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Challenges in joining conductive adhesives in structural application – Effects of tolerances and temperature

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ABSTRACT

Our investigations evaluate the usage of an electrically conductive adhesive facing the challenges of structural application when at the same time antistatic electrical properties are important. Structural adhesive joints typically have the characteristic of an electrical insulation between the adherends. To overcome this issue we incorporated 20 wt% electrically conductive graphene nano-platelets in an epoxy resin, to achieve an electrically conductive adhesive composite. Under unloaded condition the investigated composite joint provides shear strength of 11.4 MPa and a volume resistivity of $8.5 \times 10^4\ \Omega$ cm.

In summary following observations are identified: Electrically conductive adhesive composite joints are able to meet structural requirements at a temperature within the structural application range even if tolerances up to 1 mm need to be compensate. The volume resistivity of the joints is sensitive to elongation. Suppression of the load-dependent elongation by thin adhesive layer benefits the conductive robustness of the joint. If a high displacement is important, a thick adhesive layer enhances the ability of an undamaged shift of the conductive particle network by an increased deformability.

1. Introduction

Adhesive joining is a suitable bonding technology to match the requirements of today's lightweight and multi-material design. In structural applications bonding by adhesives typically leads to an electrical separation of the components. But when protection against electro-static discharge (ESD) ($<10^6\ \Omega$ cm) is important, additional efforts are necessary to achieve an electrical connection of the components. An intrinsic electrically conductive adhesive would eliminate the need for an additional manufacturing step. A well-known procedure achieving electrical conductivity in a polymer matrix is the incorporation of conductive particles. The particle fraction is raised until pathways of particles build connections between the adherends, and an electrical charge can be transported through the adhesive matrix [1,2]. With the first formation of a particle network a drop of the electrical resistivity occurs and the so-called percolation threshold is achieved [3]. As shown in Fig. 1a drop of the electrical resistivity of a composite is already observable when a connected particle network is not fully developed. This early drop of resistivity is possible due to electron tunneling between particles in close proximity [4,5]. Taking this into account we divided Fig. 1 into three sections.

Section 1 included the composite with low filler fractions which does not lead to a decrease of the electrical resistivity. In Section 2 a drop of the electrical resistivity occurs. In this section the particle network is not fully developed and the electrical resistivity of the composite is dominated by electron tunneling. In Section 3 a particle network is developed by physical particle contact which means absolute percolation is achieved. The lowest electrical resistivity is mainly limited by the contact resistances.

The drawback of this procedure is a decrease of the joint strength when high filler fractions are necessary [6–8]. To avoid catalytic effects or galvanic corrosion the use of a carbon-based additive is beneficial. Several studies show that graphene nano platelets (GNP) are adequate conductive fillers [9–11]. Graphene was introduced in 2004 by Novoselov et al. [12]. It provides low electrical resistivity and a flat, platelet morphology [13]. Non-spherical morphology of filler-particle leads to a strong influence of the processing parameters to the electrical resistivity of the composite [14,15]. While the polymer matrix provides the mechanical and chemical properties of the composite the filler fraction is kept low to maintain the properties. The application of protection against electrical discharge is already achieved by filler fraction of Section 2. Therefore the electrical properties of the structural adhesive for structural application are dominated by electron tunneling [2]. In structural application several requirements need to be matched by an adhesive joint. Besides shear strength to withstand high loads, the adhesive needs to compensate tolerances as well as withstanding environmental influences

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such as temperature of the adherends geometry without a loss of properties. Investigations by Sancaktar et al. and Wei et al. show the interrelationship of diminishing conductivity at lower adhesive thickness [17,18]

In this study electrically conductive adhesives for structural application are investigated. The adhesive composite is achieved by the incorporation of GNP in an epoxy resin. The influence of tolerances, which lead to various thicknesses of the adhesive layer, is investigated while the adhesive joint is exposed to mechanical load. Furthermore the effect of different operating temperatures in industrial application is taken into account. The evaluation of the electrically conductive adhesive joints is based on the shear strength, the conductive robustness of the joint and the fragility of the particle network within the adhesive.

2. Materials and methods

Typical representatives of structural adhesives are based on epoxy resins. We chose the 2-component system AH120/LI130-2 (Ebalta-kunststoff GmbH, Germany) which is composed of an unfilled epoxy resin and an amine curing agent. Due to the low viscosity of the system we added a thixotropic agent to achieve a practicability of the system for adhesive application. The curing is possible at room temperature, but can be accelerated by exposure to elevated temperatures. To achieve an electrical conductivity GNPs of the size up to 15 nm (IoLiTec-Ionic Liquids Technologies GmbH, Germany) were used as filler material. Measurements of the dry graphene powder show a volume resistivity lower than 1 Ω cm.

To prepare the adhesive composite in the first step a GNP fraction of 20 wt% and methyl ethyl ketone (MEK) for better sonication were added to the epoxy resin. After a homogenous mass is produced by ultra-sonication (Hielscher Ultrasonics GmbH, Germany) and stirring the MEK is removed at 60 °C for eight hours. Afterwards the hardener is added as well as the thixotropic agent because of the manageability of the joining process. By mixing all components by a dual asymmetric centrifuge a homogenous adhesive composite is achieved. The adherends are made of steel, which provides an electrical resistivity smaller than 1 Ω cm that observations can be clearly attributed to the adhesive-particle composite. The adherends provide a dimension of 100 mm × 25 mm and are joined as single lap shear specimens according to DIN EN 1465. We manufactured five samples of each series with an overlap of 12.5 mm and various adhesive layer thicknesses. After the joining procedure the samples are cured in an oven at 60 °C for four hours. Fig. 2 shows the manufacturing procedure of the adhesive composite and the final specimen.

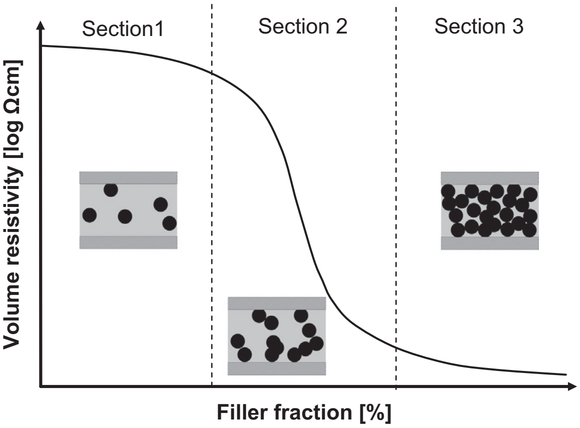

Fig. 1. Schematic representation of the volume resistivity of a polymer-particle-composite in dependence of the filler fraction.

The operating temperature is evaluated by dynamic mechanical analysis (DMA) at a temperature range from 25 °C to 160 °C, a temperature rate of 3 K/min an 1 Hz.

The shear strength tests are performed with a tensile test machine (Instron GmbH, Germany) in combination with an integrated oven to enable tests at various temperatures. The electrical resistance is simultaneously measured by an ohmmeter and the volume resistance is calculated by

$$\rho = (R \cdot W \cdot B)/L \tag{1}$$

ρ (Ω cm) being the bulk resistivity, R (Ω) the measured resistivity, W (cm) the width, B (cm) the length and L (cm) the thickness of the adhesive layer.

The results are presented as shear strength and volume resistivity of the composite in dependence of the layer thickness or temperature at an initial load of 100 N. Furthermore, for each series the reaction of the volume resistivity to load is shown to evaluate the robustness of conductivity of the joints against load. The fragility of the electrically conductive particle network is based on the changes in the volume resistivity depending on displacement. To provide comparability the changes in the volume resistivity are given in % up to the last point where a conductivity of the joint is given.

3. Results and discussion

As shown in Fig. 3 the percolation of the adhesive composite occurs when the GNP fraction exceeds 10 wt%.

The shear strength is measured by single lap shear specimens with a adhesive layer thickness of 0.3 mm and provides a cohesive failure when the GNP fraction exceeds 8 wt%. To secure a reliable value of electrical resistivity for antistatic application ($< 10^6$ Ω cm) our adhesive composites contain a GNP fraction of 20 wt%. The composite provides shear strength of 11.4 MPa, which means a decrease of 19% compared to the unmodified adhesive (14.0 MPa).

3.1. Influence of geometric tolerances (adhesive layer thickness)

To evaluate the influence of tolerances in component manufacturing, which must be bridged by the adhesive, samples with adhesive thicknesses of 0.3 mm, 0.5 mm and 1 mm are investigated. Fig. 4 shows the influence of the adhesive layer thickness on the maximum shear strength and the initial volume resistivity.

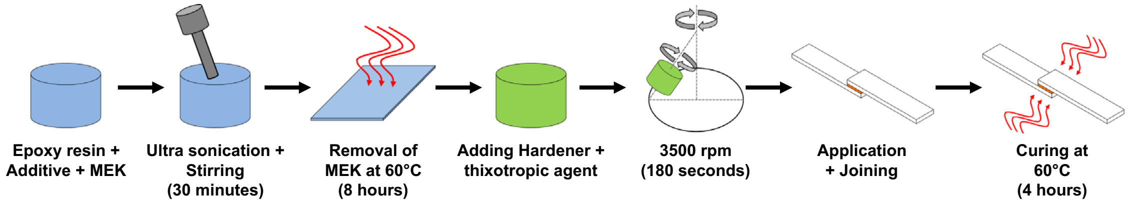

Fig. 2. Manufacturing procedure of the adhesive composite and final specimen.