

ELECTROCONDUCTIVE ADHESIVES BASED ON POLYURETHANE WITH MULTIWALLED CARBON NANOTUBES

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In the present study, we prepared and characterized electrically conductive adhesives based on polyurethane filled with two kinds of multiwalled carbon nanotubes (MWCNTs), viz. pristine MWCNTs and acid treated MWCNTs, respectively. The influence of the type of filler on the dispersibility within the polyurethane matrix and the corresponding electrical conductivity is investigated. The electrical conductivity of the prepared specimens was measured using a four-point probe. The morphology and dispersibility of the fillers were observed by field emission scanning electron microscopy and transmission electron microscopy.

Keywords: Electroconductive adhesive; polyurethane; multiwalled carbon nanotubes.

1. Introduction

As an alternative to tin-lead solders, electrically conductive adhesives (ECAs) provide conductive paths to allow contact between two electrical device components. ECAs typically consist of a polymeric resin that contributes to their physical and mechanical properties, and conductive fillers—typically metal particles such as silver, gold, or nickel particles.^{1,2} Despite the many advantages of ECAs compared with tin-lead solder, they have some limitations, including low electrical conductivity and an unstable network. The latter results from the large contact points formed by the metal particles with sizes of a few micrometers.^{3–6} In order to overcome these problems, carbon nanotubes (CNTs) have been used as conductive fillers, owing to their high aspect ratio, smaller nanometer scale, and high electrical conductivity relative to those of other conductive fillers.^{6–9}

In this study, MWCNTs were found to be feasible conductive fillers for polyurethane based ECAs due to their intrinsic electrical properties and high aspect ratio. Two types of MWCNTs were used in this study, viz. pristine MWCNTs (P-MWCNTs) and acid treated MWCNTs (A-MWCNTs) which show enhanced interaction with polyurethane in composites. The dispersibility of the MWCNTs in the polymeric matrix and their electrical conductivity were also investigated according to the type of MWCNTs.

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2. Experiment

Materials. The adhesive (OKONG Co., 894HV, Korea) consists of 30 wt% linear polyester polyurethane based on toluene diisocyanate dissolved in methylene chloride, the molecular weight of which was about 250,000 g/mol. The curing agent (OKONG Co., A800H, Korea) has a triisocyanate group based on toluene diisocyanate and trimethylol propane. MWCNTs (Iljin Nanotech Co., Korea) synthesized by thermal chemical vapor deposition (CVD) were used as a conductive filler in this study. The purity of the as-received pristine MWCNTs was 97%.

Purification of MWCNTs and dispersion of MWCNTs. Pristine MWCNTs (P-MWCNTs) and acid-treated MWCNTs (A-MWCNTs) were used as fillers. The A-MWCNTs were treated with a 1:3 concentrated nitric acid-sulfuric acid mixture at 60°C for 24 h. The purity of the A-MWCNTs was determined to be 99% by thermogravimetric analysis (TGA, Polymer Lab., Q50, UK). Acid treatment is known to introduce carboxylic acid and hydroxyl functional groups onto the surface of the MWCNTs.¹⁰ The P-MWCNTs and A-MWCNTs were dispersed in N,N-dimethylformamide (DMF), separately, using an ultrasonic generator (Kyungill Ultrasonic Co., Korea).

Preparation of adhesive filled with MWCNTs. A fixed amount of polyurethane based adhesive was first mixed into the MWCNT dispersion in DMF to dissolve it. The MWCNT concentration in the polyurethane of the adhesive was varied from 1 to 12 wt%. The pre-mixed mixture was cured by adding a curing agent at a ratio of curing agent to adhesive of 1 to 20. The resultant films containing predetermined concentrations of P-MWCNTs or A-MWCNTs were prepared by casting and evaporating the solvent.

Characterization. The reaction process between the polyurethane and A-MWCNTs was monitored by means of a Biorad Fourier transform infrared spectrometer (FT-IR, VERTEX 80v, Bruker Optics, Germany). The morphology of the cross section of the specimens was observed by field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). The electrical conductivity of the polyurethane films with MWCNTs was measured with a home-built four-point probe (FPP) apparatus (Hiresta-up MCP-HT450, Mitsubishi Chemical, Japan). Transmission electron microscopic (TEM, CM200, Philips, Japan) images were obtained to confirm the morphology and dispersibility of the MWCNTs in the polyurethane matrix. Raman spectra were collected with a 1064 nm laser source on a Raman spectrometer (RFS 100/S, Bruker, Germany).

3. Results and Discussion

The as-received adhesive consists of linear polyester polyurethane based on toluene diisocyanate. The polyurethane used in this study was cured with a triisocyanate terminated curing agent. The FT-IR spectra of the A-MWCNTs, cured polyurethane, and the polyurethane/A-MWCNTs composite are shown in Fig. 1.

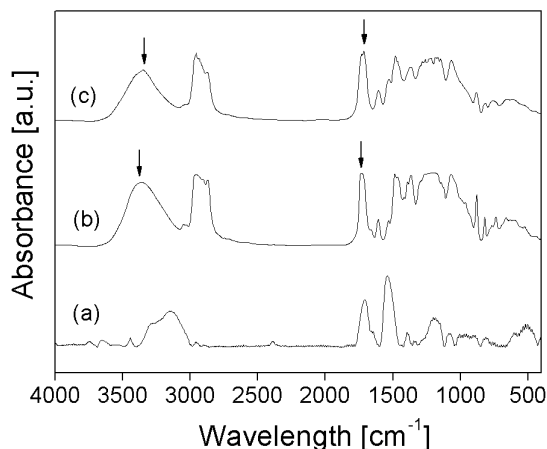


Fig. 1. FT-IR spectra of (a) A-MWCNTs, (b) cured polyurethane and (c) polyurethane/A-MWCNTs composite.

The peak observed at 1712 cm^{-1} in the FT-IR spectra corresponded to the C=O stretching of the carboxylic acid group formed on the surface of the MWCNTs by the acid treatment (Fig. 1(a)). The characteristic peaks of polyurethane are 3359 and 1733 cm^{-1} , corresponding to the N-H and C=O groups of the urethane group, respectively.¹¹ In addition, the peak at 2270 cm^{-1} related to isocyanate is not observed in Fig. 1(b) due to the curing reaction between the hydroxyl group of the linear polyurethane and the isocyanate of the curing agent, indicating that the polyurethane was cured well.

The FT-IR spectrum of the polyurethane/A-MWCNTs composite prepared by introducing the A-MWCNTs into polyurethane is shown in Fig. 1(c). From Fig. 1(c), it can be seen that the peak for the C=O group of the polyurethane/A-MWCNTs composite is shifted to a lower wavelength than that of the cured polyurethane, from 1733 cm^{-1} to 1714 cm^{-1} . It can also be seen that the peak for the N-H group is shifted from 3359 cm^{-1} in the cured polyurethane to 3350 cm^{-1} in the polyurethane/A-MWCNTs composite. We suggest that there is an interaction between the urethane group of the polyurethane matrix and the carboxylic acid group on the surface of the A-MWCNTs. This interaction is likely hydrogen bonding, which occurs between both N-H and C=O of the urethane group and the carboxylic acid group of the A-MWCNTs.¹² These functional groups led to a reaction between the polyurethane and A-MWCNTs. In addition, some of the OH groups on the surface of the A-MWCNTs possibly take part in the curing reaction with the triisocyanate terminated curing agent, as the hydroxyl group reacts with the isocyanate group to form the urethane group.¹³ These results are an indication of the good dispersibility of the A-MWCNTs within the polyurethane matrix.

Figure 2 shows the morphological features of the fractured surface observed with increasing concentration of A-MWCNTs. Well dispersed A-MWCNTs could

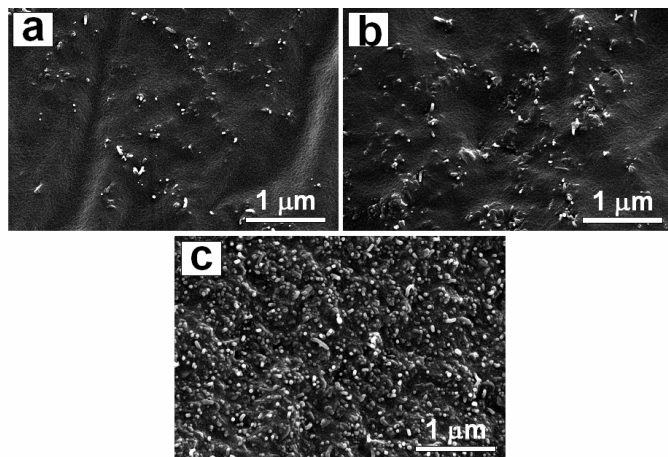


Fig. 2. FESEM images of fractured surface of polyurethane/A-MWCNTs composites; (a) 3 wt%, (b) 6 wt%, and (c) 12 wt%.

be observed within the polyurethane matrix. The white dots are broken MWCNTs, resulting from the interfacial interaction between the A-MWCNTs and the polyurethane matrix, as mentioned above. Note that the number of white dots increases with increasing concentration of A-MWCNTs. It is also seen that the A-MWCNTs retained their excellent dispersibility within the polyurethane matrix even when the A-MWCNT concentration was increased to 12 wt%. The numerous carboxylic acid groups on the MWCNT surface introduced by the acid treatment could be involved in hydrogen bonding with the urethane group of the polymeric matrix; this is supported by the shift of the peaks in the FT-IR spectra of the polyurethane/A-MWCNTs composite.

However, the fractured surface of the polyurethane/P-MWCNTs composite presented poor dispersibility within the polyurethane matrix and some P-MWCNTs were aggregated. It is well known that P-MWCNTs do not readily disperse in a polymeric matrix, due to the absence of functional groups that can interact with the polymer. In contrast to the A-MWCNTs, some of the P-MWCNTs were pulled out from the polyurethane matrix due to the poor interaction between the MWCNTs and polymer matrix.

The electrical conductivity of the polyurethane filled with two kinds of MWCNTs, P-MWCNTs and A-MWCNTs, is displayed in Fig. 3. Both the P-MWCNTs and A-MWCNTs enhanced the electrical conductivity of the ECAs to a greater extent with increasing MWCNT concentration. When 12 wt% of the A-MWCNTs was added to the polymeric matrix, an electrical conductivity of 10^{-2} S/cm was obtained. In the case where 6 wt% of the P-MWCNTs was added to the polymeric matrix, an electrical conductivity of 100 S/cm was measured. It was observed by FESEM that the A-MWCNTs were well dispersed, while the P-MWCNTs were rather less well dispersed.

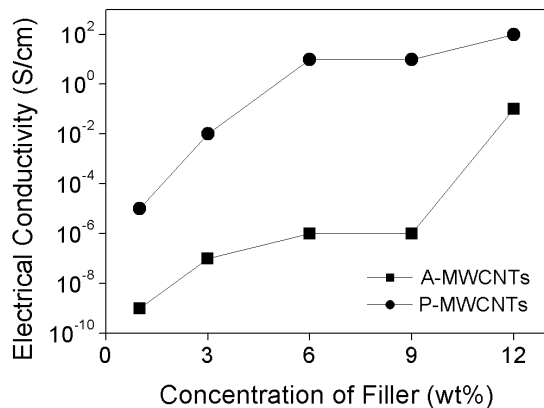


Fig. 3. Electrical conductivity of polyurethane/P-MWCNTs composite and polyurethane/A-MWCNTs composite.

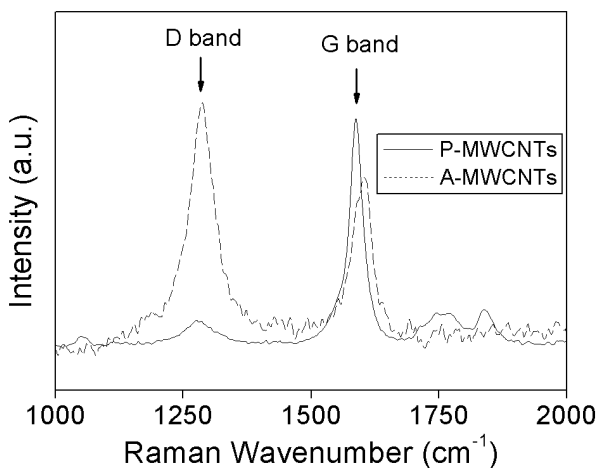


Fig. 4. Raman spectra for P-MWCNTs and A-MWCNTs.

The two characteristic peaks of the MWCNTs are exhibited at roughly 1280 and 1590 cm^{-1} , which are referred to as the D band and the G band in the Raman spectrum, respectively (Fig. 4). In general, the Raman spectra of the MWCNTs indicate the degree of disorder in the structure or crystallinity on the basis of the intensity ratio between the D and G bands, which are related to the degree of disorder and crystallinity, respectively. The intensity of the D band was increased by the acid treatment, suggesting that the crystallinity of the P-MWCNTs is higher than that of the A-MWCNTs. The intensity ratios of the D band to the G band (I_D/I_G) are 0.16 and 1.39 for the P-MWCNTs and A-MWCNTs, respectively. This implies that the disordered structure of the MWCNTs is due to the acid treatment,

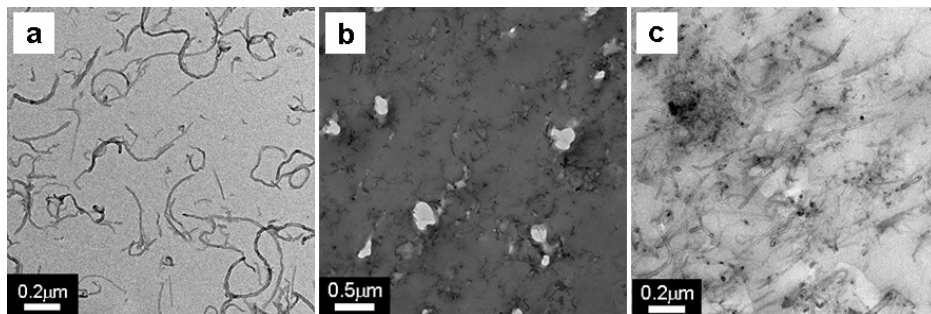


Fig. 5. TEM images of (a) A-MWCNTs, (b) polyurethane/P-MWCNTs composite and (c) polyurethane/A-MWCNTs composite.

although the acid treatment was primarily carried out for the purification of the MWCNTs as well as the introduction of functional groups onto their surface. Jang *et al.* reported that the amount of defects in the MWCNTs could be altered by varying the conditions of acid treatment, and that such a variation also affected their electrical properties.¹⁴ They reported that the poor electrical conductivity of the obtained composite could be attributed to the presence of MWCNTs whose crystalline structure was destroyed by acid treatment.

In addition, some of the MWCNTs might be cut during the acid treatment (Fig. 5(a)). Figures 5(b) and 5(c) show that the A-MWCNTs and P-MWCNTs were dispersed within the polyurethane matrix. Although the shortening of the A-MWCNTs facilitates the formation of a well dispersed polyurethane/A-MWCNTs composite, the A-MWCNTs would have little opportunity to come into contact with the adjacent A-MWCNTs within the polymeric resin, because the length of the MWCNTs is shortened. The P-MWCNTs were likely to form agglomerates, whereas those that retained their long length easily formed contact points with each other. Therefore, the incorporation of a higher concentration of A-MWCNTs into the polyurethane matrix compared to that of the P-MWCNTs, thus providing the desired electrical conductivity in the case of the former, could be attributed to the presence of defective and shortened A-MWCNTs. As fillers for ECAs, the properties of MWCNTs can be controlled by altering their morphological characteristics, such as their length, as well as the state of the carbon nanotube walls.

4. Conclusions

We prepared an ECA based on polyurethane filled with MWCNTs as conductive fillers. MWCNTs were selected because of their high aspect ratio, nanometer scale, and good dispersability. Carboxylic acid and hydroxyl functional groups were introduced onto the surface of the MWCNTs by acid treatment, and thus hydrogen bonding occurred between the carboxylic acid groups of the A-MWCNTs and the

urethane groups of the polymeric matrix. As a result, the A-MWCNTs showed increased interfacial interaction and were readily dispersed within the polymeric matrix. Nevertheless, the electrical conductivity of the polyurethane/A-MWCNTs composite was obtained at a higher concentration of A-MWCNTs than that of P-MWCNTs due to the reduction in the crystalline structure of the MWCNTs caused by the acid treatment. Therefore, the conductive properties of the conductive adhesive could be tailored by controlling the state of the MWCNTs used as conductive fillers for the ECAs.

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