Composites Science and Technology 72 (2012) 1841–1847

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Conductivity enhancement of silver filled polymer composites through electric field alignment

G.K. Johnsen [a,*], M. Knaapila [a], Ø.G. Martinsen [b,c], G. Helgesen [a,b]

[a] Physics Department, Institute for Energy Technology, NO-2027 Kjeller, Norway
[b] Department of Physics, University of Oslo, NO-0316 Oslo, Norway
[c] Department of Clinical and Biomedical Engineering, Oslo University Hospital, Rikshospitalet, Norway

ARTICLE INFO

Article history:
Received 3 May 2012
Received in revised form 6 July 2012
Accepted 10 July 2012
Available online 25 July 2012

Keywords:
A. Polymer–matrix composites
A. Metals
B. Electrical properties
C. Anisotropy
D. Optical microscopy

ABSTRACT

We show how an alternating electric field can be used to align silver micron or sub-micron sized particles into microscopic wires in diverse polymer matrices based on the dielectrophoretic effect. The electric field is set by an electrode pair and the wires form conductive pathways through the matrix, bridging these electrodes electrically. The matrix is cured after alignment, locking wires in permanent pathways within the polymer. The wires are then characterized by ac impedance spectroscopy. The alignment can take place either in-plane or out-of-plane, and yields a directional conductivity in the alignment direction parallel to the electric field lines. The samples can be centimeters wide containing thousands of wires in parallel, but even an individual wire can be grown and controlled. The initial mixture contains less than 1 vol.% of silver and is an electrical insulator. The bulk conductivity enhancement, due to the alignment, may be 5 orders of magnitude, typically from 1×10^{-5} S/m to 1 S/m as the particle alignment converts the sample conductivity from polymer dominated to silver dominated. For the aligned isolated silver wires, the jump in conductivity, confined to the volume filled by the wire can be seen to be as high as 9–10 orders of magnitude, resulting in conductivities as high as 1×10^{5} S/m, thus approaching those of pure metal. This technique offers new ways on how e.g. conducting polymer composites and conducting glues could be produced.

1. Introduction

By applying an alternating electric field between a suitable set-up of two or more electrodes, conductive particles dispersed in a fluidlike polymer or polymer precursor matrix can be manipulated to align into thin conductive strings, bridging the electrodes electrically even at particle filler ratios tenfolds below the percolation limit. The driving mechanism behind such a field alignment is dielectrophoresis (DEP) by which a polarizable, but charge-neutral particle feels a net force parallel to the electric field lines [1]. The only requirements for an existing DEP force are the field gradient be non-zero as well as must the particles and matrix have non-equal electric permittivities. If the particle is more polarizable than the dispersing matrix, the particles will move in the direction of increasing field strengths, and so the particles will start aligning into wires at the electrodes since the DEP force points towards the electrode edges [2]. Once the wires are complete, the matrix can be cured rendering solid anisotropic material.

In industries such as electronics packaging, electric interconnections are traditionally established by soldering that ensures high electronic contact [3]. However, such a soldering also involves environmental unfriendly metals as well as high temperatures yielding mechanical stress, factors which are both unwanted [4]. Therefore, electrical conductive adhesives are experiencing increased attention [3,5], and potential applications include fills for semiconductor packaging [5], interconnection of solar cells [6] as well as in making electro-mechanical connections in touch screens [5,7]. Commercially available isotropic conductive adhesives are generally based on silver particle loadings of as high as 70–90 wt.% in an insulating polymer [3,5,8–10]. The high silver particle loading, well above the percolation limit, ensures conductive paths in all directions within the adhesive due to unavoidable particle–particle contacts. However, such high silver loadings are cost inefficient, suppress polymer properties such as adhesion to e.g. metal surfaces [3,11], optical transparency, as well as generating an often unavoidable macrophase separation [12]. Printing of pastes becomes difficult as high loadings of nanomaterials cause a drastic increase in viscosity of the paste [11]. Due to the reduced optical transparency caused by the filler particles, curing of the matrix cannot be performed by the well-controlled UV process [13], but must be performed by thermal methods or other time- and cost inefficient methods [11]. Orienting graphite sheets, dispersed in a polymer resin, by a dc electric field has proven to increase the

* Corresponding author.
E-mail address: gormj@fys.uio.no (G.K. Johnsen).

0266-3538/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compscitech.2012.07.011

optical transparency significantly [14]. From a practical working point of view, UV curing is a superior principle to control the curing of the polymer. Thus, a semitransparent polymer composite, due to a significantly reduced particle loading, that also conducts will be useful in many application areas.

One method to produce conductive adhesives at low filler ratios consists of using specific high aspect ratio particles as fillers, as this may result in a lower percolation limit [5,15]. The particles can be chosen long enough to reach from one electrode to the next, yielding anisotropic conductive adhesives [15,16]. However, this may impose restrictions on the maximal distance between the electrodes, as well as provide an uncertain method for making conductive bridges as the particle may not hit both electrodes.

It would therefore be an advantage if the conductive adhesives and similar composites were constructed by a much lower particle filler ratio by aligning small particles into thin, highly conductive wires. Such an alignment might be performed either across the materials thickness or parallel to its surface, all depending on the final product purpose. This would also enable a directional conductivity, if desired, yielding conductivity only in the direction of interest as a curing of the polymer locks the aligned wires in a stable configuration [17]. Anisotropic structuring of carbon based filler particles, although of high volume fractions, generated by different alignment methods, has previously shown to enhance the adhesives mechanical properties [14,16] as well as the thermal conductivities [18] along the direction of alignment.

Electric field alignment studies of various carbon filled polymers have previously been carried out, in some also with conductive adhesive applications in mind. Materials used for these purposes have been carbon nano cones [17,19], carbon nano tubes [20–22] carbon black [7,23,24], and carbon fibers [25]. These materials allow bulk conductivities up to 10^{-1} S/m [25]. Elsewhere, studies of dielectrophoretic growth of metallic wires [26], electric field alignment of gold nano particles [27], silver nanowires [28] as well as magnetic alignment of nickel particles [29] have also been performed, but not with micro or nano-sized silver particles as fillers with the purpose of high conductive aligned wires with conductive adhesives applications in mind.

In this paper we have used silver particles as fillers with the purpose of making high conductive adhesives at low particle filler loadings. We show that the particle loading, resulting in conducting wires, can be as low as ten times below the percolation limit when the polymer matrix is subject to an alternating electric field, and we seek a method for making conductive adhesives at minimal loading ratios and cost. The silver particles are aligned into thin conductive wires from an initially isotropic and low fraction polymer with no macroscopic electric conductive properties, yielding anisotropic conductivity and a significant jump in conductivity in the direction of the applied electric field. We present results of electric field alignment of silver particles of micro or sub-micro particle size, both in terms of individual wires as well as larger bulk samples, consisting of thousands of wires in parallel, and investigate their general electrical properties. In total, we show how conductive adhesives, consisting of silver aligned wires, can be constructed from a very low particle fraction, enhancing the polymer properties. The results of this study have implications on how conductive adhesives are produced, with implications in areas such as solar cell interconnections, conductive, transparent films, sensor applications and electronics packaging.

2. Materials and methods

2.1. Materials

The silver particles used in this study were commercially available flakes (>99.9%, <10 μm) provided by Sigma–Aldrich. Two different adhesive polymers were used for dispersing the silver particles. A two component thermoset polymer containing Araldite AY 105-1 epoxy resin (Huntsman Advanced Materials) with Ren HY 5160 or HY 5162 amine hardener (Vantico AG), and a UV-curable Dymax 3094 acrylated urethane based polymer (Dymax Corp.). Both choices of polymers were of technical quality and supplied by Lindberg & Lund (Norway). Mixing of the silver particles with the polymers was performed by a 120 rpm stirring at room temperature for 20 min or more. For alignment studies the particle concentrations were ranging from 0.1 to 0.5 vol.% which is well below the expected value for the percolation limit.

2.2. Electric field alignment

The alignment procedure and used alignment geometries are illustrated in Fig. 1. For the generation of single wires, the silver matrix was placed to form a uniform, thin layer on top of tip-like electrodes (Fig. 1A). The thickness and width of these electrodes were 100 nm and 3 μm, respectively, and the tip-tip distance was in the range of 10–100 μm. For larger samples with multiple wires, the alignment of the silver particles was either performed horizontally (in-plane alignment; Fig. 1B) by placing the matrix on a glass microscope slide with prefabricated electrode fingers under optical microscopy observations, or vertically between a top and bottom metallic electrode (out-of-plane configuration: Fig. 1C), as described in more detail in earlier works [19]. The distances between the alignment electrodes were in the range of 50–1000 μm in both geometries. In all our experiments, the silver–polymer dispersion was placed onto the electrode-set-up immediately after the mixing. In this procedure there was no time for significant particle precipitation.

Before any alignment procedure to be initiated to a matrix, its resistance through the electrodes was measured by a Fluke 179 multimeter. The ac electric field needed for particle alignment was provided by a B&K Precision function generator combined with a Model 2210 amplifier (Trek Inc.). The signal frequency used was 1 kHz sinusoidal, and electric field strengths (rms values) were typically of 1–4 kV/cm, lasting from 10 s up to several minutes. The alignment of the silver particles was monitored by optical microscopy, and the enhancement of the matrix conductivity was studied by dc and ac electrical measurements. Curing of Araldite matrix was performed by moderate heating at 60 °C for 1 h. Curing of the Dymax matrix was performed by UV light using Dymax Blue Wave 200 UV source.

2.3. Electrical characterization

The detection of the conductivity enhancement was observed by the sudden drop of resistance, measured by a Fluke 179 multimeter. The process was monitored in an optical microscope (Nikon Optiphot), with possibilities of continuous image recording (DinoCapture 2.0). The silver conductivity data estimates, both for the single wires as for the bulk samples, were performed using Ohm's law for volume conductors. For the single wire conductivity estimates, a most correct value of the volume of each wire was achieved based on the optical images of the completely connected wires. The wires were modeled as massive cylinders with a best estimate of the diameter obtained based on the optical data. For the in-plane aligned conductive sheets, the factor to be determined for conductivity estimates was the vertical thickness of the film, which was set to 50 μm.

The impedance analysis of the aligned wires was performed after the samples had been cured, locking the wires in a conducting configuration, suitable for e.g. transportation and further electric characterization. In that respect, the dc electric conductivity study was completed with an ac electric impedance spectroscopy for the