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Electro-conductive resins filled with graphite for casting applications

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Abstract

Electro-conductive resins, convenient for casting and coating applications were investigated in this paper.

Electrical conductivity of epoxy and polyurethane resins, filled with two different grades of synthetic graphite (different average size) was studied. It was found that all the investigated composites became electro-conductive when filled with 22-vol% of the filler.

The impact strength of epoxy and polyurethane resins filled with graphite was also investigated. A decrease in impact strength with an increase in filler content was observed in all cases. The highest values of impact strength were found for polyurethane/graphite KS 6 composites.

The strength of adhesion of the filled resins to aluminum was also determined. A decrease in the strength of adhesive joints to aluminum foils with an increase in filler content was observed in all cases. The strongest adhesive joints were found for the epoxy/graphite KS 6 composites.

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1. Introduction

A high electrical charge on the surface of plastics causes some problems, like handling during transport, storage and packing, dust contamination, affecting both appearance and performance of end products, risk of electrical shocks to employees working at the machines, as well as the risk of electrical discharge causing fire or explosion [1–3]. To reduce the surface or/and volume electric resistivity and hence dissipate high electric charge density on the surface of plastics, either antistatic agents or electro-conductive fillers are used [4–11].

High performance antistatic or/and electrically conductive materials, used for casting (plank, etc) or coatings, are usually designed by combining the thermosetting resin and efficient electrically conductive fillers [12–14]. There are usually a few types of basic polymeric matrices available for casting—acrylics, polyesters, polyurethanes (PU) and epoxies. The filling of the system is usually focused only on the resin, and the cross-linking agent is unfilled. Resins can be cast as a pourable liquid and/or are properly filled using various inorganic or organic fillers. Most resins can be cast in properly separated flexible molds made of polysulfide and PU. To work with PU requires usually some special equipment. Casting acrylic resin means subjecting the polymer/monomer “dough” to high pressure and temperature in an autoclave, using special molds. Because of this, and because of the fact that uncured acrylic is highly toxic, most users should avoid using this method

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and rather cast PU resins that set at room temperature [15].

Graphite is frequently used as an electroconductive filler, due to its moderate cost and good conductivity [16]. Graphite has also a positive influence on the mechanical properties, as well as thermal and dimensional stability.

This paper concentrates on a study of the electrical properties (electrical conductivity, electrostatic parameters) of epoxy and PU resins filled with two grades of synthetic graphite, as well as on the investigation of some mechanical properties such as impact strength and strength of the adhesive joint to aluminum foils.

2. Experimental

A two-component PU adhesive Veropal (Synpo, Czech Republic)—polyol with a viscosity at 25 °C 800 mPa s and methylene diphenyl diisocyanate as a cross-linking agent having a viscosity of 1000 mPa s and two-component epoxy adhesive consisting of the epoxy oligomer ChS Epoxy 531 (based on Bisphenol-A-diglycidylether) (Spolchemie, Czech Republic) modified by the reactive solvent 1,6-hexanediol-diglycidylether (Sachem, USA), and having a viscosity at 25 °C of 2.2 Pa s and the curing agent Aminoamid DE 400 based on diethylene triamine (Bohemiachem, Czech Republic), were used as the polymer matrices.

The extra fine graphites Lonza KS 6 and KS 15 (Lonza, Switzerland) in the form of flakes were used as the filler. The purity of the graphite powders analyzed for determination of carbon content was: C \geq 99.9%, the ash content $<$ 0.1%. A large crystallite size [$>$ 100 nm] as well as an ideal interlayer spacing smaller than 0.3354 nm are indicative of the high degree of graphitization of graphite powders. The density (in Hg)—2.19 g/cm³, specific surface— \geq 50 m²/g, particle size (determined by laser diffractometry)—90% of particles were smaller than 15 μ m (KS 15) or 6 μ m (KS 6).

The composition of the aluminum alloy AlMgSi0.5 was: 98.45-wt.% Al, 0.7-wt.% Mg, 0.5-wt.% Si, 0.2-wt.% Fe and 0.15-wt.% Mn.

The electrically conductive materials were prepared by mixing both components of epoxy or PU resins with the respective electrically conductive fillers at room temperature for 20 min at a mixing speed 20 rpm using a lab-scale mixer (Koba, SR). The components of epoxy or PU resins, i.e. epoxy resin and hardener or polyol and hardener, were mixed together in the weight ratio 2:1.

The single overlapped adhesive joints were prepared after degreasing of the aluminum alloy slabs with toluene and subsequent bonding. The dimensions of the aluminum slabs were 60 \times 10 \times 2 mm; the thickness of the adhesive layer was 0.1 mm. The bonded area of each adhesive joint was 1 cm². All adhesive joints were

hardened 24 h at room temperature, and consequently for 3 h at 100 °C.

For measurements of electrical properties, circular discs with a diameter 30 mm and a thickness about 0.5 mm were prepared by casting into silicone rubber forms. The samples were tested after 7 days of adhesive hardening at room temperature.

The volume electrical conductivity of adhesives was measured according to ASTM D-257. A three-electrode electrometer arrangement was used for the DC-measurement of the electrical resistivity. The voltage level varied in the range 0.1–500 V.

The specimens (80 \times 10 \times 3 mm) for determination of impact strengths were prepared by casting in silicone rubber forms. After 7 days of hardening at ambient temperature, the samples were tested at room temperature using a Charpy pendulum working in the range 0–4 J/cm².

The strengths of adhesive joints were measured by tensile testing of aluminum single overlapped adhesive joints, with dimensions 60 \times 10 \times 2 mm using an 5 kN universal testing device Instron 4301 (Instron, England) at a constant cross-head speed of 10 mm/min. The measured data were processed using computer software that enables the statistical evaluation of the results.

Antistatic properties of the composite adhesives were measured using an integrated electrometer Polystat PS-1 (JZD Jizera, Czech Republic). The 1-mm thick discs were prepared with epoxy and polyurethane casting resin using a silicone rubber form. After hardening the specimens were cleaned with n-heptane, fixed in a stainless steel device holder and charged during 20 s in 15 kV electric field using a corona discharge plasma. The maximum surface potential of sample and its changes with time were periodically measured.

3. Results and discussion

3.1. Electrical conductivity

The dependence of electrical conductivity of epoxy and PU resin, filled by synthetic graphite, is shown in Figs. 1 and 2.

The concentration of the filler, when internal conductive network of particles is formed within the polymeric matrix and the material becomes electroconductive is called *percolation concentration* (ϕ_c). A number of factors have been identified as being important for the formation of conductive networks in filled polymers, including the morphology of the filler and its surface activity, the wettability of the filler by the polymer, solidification rates after mixing and post-processing the rheology of the polymer during the mixing process, etc. This complexity makes difficulties in prediction of percolation concentration as well as the dependency of

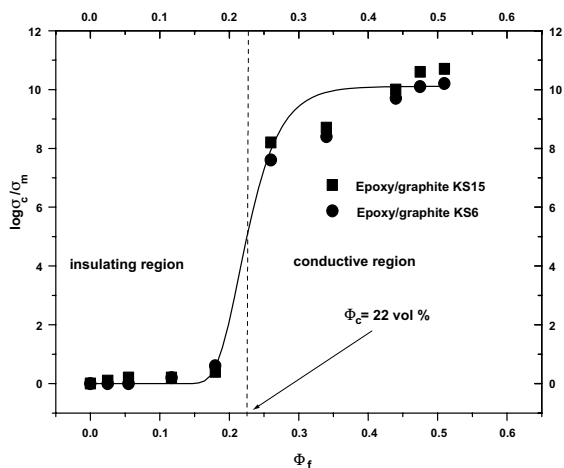


Fig. 1. Electrical conductivity of epoxy resin filled with graphite KS 15 (squares) and graphite KS 6 (circles). Solid line = fitting according to Eq. (1).

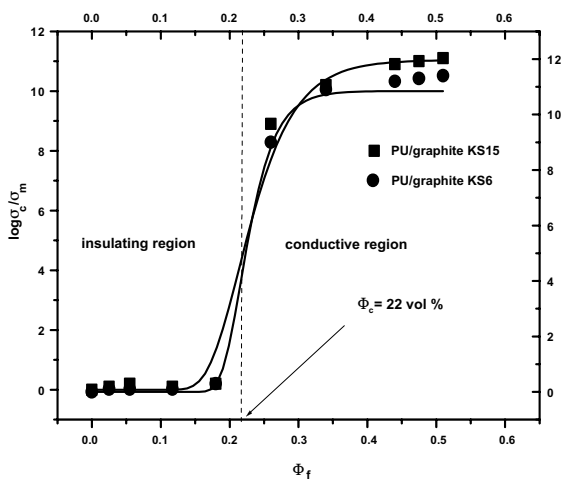


Fig. 2. Electrical conductivity of polyurethane filled with graphite KS 15 (squares) and graphite KS 6 (circles). Solid line = fitting according to Eq. (1).

electrical conductivity on the filler content. The most prominent models were reviewed by Lux [17]. He concluded that currently no model exists which is able to explain all the different experimental results as well as to be able to account for the extensive influence of different parameters and processing methods on the percolation process. In the past, we have suggested the empirical function given by Eq. (1) [18,19], which appropriately fits experimental dependencies electrical conductivity versus volume filler content.

$$\log(\sigma_c/\sigma_m) = B(1 - e_r^{-a\phi})^n \tag{1}$$

B , a , n are adjustable parameters, σ_c is the electrical conductivity of the composites, σ_m the electrical conductivity of the polymeric matrix, and ϕ_f the volume portion of the filler. A percolation point (ϕ_c) has been arbitrary identified as an inflexion point in this empirical fitting curve.

An inflexion point (ϕ_i) was calculated according to Eq. (2) [18,19]:

$$\phi_i \equiv \phi_c = \ln(n)/a \tag{2}$$

The reason, why percolation concentration was arbitrary defined is that in real situation, when only limited number of experimental points is available, the unambiguous determination of exact percolation concentration is difficult.

It was found that the percolation concentration depends on neither the grade of the graphite nor on the type of polymeric matrix. In all investigated cases, the value of 22-vol% of the filler was determined as the concentration where material becomes conductive. It was also found that the matrix (Epoxy, PU) as well as the type of graphite has no significant influence on the electrical conductivity of composites, as seen in Figs. 1 and 2.

3.2. Antistatic properties

Epoxy and PU resins are often used for coating of an inorganic or metallic surface. If they are filled with conductive filler, the coatings become antistatic.

The antistatic properties, expressed by discharging characteristics of epoxy and PU composite adhesives filled with two grades of graphite are summarized in Tables 1 and 2.

The discharging characteristics of the samples, i.e. the maximum surface electrostatic potential (V_{max}) and the half-life of electrostatic discharging ($\tau_{1/2}$) [18], were investigated for epoxy resin (Table 1) and for PU (Table 2). The results obtained from the measurement of the antistatic properties of epoxy and PU composite adhesives showed that the antistatic properties were reached

Table 1
Discharging characteristics of epoxy filled with graphite KS 6 and KS 15 (the values in the brackets)

Content of graphite KS 6 (KS 15) (vol%)	$V_{max} \times 10^{-1}$ (kV)	$\tau_{1/2}$ (s)
0	72 (76)	–
2.5	68 (72)	–
5.5	56 (60)	–
11.7	48 (54)	152 (166)
18	36 (40)	94 (120)
26	8 (12)	8 (10)
34	6 (8)	4 (8)
44	2 (2)	2 (2)

Table 2
Discharging characteristics of PU filled with graphite KS 6 and KS 15

Content of graphite KS 6 (KS15) (vol%)	$V_{\max} \times 10^{-1}$ (kV)	$\tau_{1/2}$ (s)
0	76 (78)	—
2.5	72 (74)	—
5.5	64 (66)	—
11.7	54 (62)	166 (196)
18	44 (50)	128 (138)
26	10 (10)	20 (36)
34	6 (10)	4 (8)
44	2 (2)	2 (2)

at the lower concentration of the graphite in the case of epoxy composite adhesives in comparison with PU adhesives. Electrically conductive adhesives, having a leakage half-life of electrostatic discharge lower than 10 s, are considered as antistatic materials. This goal was reached for a graphite content in the epoxy-based composites exceeding 22-vol%, e.g. for 26-vol% of graphite in the composite adhesive (Table 1 for epoxy and Table 2 for PU), and the half-life of electrostatic discharge was 10 s or lower. The epoxy and PU composites with graphite KS 15 (Tables 1 and 2, values in brackets) give higher values of the surface electrostatic potential and of the half-life of electrostatic discharge, compared to the graphite KS 6.

3.3. Impact strength

The dependence of impact strength of epoxy and PU resin filled with graphite KS 15 and graphite KS 6 on the volume portion of the filler is shown in Figs. 3 and 4. A decrease in impact strength and toughness with an increase in filler content was observed in all cases. This behavior is common for polymers filled with particulate filler. The particulate filler initiates a crack formation via stress concentration on the filler surface [20–22]. As far investigated composites, the impact strength of materials, filled with graphite KS 6 is higher than the impact strength of materials filled by graphite KS 15 (Fig. 3), probably due to its higher specific surface. This behavior was observed for both epoxy and polyurethane matrix.

It was found that the impact strength of PU/graphite composites is higher than that of impact strength of epoxy/graphite composites for both grades of graphite. This behavior is the result of the higher elasticity of PU.

3.4. Adhesion of epoxy/graphite and PU/graphite resins to aluminum

The adhesion of epoxy as well as PU resin filled with graphite particles to aluminum was investigated. The

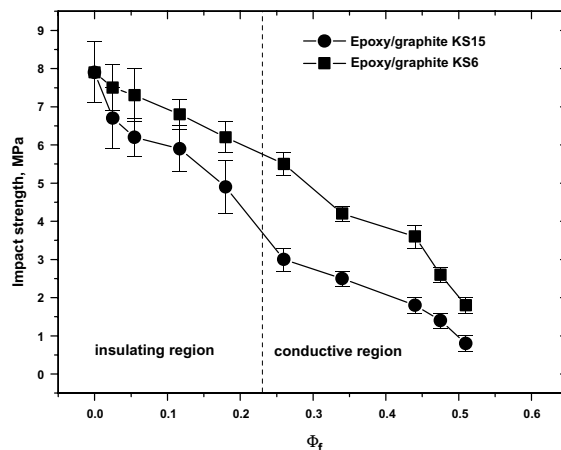


Fig. 3. Impact strength of epoxy resin filled with graphite KS 15 (circles) and graphite KS 6 (squares).

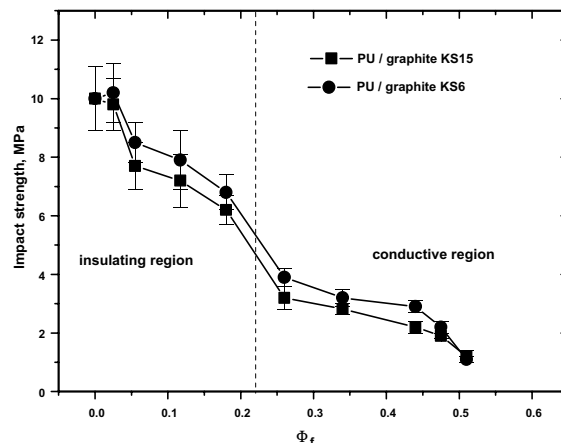


Fig. 4. Impact strength of polyurethane filled with graphite KS 15 (squares) and graphite KS 6 (circles).

adhesive joints created by two aluminum slabs were bonded together by the filled resins, and then mechanically strained. The dependence of the strength of adhesive joint on the filler content is shown in Figs. 5 and 6.

It is seen that the strength of adhesive joint decreases with an increase in filler content in the whole concentration range, for all investigated resins. Despite the fact that the strength of the adhesive joints decreases with an increase in the filler content, the composites can be successfully used as electrically conductive adhesives, since the improvement in the electrical properties of adhesives, through the dispersion of the conductive filler in the polymeric matrices, is much more significant than the deterioration of strength of the adhesive joints.

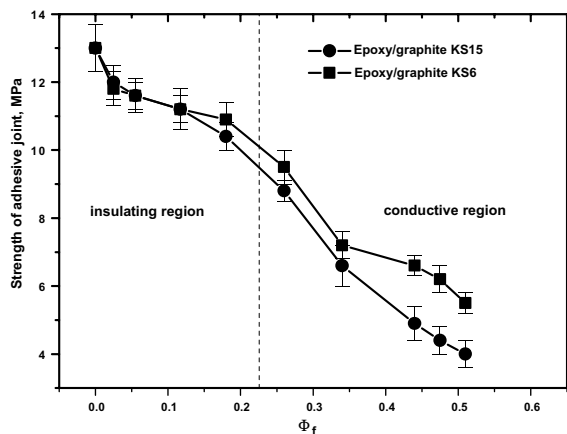


Fig. 5. Strength of adhesive joint formed by epoxy resin filled with graphite KS 15 (circles) and graphite KS 6 (squares).

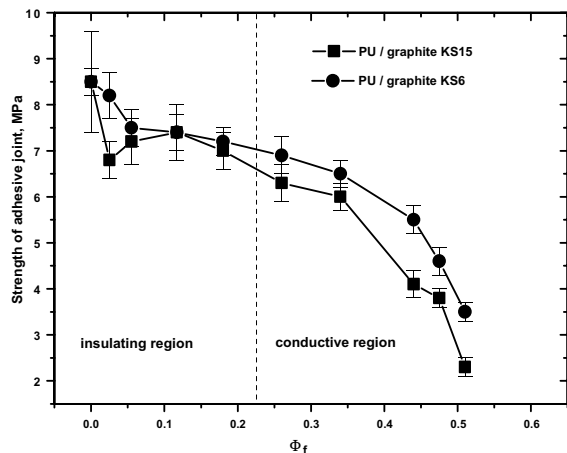


Fig. 6. Strength of adhesive joint formed by polyurethane filled with graphite KS 15 (squares) and graphite KS 6 (circles).

It was found that the strengths of adhesive joints, based on the epoxy resin, are significantly higher than those based on PU in the whole concentration region, since epoxy matrix has a higher adhesion to aluminum than PU (values of 12.5 MPa for neat epoxy resin and 8 MPa for PU). This effect is more pronounced at lower filler content (Fig. 5), when the particles of the filler are better wetted. Comparing the different grades of graphite shows that graphite KS 6 increases the strength of adhesive joint more than graphite KS 15, probably due to its higher specific surface.

The highest strengths of the adhesive joints were found for epoxy/graphite KS 6 composites.

4. Conclusions

A percolation concentration of electrically conductive resins, filled with different grade of graphite, was determined to be 22-vol% for all the investigated composites. The grade of graphite, as well as type of polymeric resin, had no significant influence on either percolation concentration, or electrical conductivity. These results were confirmed by measurements of anti-static properties because the electrostatic material was obtained after reaching the percolation concentration of graphite in the composite adhesive.

A decrease in impact strength with an increase in filler content was observed in all cases. The highest impact strength was observed for PU/graphite KS 6 composites.

A decrease in the strength of the adhesive joint to aluminum with an increase in filler content was observed in all cases. The highest adhesive joint strengths were observed for adhesives based on epoxy/graphite KS 6.

Acknowledgements

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