% w/w Zn), and finally it increases one order of magnitude (30–40% w/w Zn). The course of both curves can be phenomenologically interpreted as follows.

It is remarkable that the electrical conductivity of the composites (without carbon fibers) with even a low content of Zn particles increases compared to the cured novolac (matrix without Zn particles). The addition of the metal particles of Zn in the novolac resin leads to a new material, and the electrical conductivity increases (and indeed about 1.5 orders of magnitude by addition of only 2.5% w/w, N-Zn2.5). This increase can be explained based on the ion–dipole interactions between a positive ion of Zn^{2+} and two negatively charged polar groups (e.g., $O^{-}\delta$) of two macromolecules. Novolac resin contains such polar groups (—OH), which have dipole moment of $4.7 \times 10^{-30}\ C \times m$ for the phenolic unit of novolac.[11] Dipole interactions of dispersed metal particles in polymer matrix (as Ag–nylon 11 interactions) have been described in the literature.[18] Thus, the initial increase of conductivity can be attributed to the ion–dipole interactions,

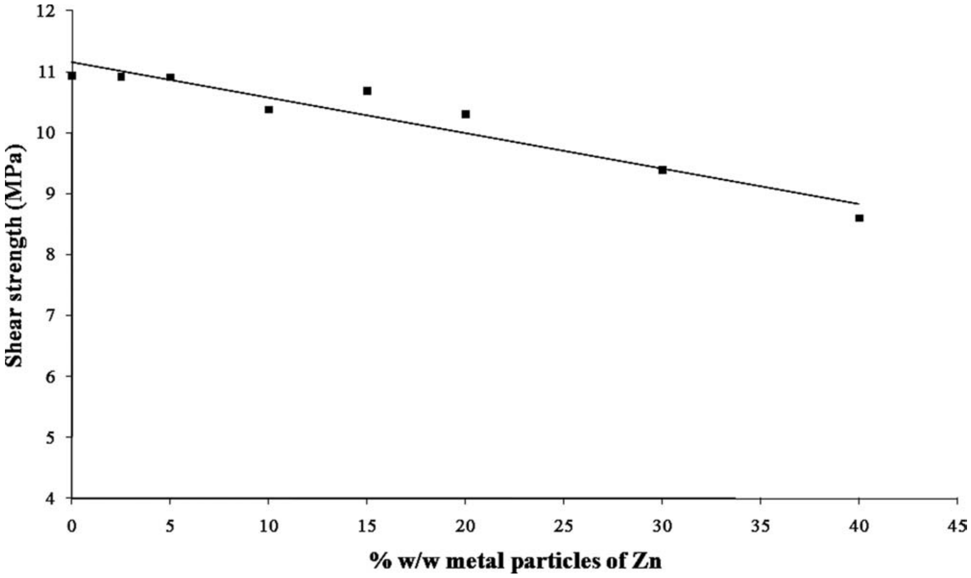


Figure 4 Shear strength of the composites of the group N-Zn-CF (with 15% v/v carbon fibers) versus % w/w metal particles of Zn.

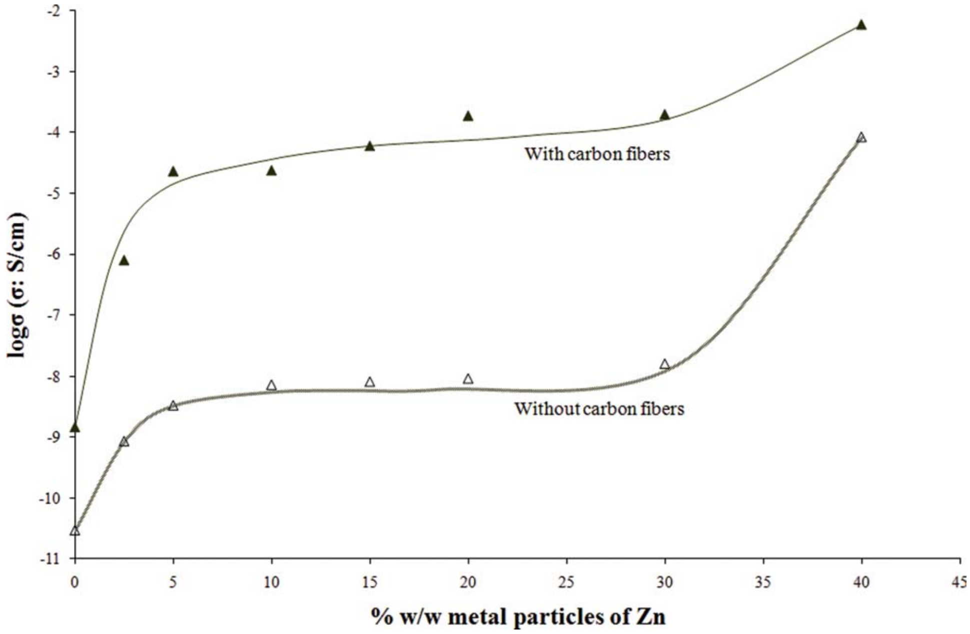


Figure 5 Electrical conductivity of the composites of the groups N-Zn and N-Zn-CF (with 15% v/v carbon fibers) versus % w/w metal particles of Zn.

which create charge carriers.[19] The second and third parts of the curve are typical for a composite material made of conductive filler and an insulating matrix.[20] In the region of low filler concentrations, there are no contacts between adjacent filler particles. With rising filler concentration, agglomerates of the filler particles begin to form, wherein the filler particles are in contact with each other. At a certain filler content (third part), the growing agglomerates reach a size, which makes it possible for them to touch each other and forms a network of the conducting phase within the insulating one and the conductivity of the composite shows a drastic increase. Taking into consideration that the metal particles of Zn were in the form of fine powder (<60 μm), the conduction mechanism of particle filled composites can be described using direct particle–particle contact model, which is dominant for large particles (e.g., for carbon blacks with particle diameter larger than 0.1 μm or short carbon fibers).[21]

According to Table II, the electrical conductivity of the composite with carbon fibers (N-CF15) is almost two orders of magnitude higher than that of cured novolac (N), due to the presence of the conductive continuous carbon fibers. The abrupt increase of the electrical conductivity with the addition of a small amount of the metal particles of Zn indicates that the metal particles are inserted between adjacent carbon fibers forming conductive paths (i.e., carbon fibers–metal particles). This interpretation is in agreement with the SEM images indicating short distances between the carbon fibers in the composite [Fig. 1(d)], whereas the small spaces can be covered with a small amount of the conductive particles of Zn. In the second part of the curve, the slight increase of the electrical conductivity indicates that the addition of more metal particles of Zn leads to the formation of further conductive paths. The significant increase of the electrical conductivity by one order of magnitude in the third part indicates the appearance of a new mechanism, which can be attributed to the formation of new conductive paths between metal–metal particles.

Based on the above description, it is obvious that the percolation threshold of the composites without carbon fibers (N-Zn) is in the third part (i.e., above 30% w/w) and that of the composites with carbon fibers (N-Zn-CF) is in the first part (i.e., below 5% w/w). In below, we attempt to determine the percolation threshold of both groups of composites. According to the literature,[11,22–24] most composite conductors are made up of conducting particles suspended in an insulating matrix. Particle contact requires 10–30 vol % conductor at the percolation threshold when the metal and insulator grains are comparable in size. But when the metal grains are much smaller, they are forced into interstitial regions between the insulating particles and into contact with one another, which results in a lower percolation threshold (3–10 vol %).

A significant approach to determine the percolation threshold of the electrical resistivity of conducting particles in an insulating matrix was made by Bueche.[14] He applied the Flory theory of polymer gelation during of polymerization of small molecules each of which is multifunctional in the previous system by replacing the term "molecule" with the

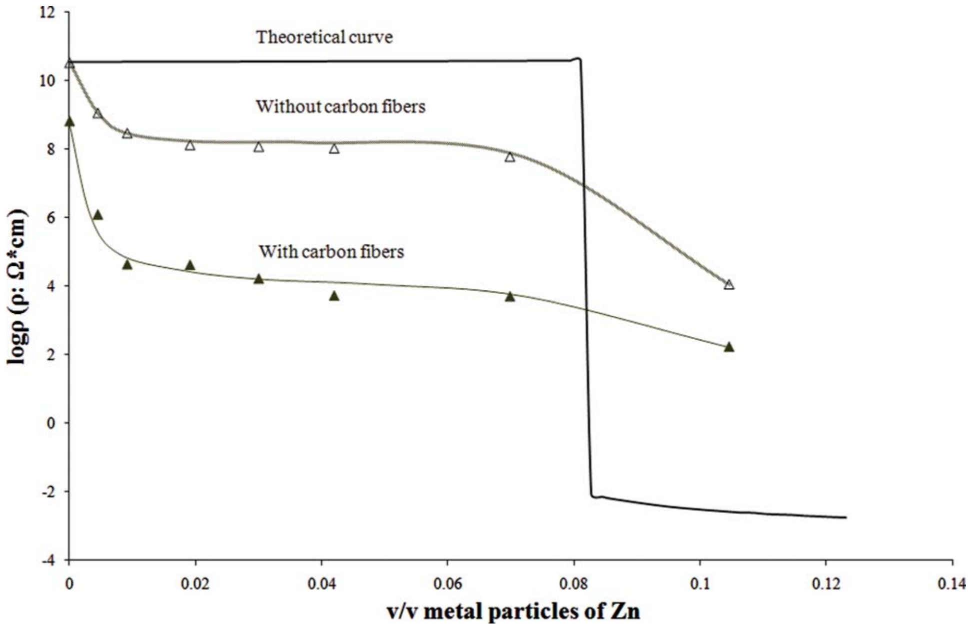


Figure 6 Electrical resistivity of the composites of the groups N-Zn and N-Zn-CF (with 15 % v/v carbon fibers) versus v/v metal particles of Zn and theoretical curve based on the theory of Bueche.[14]

term "conducting particle." Specifically, he proposed that the resistivity of a composite formed by a nonconducting matrix filled with conducting particles follows the Eq. (3):

$$\frac{\rho}{\rho_m}=\left[1-V_p+V_p w_g\left(\frac{\rho_m}{\rho_p}\right)\right]^{-1} \tag{3}$$

where ρ, ρ_m, and ρ_p is the resistivity of the composite, the matrix, and the particles, respectively, V_p is the volume fraction of the particles, and w_g is the fraction of the particles that contributes to the formation of a conducting network. The latter can be calculated from the Eq. (4):

$$w_g = 1-\frac{(1-a)^2 y}{(1-y)^2 a} \tag{4}$$

where α is the probability for the appearance of a contact between neighboring particles and y is the smallest root of Eq. (5):

$$a(1-a)^{f-2}=y(1-y)^{f-2} \tag{5}$$

where f is the maximum number of contacts a particle can make with its neighbors. The values of f and α depend on the shape and the lattice of the particles. For example, when spherical particles with hexagonal closed-packed lattice are considered, then $f = 12$ and $\alpha = V_p/0.74$.[5,14]

By defining the values of f and α, Eq. (5) can be solved and y can be determined. Then, w_g can be calculated from Eq. (4) and finally the resistivity ρ of the composite is calculated for any given V_p. Figure 6 shows the electrical resistivity of the composites of the groups N-Zn and N-Zn-CF (with 15% v/v carbon fibers) versus v/v metal particles of Zn and the corresponding theoretical curve to determine w_g based on Eq. (4) using the values: $f = 12$ and $\alpha = V_p/0.74$. Thus, the theoretical curve does not fit the whole experimental curve, but it gives only the abrupt change of the resistivity which occurs at w_g. The interception of the theoretical curve in its abrupt part with the experimental curves indicates the threshold, which is in 0.081 v/v of Zn metal particles (8.1% v/v, corresponding to 33.5% w/w for the group of N-Zn composites). The corresponding resistivity value is $\log \rho = 7$ (i.e., $\log \sigma = -7$) for the composites of the group N-Zn.

The group N-Zn-CF is a more complicated system, because it additionally contains conductive continuous carbon fibers. As it was previously mentioned, the Flory theory of polymer gelation during polymerization is valid for small molecules (i.e., conductive particles by Bueche approach). The Flory theory is not valid if the small molecules are replaced by macromolecules. It is obvious that continuous carbon fibers do not correspond to small molecules but to macromolecules. Therefore, for the group N-Zn-CF, the percolation threshold cannot be determined from this approach.

Besides this approach, simple models of the ordering of globular particles in the nonconducting matrix revealed that conductivity σ of a percolating system depends on the concentration of conducting particles V_p as a power law[17,21,23–25]:

$$\sigma = \mathrm{K}\left(V_\mathrm{p} - V_\mathrm{p,c}\right)^t \qquad (6)$$

where $V_\mathrm{p,c}$ is the percolation limit, K, and t are constants for a given system. The values of K and t can be determined as the intercept and the slope, respectively, of the straight line presented in the double logarithm plot : $\log \sigma - \log(V_\mathrm{p} - V_\mathrm{p,c})$, by trial-and-error procedure of the $V_\mathrm{p,c}$ value. The optimum value of $V_\mathrm{p,c}$ is the one that leads to the line with the best regression (correlation coefficient of the line). This equation is valid for $V_\mathrm{p} \geq V_\mathrm{p,c}$. For the composites without carbon fibers (N-Zn), according to Figure 5, this condition is valid only for the composite N-Zn40. It was not possible to manufacture composites containing higher than 40% w/w metal particles of Zn with satisfying quality and mechanical properties. Concerning the group of N-Zn-CF, these composites contain conducting particles and continuous carbon fibers consisting of a system, which is not directly described by the Eq. (6). On the other hand, there are available experimental data for $V_\mathrm{p} \geq V_\mathrm{p,c}$, and we have attempted to apply the Eq. (6). By using the data between 2.5 and 30% w/w metal particles of Zn, the best fitting of the experimental curve with the Eq. (6) is given with the following values of the parameters: $V_\mathrm{p,c} = 0.0034$ (0.34% v/v, i.e., 1.92% w/w metal particles of Zn), $t = 1.3$, and $K = 10^{-2.1}$ S/cm. Although the value of t for composites is most often found to lie in the "universality" range of 1.65–2.0, it is sometimes found to be somewhat below these values and often has a value in excess of 2.0,[23] depending on parameters such as the filler distribution, filler shape, filler/matrix interactions, and the processing technique.[20]

Thus, the experimental curve of the electrical conductivity of the composites with carbon fibers versus the metal particles of Zn (% w/w) (Fig. 5), which shows an abrupt increase of four orders of magnitude for the electrical conductivity in the initial part, between 0 and 5% w/w Zn, confirms with the previously determined percolation threshold of 0.34% v/v, that is, 1.92% w/w metal particles of Zn. The verification of the Eq. (6) for $V_\mathrm{p} \geq V_\mathrm{p,c}$ by using the experimental data between 2.5 and 30% w/w metal particles of Zn, that is, partially of the initial part (above percolation threshold), and the second part of the curve indicates that there are the same conductive paths between carbon fibers and conducting particles of Zn. On the other hand, the Eq. (6) is not valid when also the data at 40% w/w metal particles of Zn are included. That is, an indication that above 30% w/w Zn also another conduction mechanism takes place. The latter should be attributed to the conductive paths between metal–metal particles due to their high amount.

According to the experimental and computational previously described results: (a) the composites without carbon fibers (N-Zn) have percolation threshold at 8.1% v/v (i.e., 33.5% w/w), with corresponding electrical conductivity $\sigma_\mathrm{thr} = 10^{-7}$ S/cm and (b) the composites with carbon fibers (N-Zn-CF) have percolation threshold at 0.34% v/v (i.e., 1.92% w/w), with corresponding electrical conductivity $\sigma_\mathrm{thr} = 10^{-6.5}$ S/cm. These results will be compared to that of the literature. For composites of epoxy resins filled with carbon black, with particle size of 14 nm, the percolation threshold was 0.5% v/v, $t = 2.0$, and $\sigma_\mathrm{thr} = 10^{-5}$ S/cm, and, with particle size 300 nm, the corresponding values are 17.5% v/v, $t = 1.85$, and $\sigma_\mathrm{thr} = 10^{-6}$ S/cm.[21] For composites of epoxy resins filled with short carbon fibers, with length of 1.15 mm, the percolation threshold was 1.47% v/v, $t = 3.0$, and $\sigma_\mathrm{thr} = 10^{-8}$ S/cm, with length of 2.85 mm the corresponding values are 0.25% v/v, $t = 3.0$, and $\sigma_\mathrm{thr} = 10^{-5}$ S/cm,[25] and with length of 1 mm the percolation threshold was 0.93% v/v, $t = 3.0$, and $\sigma_\mathrm{thr} = 2 \times 10^{-7}$ S/cm.[21] It is obvious that the new composites of novolac resin with conductive continuous carbon fibers (15% v/v) and with very low content of metal particles of Zn (0.34% v/v) have $\sigma_\mathrm{thr} = 10^{-6.5}$ S/cm, which is comparable or better than that of other types of composites. Additionally, these new composites have high flexural strength (lower than that of the composite reinforced with carbon fibers without Zn particles, but still acceptable) and almost the same shear strength. The required electrical conductivity for antistatic applications is in the range below 10^{-9} S/cm, for electrostatic dissipation applications is 10^{-5} to 10^{-9} S/cm,[17] for low-level electrostatic discharge elimination (ESD) is 10^{-11} to 10^{-8} S/cm and for high level ESD is 10^{-8} to 10^{-6} S/cm.[12] For applications where conductivity in the range of 10^{-5} S/cm is required, then composites with metal particles of Zn of 0.92% v/v (5% w/w) can be used, which have simultaneously acceptable mechanical properties.

CONCLUSIONS

Composites were manufactured by using novolac with only 15% v/v carbon fibers and with metal particles of Zn (N-Zn-CF), and their percolation threshold was determined at 0.34% v/v (1.92% w/w). The abrupt increase of the electrical conductivity with the addition of a small amount of the metal particles of Zn indicates that the metal particles are inserted between adjacent carbon fibers forming conductive paths (i.e., carbon fibers–metal particles). On the other hand, the composites of novolac without carbon fibers (N-Zn) show a higher percolation threshold attributed to the formation of conductive paths between metal–metal particles, which is typical for composites made of conductive filler and an insulating matrix. These new materials combine good mechanical properties and electrical conductivity and could be used in a wide variety of applications.

References

1. Chung, D. D. L. Carbon Fiber Composites; Butterworth-Heinemann: Boston, 1994.
2. Kolbe, J. J Adhes 2009, 85, 381.
3. Tee, D. I.; Mariatti, M.; Azizan, A.; See, C. H.; Chong, K. F. Comp Sci Tech 2007, 67, 2584.
4. Kim, W. J.; Taya, M.; Nguyen, M. N. Mech Mater 2009, 41, 1116.
5. Huang, J. C. Adv Polym Tech 2002, 21, 299.
6. Cui, L.; Zhang, Y.; Zhang, Y.; Zhang, Z.; Zhou, W. Eur Polym J 2007, 43, 5097.
7. Yin, Q.; Li, A. J.; Wang, W. Q.; Xia, K. G.; Wang, Y. M. J Power Sour 2007, 165, 717.
8. Fladin, L.; Chang, A.; Nazarenko, S.; Hiltner, A.; Baer, E. J Appl Polym Sci 2000, 76, 894.
9. Feller, J. F.; Linossier, I.; Grohens, H. Mater Let 2002, 57, 64.
10. Choi, M. H.; Jeon, B. H.; Chung, I. J. Polymer 2000, 41, 3243.
11. Blythe, A. R. Electrical Properties of Polymers; Cambridge University Press: Cambridge, 1979.
12. Laasko, J.; Oesterholm, J.-E.; Jaervinen, H. U.S. Pat. 5,662,833 (1997).
13. Pinto, G.; Maaroufi, A. K. J Appl Polym Sci 2005, 96, 2011.
14. Bueche, F. J Appl Phys 1972, 43, 4837.
15. Simitzis, J. Angew Makromol Chem 1989, 165, 21.
16. Braun, D.; Cherdron, H.; Kern, W. Praktikum der Makromolekularen Organischen Chemie; Dr. Alfred Huthig Verlag: Heidelberg, 1971.
17. Vilcakova, J.; Saha, P.; Quadrat, O. Eur Polym J 2002, 38, 2343.
18. Akamatsu, K.; Deki, S. Nanostr Mater 1997, 8, 1121.
19. Linford, R. G. In Applications of Electroactive Polymers; Scrosati, E.B. Ed.; Chapman & Hall: London, 1993.
20. Lux, F. J Mater Sci 1993, 28, 285.
21. Carmona, F.; Mouney, C. J Mater Sci 1992, 27, 1322.
22. Malliaris, A.; Turner, D. T. J Appl Phys 1971, 43, 614.
23. McLachlan, D. S.; Blaszkiewicz, M.; Newnham, R. E. J Am Ceram Soc 1990, 73, 2187.
24. Struempler, R.; Glatz-Reichenbach, J. J Electroceram 1999, 3, 329.
25. Carmona, F.; Prudhon, P.; Barreau, F. Sol State Comm 1984, 51, 255.