https://doi.org/10.31436/iiumecp.v1i1.2985

SURFACE RESISTIVITY OF CARBON NANOTUBE FILLED PRESSURE SENSITIVE ADHESIVE AFTER ANNEALING PROCESS

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ABSTRACT: Pressure-sensitive adhesives (PSAs) exhibit adhesive properties upon applying light pressure. The light pressure adhesion of PSAs makes them suitable for potential applications in electronic packaging. However, to apply PSAs in electronic packaging, it is essential for them to possess electrostatic discharge (ESD) properties and high clarity. The attainment of ESD properties in PSAs can be achieved by either mechanically incorporating conductive fillers or chemically functionalizing the PSA compound. In this study, we aimed to achieve electrostatic discharge (ESD) properties in PSA using CNT as a conducting filler. CNT was selected for its strong conductivity compared to carbon black (CB). To accomplish this, CNT was mixed into the PSA formulation, which contained Chivacure 300 as a photoinitiator, silicone-urethane acrylate as an oligomer, and 2-ethyl-hexylacrylate and methyl methacrylate as monomers. The resulting PSAs were then coated onto polyethylene terephthalate (PET) film and cured with Ultraviolet light-emitting diode (UV-LED) light. However, the effect of CNT content on achieving a balance between ESD properties was insignificant. Therefore, an annealing process was introduced further to enhance the electrostatic discharge properties of the PSA. After the annealing process, it was found that PSAs with 0.75 phr of CNT achieved the desired electrostatic discharge (ESD) properties. Therefore, we examined the impact of the annealing process on the electrostatic properties and found that the inclusion of the annealing process significantly improved the electrostatic properties of pressure sensitive adhesives.

KEYWORDS*: Pressure Sensitive Adhesive, Multiwall Carbon Nanotube, Electrostatic Discharge, Ultra-Violet Light Emitting Diode, Annealing*

1. INTRODUCTION

Electrostatic Discharge (ESD) properties are one of the most important characteristics of pressure sensitive adhesive (PSAs) cover tape in order to prevent damage to electronic devices. In the context of the EOS/ESD Association (2008), material with different conductivity has been grouped according to their surface resistance. The requirement pertaining to ESD properties is very specific for packaging material, where it is mandated to achieve less than or equal to10^5 ohms to less than 10^{11} ohms by the International Electrotechnical Commission. To achieve surface resistance properties, various methods have been developed such as surface coating of static dissipative solutions, direct functionalization of filler onto matrix and compounding with filler. To our knowledge, compounding with filler is the most common technique, with several advantages over other methods, including stable surface conductivity, no environmental humidity effect, a more mature process, and lower cost. Conventionally, it is known that carbon black is the most common antistatic filler to use on PSA. Nonetheless, carbon black has several drawbacks, such aside requiring a higher amount of carbon

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black to achieve the threshold level at which it exhibits the ESD properties(Antosik *et al.*, 2021). An studies has shown with inclusion of CB onto PSA tape would deteriorate the clarity and adhesion strength of the PSA (Park *et al.*, 2014). Threshold levels are often defined as the minimum content of the filler required to convert an insulative polymer to an antistatic polymer. Carbon nanotubes (CNT) discovered by Lijima in 1991 have emerged as one of the potential antistatic fillers. CNTs offer advantages such as higher conductivity, a higher surface ratio, better mechanical properties, and thermal resistance. However, the high surface ratio of CNTs often poses challenges when dispersing them into polymers. As a result, various techniques have been implemented to overcome the strong pi-bond between CNTs. These techniques can be broadly categorized into mechanical dispersion and functionalization dispersion methods. Mechanical dispersion involves physical mixing techniques such as sonification, calendaring, high-speed stirring, and extrusion, without altering the chemical properties of CNTs (Ma *et al.*, 2010). On the other hand, functionalization dispersion requires aggressive chemical reactions to change the surface properties of CNTs for better dispersion in polymers. However, even with physical mixing or chemical alteration, achieving a low percolation threshold (<1wt%) for effective dispersion of CNTs onto polymers, especially in PSA cover tape applications, is challenging due to the high percolation threshold (>2-3wt%) required. High percolation levels can result in deterioration of the host material's characteristics, such as transparency and peeling force, as reported in the literature (Czech *et al.*, 2011). Therefore, post-processing techniques, such as thermal annealing, have been introduced to further enhance the conductivity of CNTs in pressure-sensitive adhesive cover tape applications. Thermal annealing is associated with dynamic percolation, which refers to the network formation attribute through temperature changes resulting in self-assembly in quiescent melt. The focus of this paper is to understand and identify the impact of thermal annealing on carbon nanotube compounded on pressure-sensitive adhesive properties.

2. MATERIALS AND METHODS

2.1. Chemicals And Materials

Silicone urethance acrylate oligomer was obtained from Dymax Corporation, while 2-ethylhexylacrylate(2-EHA), methyl methacrylate(MMA),trimethlylopropane triacrylate (TMPTA), multiwall carbon nanotube, Sulphuric acid, and Nitric acid were purchased from Sigma Aldrich (Malaysia). The photoinitiator oligo[2-hydroxyl-2-methyl-1-[4-1(methylvinyl)phenyl]propanone] (Chivacure 300) was received from Chitec Sdn Bhd. Other chemicals were used without further purification.

2.2. Preparation of Pressure Sensitive Adhesive Filled Pristine CNT

The curable coating formulation was prepared by dissolving photoinitiator in the reactive monomers (2-EHA, MMA and TMPTA) for 1 hour at room temperature. Then, the oligomer and CNT of various compositions were added to the mixture and mixed mechanically for 1 hour, followed by ultrasound treatment for another hour. The prepared samples were then coated on PET film using a bar applicator with a coated thickness of 0.1mm and size of 130mm length X 80mm width. The samples prepared in such length and width are due to the minimal sizes required by the standard STM 11.11-2021. Lastly, the formulation was irradiated under UV LED radiation for 15 minutes.

2.3. Surface Resistance Analysis

In accordance with the standard STM 11.11 – 2021, the surface resistance of the static discharge pressure sensitive adhesive was measured by surface resistance meter (Prostat - 801). The coated adhesive sample was prepared with size of 130mm length X 80mm width. Then the electrode was placed on the middle of the coated surface and measured, for which this is a standard measurement that has been adopted by EOS/ESD Association for packaging material.

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3. RESULTS AND DISCUSSION

To apply PSA to ESD products, it is necessary for the adhesive to possess a certain degree of surface resistance. The EOS/ESD Association specification mandates that the pressure-sensitive adhesive must have a minimum surface resistance of less than 10^{11} ohms. Hence, to meet this requirement, it is critical to incorporate a specific concentration of carbon nanotubes into the adhesive formula. The crucial concentration of carbon nanotubes required to meet the specification is commonly referred to as the percolation threshold. To achieve this threshold, various studies have explored the thermal effects of composite materials, which have shown a positive impact on the percolation threshold. Figure 1 shows the surface resistance of an annealing sample and non-annealing sample.

Figure1.0 Surface Resistance of Annealing Sample Vs Non Annealing Sample

Based on the result, it is observed that the sample without annealing treatment it unable to achieved static dissipative PSA on sample with annealing treatment it only required 0.75phr to achieve static dissipative ($8.1X10^{10}$ ohm). Based on the observations from the annealed sample, it can be concluded that the inclusion of conductive filler in an insulative material can lead to a transition in the material's behavior from being insulative to becoming static dissipative. This phenomenon is commonly referred to as the percolation threshold. In our study, it was observed that annealing the sample at 100°C resulted in a self-assembly process of carbon nanotubes, leading to their reorganization and closer proximity to each other, thereby forming a conductive network. In contrast, samples that did not undergo annealing showed carbon nanotubes remaining separated from each other, resulting in insulative behavior, despite the addition of conductive additives to the matrix. The similar conclusion has been made by McIntyre *et al.* (2020), annealing would cause reorganization of the CNT. Price *et al.* (2018) cited that CNT possess a high Van Der Waals forces; such forces are the barrier for which to disperse CNT evenly on the matrix. Hence, in this research, ultrasonification is applied to disperse CNT onto PSA material followed by annealing treatment to the sample. According to Frømyr *et al.* (2012), ultrasonification able create a high shear force to disperse CNT evenly onto the polymer matrix. Nonetheless, ultrasonification would cause the CNT farther apart from each other forming a random conductive network that causes an increase in electrical resistance (Pang *et al.*, 2014). Figure 2 below illustrates the ultrasonification dispersing CNT on PSA. As shown on Figure 2, the high Van der Waals forces cause the CNT to be lumped together, whereas dispersion via ultrasonification causes the CNT to be randomly dispersed, forming a random conductive network.

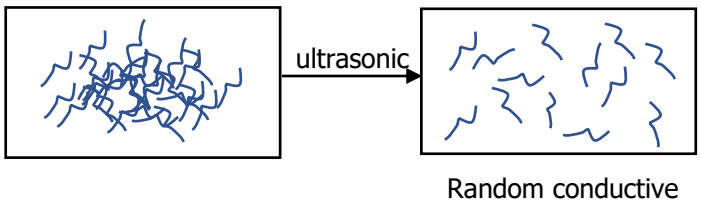

Figure 2.0 Ultrasonic Dispersing CNT on PSA

Upon annealing the sample, ultrasonification caused the CNTs to be dispersed further apart from each other. However, the thermal influence resulted in the re-aggregation of CNTs, forming a segregated

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conductive network that led to a reduction in electrical resistance. This re-aggregation of CNT under 100ºC, is known as dynamic percolation, for which the factor causes the same concentration of CNT but behaves differently. In our study, the annealed sample containing 0.75 phr of CNT exhibited an electrical resistance of $8.1x10^{10}$ ohm, while the non-annealed sample had a higher resistance of $1.1x10^{11}$ ohm. Figure 3 shows a pictorial explanation of the random conductive network and segregated conductive network. It explained a schematic diagram where dispersion of CNT via ultrasonification followed by re-aggregation of CNT forming a conductive network.

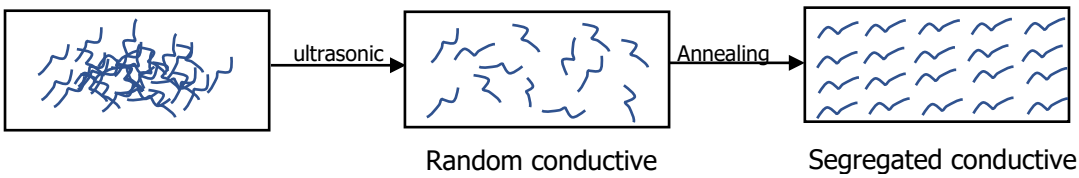

Figure 3.0 Schematic diagram of random conductive network and segregated conductive network.

According to Badard *et al.* (2017), the critical exponent (t) in the scaling law represents the dimensional structure of the carbon nanotubes within the pressure-sensitive adhesive. Based on our result shown that the critical exponent (t) value for the annealed sample was 2.26 with reference to the scaling law. Salaeh *et al.* (2020) have classified a universal critical value in which critical exponent less than or equal to two are represent a two dimensional structure and critical value greater than two are represents a three dimensional structure. According to this classification, it can be concluded that the annealed sample has a three-dimensional structure, which is likely to improve the conductivity of the PSA. Conversely, the non-annealed sample remained an insulating material as the concentration increased. Such a major dispute between the samples is due to two factors, where annealed samples undergo thermal expansion and dynamic percolation, whereas non-annealed samples depend on mechanical mixing to disperse CNT on the PSA. According to Zhang *et al.* (2015), thermal expansion increases the gap between CNTs, thereby reducing conductivity. This study observed thermal expansion in the annealed sample with 0.25 and 0.5 phr of CNTs, which resulted in higher electrical resistance compared to the non-annealed sample. As reference to Ansari *et al.* (2019) an thermal expansion of CNT reinforce material would happened within an material, hence in our studies it is proven that thermal expansion had occurred within the CNT and PSA. The second factor is the dynamic percolation event occurred within the PSA matrix which causes an increase in conductivity of 0.75 phr ($8.1X10^{10}$ ohm) in which with the application of the annealing the isolated carbon nanotube has been restructuring themselves into an infinite path because of the formation of the conductive network.

4. CONCLUSION

In conclusion, we have introduced annealing process to prepare pressure sensitive adhesive, whereby such methodology enables us to prepare a static dissipative pressure sensitive adhesive with a lower amount of CNT. The surface resistance reduction has been significantly reduced to 0.75 phr exhibiting static dissipative pressure sensitive adhesive after undergoing thermal annealing process at 100°C for which it led to a reaggregation of CNT on the PSA.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of research funding from the Universiti Teknologi Malaysia: UTMFR vote no. 22H56, UTMFR vote no. 20H81 and Ministry of Higher Education Malaysia (MOHE): FRGS/1/2020/TKO/UTM/02/9 and FRGS/1/2017/TK05/UTM/02/16

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