Journal of Industrial and Engineering Chemistry 20 (2014) 4108–4111

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

The effects of graphene on the properties of acrylic pressure-sensitive adhesive

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ARTICLE INFO

Article history:
Received 30 October 2013
Accepted 4 January 2014
Available online 10 January 2014

Keywords:
Acrylic pressure sensitive adhesive
Graphene
Surface resistivity
Peel strength
Nickel

ABSTRACT

Graphene was examined as a conductive filler to reduce the surface resistivity of an acrylic pressure-sensitive adhesive (PSA). The graphene effectively reduced the surface resistivity; however it also reduced the peel strength of the PSA. This peel strength reduction could be minimized when the graphene was not mixed homogeneously but embedded in the PSA as a separate layer. In addition, the surface resistivity was reduced much more effectively. Typically, the surface resistivity reduced to one-millionth, when 1 part of graphene was imbedded as a separate layer in 100 parts of PSA, compared to that of homogeneously dispersed composite.

1. Introduction

Protective tapes for electronics should have electrostatic discharge properties in order to prevent the damage on the electronics by the electrostatic discharge that occurs upon tape removal. Therefore the pressure-sensitive adhesive (PSA) used for preparation of the protective film should combine typical PSA characteristics with electrical conductivity. Conductive fillers such as metal powders or carbon-based fillers, a special grade of graphite or carbon black for example, are used as antistatic additives. However, in order to effectively exhibit antistatic properties, the filler loading should be greater than several percent; unfortunately, a filler loading at this level can damage important PSA characteristics such as tackiness [1,2].

Nano-carbons, such as graphene or carbon nanotubes (CNT), have a very low percolation threshold of electrical conductivity, near 1 wt% in polymer nanocomposites, because they have high conductivity and a large aspect ratio [3–6]. Therefore, they can be utilized as an effective antistatic additive for PSA.

Because graphite oxide (GO) is thermally reduced and exfoliated at high temperatures under an inert atmosphere, bulk quantities of graphene can be produced in an economical and eco-friendly manner through the rapid heating of highly oxidized GO [7]. These exfoliated sheets are typically composed of few-layers graphenes with specific surface areas ranging 400–1500 m^2/g [8,9]. They can be finely dispersed in various solvents or polymers without any additional modification because they contain oxygen-containing functional groups that remain even after thermal reduction [5,9,10]. The advantages in productivity, simplicity of the thermal exfoliation, and good compatibility with polymers make the thermally reduced graphene promising for many applications in which flat and perfect single-layer graphene is not mandatory and quantity is more than important [11].

The thermally reduced graphene exhibits a percolation threshold value as low as 0.39 wt% in the nanocomposite of polyurethane without further modification of the graphene [5]. Accordingly, graphene is a strong candidate as an antistatic additive for PSA. However, to the best knowledge of the authors, there are no reports to date regarding graphene-modified PSA. This paper reports the effect of graphene on acrylic PSA characteristics and suggests a novel method that can effectively reduce electrical resistivity with minimal loss of peel strength.

2. Experimental

Graphene was formed by the thermal reduction of GO, which was prepared by the oxidation of expandable graphite using the Brodie method, as described in a previous report [12]. The surface area of graphene, as measured by the BET method, was 428 m^2/g. The electrical conductivity was 26.8 S/cm and the number average particle size, measured with a laser diffraction particle size analyzer after suspension in ethanol, was 8.3 μm [12]. Typical morphology of graphene observed by transmission electron microscope (TEM) is shown in Fig. 1. More information about

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http://dx.doi.org/10.1016/j.jiec.2014.01.008

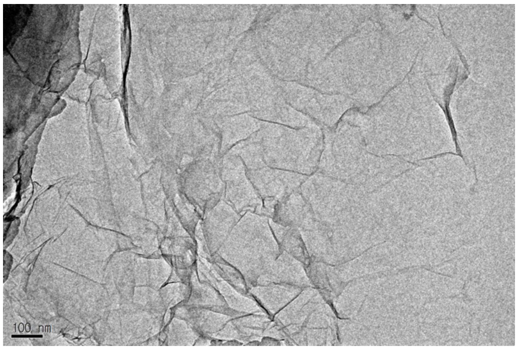

Fig. 1. Morphology of the graphene observed by TEM.

the graphene is provided in our papers published previously [5,12,13].

Acrylic PSA was prepared by solution polymerization of 2-ethylhexyl acrylate (190.0 parts) and acrylic acid (10.0 parts) in ethyl acetate at 80 °C using 2,2′-azobisisobutyronitrile (1 part) as a radical initiator. The polymerized PSA solution was cooled to 50 °C so as to dilute with ethyl acetate yielding 40 wt% solid content, and mixed at room temperature for 30 min with 0.8 parts of the cross-linking agent, N,N,N′,N′-tetrakis(2,3-epoxypropyl)-m-xylene-α,α′-diamine.

The acrylic PSA, modified by graphene through an in situ polymerization method, was prepared by the same method as in the preparation of pristine acrylic PSA, except the monomer solution was mixed with the graphene dispersion in ethyl acetate before polymerization. One gram of graphene was agitated in 150 mL of ethyl acetate for 30 min and then sonicated at room temperature for another 1 h to obtain the graphene dispersion in ethyl acetate.

To prepare acrylic PSA modified by graphene through a physical mixing method, the graphene dispersion and the acrylic PSA solution were mixed by agitation at room temperature for 30 min, followed by sonication for another 30 min. The mixture was agitated for an additional 24 h.

To prepare acrylic PSA modified by a nickel powder (Vale, T255, filamentary structure, Fisher sub-sieve size: 2.2–2.8 μm) through a physical mixing method, the acrylic PSA solution was mixed with nickel powder by agitation at room temperature for 30 min and then sonicated for another 30 min. The mixture was further agitated for an additional 24 h.

The PSA was coated on a poly(ethylene terephthalate) (PET) film to make a protective film or coated on a conductive fabric (Solueta, Korea, 300CN, surface resistivity: 7.9×10^3 Ω/square) to yield an electro-magnetic interference (EMI) shielding film. The solids content of the PSA was adjusted before coating to be 40 wt% by either adding or evaporating ethyl acetate. After coating, the protective film was heated slowly from 50 °C to 80 °C and kept at 80 °C for 2 h to dry and to crosslink the PSA. After drying, a release paper was attached on the PSA surface and the covered films were annealed further at 80 °C for 24 h. The coating weight of solid PSA, after drying, was adjusted to about 60 g/m^2 (coating thickness: about 60 μm). All film samples in Table 1 have a single PSA layer on the substrate (Fig. 2(a)) except those of *Series 6*, which have a three-layer structure (Fig. 2(b)). In the preparation of the *Series 6* samples, one-fourth of pristine PSA, graphene/PSA mixture (1/1 by weight on solid base), and then three-fourths of pristine PSA were sequentially coated and dried on the substrate to generate a three-layered structure. The thicknesses of the top and bottom PSA layers estimated from the recipe were 45 μm and 15 μm respectively. The sample designation codes in Table 1 provide information about the sample. For example, in the sample designation code of G10S1P, G10 means that the sample contains 1.0 part graphene per 100.0 parts PSA solid (1.0 phr); the S means that the sample was prepared by an in situ method; and the last 1P means that it has single-layer structure on PET. The sample designation code N20P1C means that 2.0 parts nickel powder per 100.0 parts PSA solid (N20) was physically mixed (P) and coated on conductive fabric as a single-layer structure (1C). The amount of graphene in G05P3P is 0.5 parts per 100.0 parts of total PSA solid which was used to make the three-layered structure on PET. The keywords of each Series in Table 1 are indicated next to the Series number.

The surface resistivity of the PSA surface on the films was measured with a SIMCO ST-3 surface resistivity tester. To measure the 180° peel strength, strips of films (20 mm × 55 mm) were attached to the surface of stainless steel test panel by rolling twice with a 5 kg roller at a speed of 50 mm per second. The 180° peel strength was measured 5 times for each sample with a tensile tester (OTU-2, Oriental TM Co., Korea) at a peeling speed of 100 mm/min. The morphology of graphene dispersed in PSA was observed with an Eclipse LV100 (Nikon) optical microscope equipped with an Artcam-300MI-DS digital camera. The morphologies of graphene itself and the graphene dispersed in PSA were examined also with a TEM (Hitachi H-8100). In order to examine the morphology of graphene, it was dispersed in dimethylformamide (DMF) and sonicated for 30 min. One drop of the suspended sample, about 0.005 wt% graphene, was dripped on a carbon film supported on a 200 mesh copper grid, and the DMF was evaporated at 80 °C under a vacuum. To examine the morphology of graphene dispersed in PSA, the PSA solution in ethyl acetate, having about 40 wt% solid content, was diluted with ethyl acetate to about 0.4 wt%. One drop of the diluted solution was dripped on a carbon film supported on a 200 mesh copper grid and then dried.

3. Results and discussion

In *Series 1*, where the PSA was coated as a single layer (Fig. 2(a)) on conductive fabric whose surface resistivity is 7.9×10^3 Ω/square, the resistivity is improved even with 0.1 phr loading of graphene with a marginal decrease in peel strength. This shows that only 0.1 phr graphene can help the current to pass through the PSA layer to the conductive fabric. However, when nickel powder was used as a conductive filler (*Series 2* in Table 1), the surface resistivity began to decrease evidently at a loading of 7 phr. These results show that the thermally reduced graphene can be utilized effectively for an adhesive on a conductive fabric to yield an EMI shielding film with minimal damage on peel strength.

The *Series 3* samples shown in Table 1, which were prepared by an in situ polymerization method, showed that the surface resistivity markedly decreased when the content of graphene increased above 1.0 phr. This shows that the dispersed graphene can make an effective conductive channel at a higher concentration of around 1.0 phr in case the PSA is coated on an electrically insulative PET film rather than on a conductive fabric as in *Series 1*. In addition, the peel strength decreased drastically as the graphene loading increased, which shows that finely dispersed graphene dried out the polymer with associated loss of tackiness due to strong interactions between the graphene and PSA polymer [1]. The *Series 4* samples, which were prepared by a physical mixing method, also showed similar changes of surface resistivity as graphene loading increased, however the decrease in peel strength was less evident than that of *Series 3*. In a previous study, it was observed that an ethyl methacrylate grafted on graphene, when polymerized by a radical mechanism in the presence of graphene, and this grafting enhanced the interaction between graphene and the matrix polymer [14]. When viewed from this angle, the previous results show that the PSA polymers grafted on graphene during the in situ preparation of *Series 3* enhanced the interaction between the graphene and the matrix PSA polymer; this