우수한 전기전도성을 함유한 탄소나노튜브를 포함하는 반도체 IC Tray 대전방지용 PMMA/PU 복합소재 합성

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Synthesis of PMMA/PU Composite Material Incorporating Carbon Nanotubes for Antistatic Semiconductor IC Tray with Excellent Electrical Conductivity

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초 록

반도체 웨이퍼 운반용 tray에 사용하기 위한 반도체 대전방지용 물질을 합성하기 위해 탄소나노튜브를 포함하는 폴리(메틸메타크릴레이트)(PMMA)와 폴리우레탄(PU)의 in-situ polymerization이 설계되고 진행되었다. 새롭게 합성된 복합체는 상업용 장치 제조 공정을 모방한 조건에서 열적특성과 전기전도성 특성을 평가하였다. 이들의 관련 성능을 비교한 결과, 탄소나노튜브를 함유하고 있는 PMMA와 PU 모두 탄소나노튜브 함량이 올라갈수록 열적인 특성이 향상되었으며, 전기전도성 역시 함량이 올라갈수록 증가하는 우수한 성능을 나타내었다. In-situ polymerization을 통한 복합체의 morphology는 FE-SEM을 통하여 확인한 결과 상용성이 우수한 상태로 확인되었다. 탄소나노튜브를 포함하는 PMMA와 PU 모두 반도체 대전방지용 물질로서 사용할 수 있는 우수한 표면저항 값인 10^3 Ω/□의 특성 결과를 확인할 수 있었다.

Abstract

To synthesize an antistatic material for use in semiconductor wafer transport trays, in-situ polymerization of poly(methyl methacrylate) (PMMA) and polyurethane (PU) incorporating carbon nanotubes was designed and conducted. The newly synthesized composites were evaluated for their thermal and electrical conductivity properties under conditions mimicking commercial device manufacturing processes. Comparative analysis of their respective performances revealed that both PMMA and PU containing carbon nanotubes exhibited enhanced thermal properties and superior electrical conductivity as the nanotube content increased. Morphology of the composites synthesized via in-situ polymerization was confirmed to be excellent through FE-SEM analysis, demonstrating good dispersibility. Both PMMA and PU incorporating carbon nanotubes showed outstanding surface resistance values of 10^3 Ω/□, indicating their suitability as antistatic materials for semiconductor applications.

Keywords: Electrical conductivity, Carbon nanotube, In-situ polymerization, Semiconductor, Polyurethane

1. Introduction

With recent technological advancements, research and development of polymer-based antistatic tray materials have gained significant attention in the semiconductor industry. Static electricity generated during storage and transportation of semiconductor products can transfer energy to microcomponents, potentially causing changes in their proper-

ties and structure. These changes can induce defects within the components, altering their electrical characteristics and negatively impacting overall performance. Conventional plastic products, acting as insulators, tend to accumulate static electricity, resulting in various issues such as dust accumulation affecting appearance, instrument malfunctions due to electrostatic discharge, and disturbances in video and audio equipment[1]. To mitigate static electricity, materials should possess sufficient electrical conductivity to allow accumulated charges to dissipate by facilitating their movement out of the material. Therefore, polymer materials with conductivity, known as antistatic materials, are essential for addressing these challenges. To address this issue, recent research has focused on antistatic materials incorporating conductive

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polymers with Carbon Nanotubes (CNT). Since their discovery by Dr. Iijima at NEC in Japan, CNT have been actively researched both domestically and internationally[2,3]. CNT exhibit exceptional properties compared to traditional materials: they are approximately 100 times stronger than steel, have electrical conductivity about 1000 times greater than copper, and possess thermal conductivity comparable to diamond. Furthermore, due to their high aspect ratio morphology, CNT have a significantly higher surface area compared to many other materials. These unique characteristics have led to extensive research efforts aiming to apply CNT in various fields including electrical engineering, electronics, semiconductor manufacturing, and aerospace industries[4-7]. CNT are categorized into single-walled (SWCNT), double-walled (DWCNT), and multi-walled (MWCNT) types. Particularly, MWCNT are known to exist in aggregated forms ranging from tens to hundreds of nanometers due to Van der Waals forces[8-14]. MWCNT, consisting of multiple walls compared to SWCNT, generally exhibit higher mechanical strength and are structurally more stable. Additionally, their manufacturing process is simpler, making them significantly more advantageous in terms of price and commercialization compared to SWCNT, positioning them as suitable candidates for antistatic IC tray applications. Poly(methyl methacrylate) (PMMA), an excellent thermoplastic resin, is renowned for its exceptional surface properties and transparency. Developed independently around the 1930s by R. Hill in the UK and W. Bauchr in Germany, PMMA has since been widely used in various applications due to its weather resistance, moldability, and high surface strength. It finds extensive use in applications such as window glass, automotive components, lighting fixtures, electronic products, advertising decorations, and more[15-17]. PU is a polymer compound formed through the addition reaction of a polyol containing chemically active hydroxyl groups (OH) and a diisocyanate containing isocyanate groups (NCO). PU exhibits a chain-like structure composed of urethane bonds (NHCOO) linked sequentially. PU can be tailored to achieve a wide range of properties and can be applied across diverse fields such as coatings, adhesives, fibers, synthetic leather, and more[18-19]. PMMA and PU are both low-conductivity polymers, but they are easy to synthesize and can achieve stability by increasing their molecular weight. Specifically, PMMA is a representative addition-type chain polymer known for good surface characteristics and transparency. PU, on the other hand, is a representative condensation-type step polymer that offers flexibility with the ability to control various properties. By incorporating MWCNT into these two materials, conductivity can be effectively enhanced. Therefore, we chose to synthesize these two polymers to enhance conductivity through the incorporation of MWCNT. Previously reported studies combining multi-walled carbon nanotubes (MWCNT) with PMMA through *in-situ* polymerization resulted in surface resistance values insufficient for commercialization, around 10^4 $\Omega/\square$. Similarly, reports on blending polymers with CNT also indicated data around 10^6 $\Omega/\square$, which fell short of commercialization standards. The typical surface resistance required for electrostatic discharge protection in semiconductor IC trays is known to be in the range of 10^6 to 10^9 $\Omega/\square$. We have achieved a surface resistance value of less than 10^3 $\Omega/\square$, which satisfies this requirement[20,21]. In this study, we aimed to optimize the performance of MWCNT by identifying the optimal polymerization conditions. By introducing MWCNT into the copolymerization of PMMA and PU, we formed homogeneous *in-situ* polymer composites, where two materials with different properties were mixed. We sought to investigate the tendencies of PMMA and PU composites based on the weight fraction of MWCNT. The synthesized MWCNT/PMMA and MWCNT/PU composites were analyzed using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to observe thermal behavior based on the weight fraction of MWCNT. Additionally, we confirmed electrical conductivity by measuring surface resistance to verify if the synthesized composites possessed suitable conductivity for antistatic applications.

2. Experiment

2.1. Materials and instrumentation

MWCNT was purchased from Do Woo Electric Wire Co.,Ltd. All other chemicals used in the experiments were purchased from reputable suppliers including Sigma-Aldrich and Tokyo Chemical Industry (TCI). These reagents were of minimum 98% purity and were used without further purification processes. Thermal changes were monitored by differential scanning calorimetry (DSC) using a Q-1000 instrument (TA Instruments) under a nitrogen (N_2) atmosphere to determine the glass transition temperature (T_g) of the compounds. Thermal decomposition temperature (T_d) was determined by conducting thermal gravimetric analysis (TGA) using a TGA Q5000 IR instrument (TA Instruments). Surface resistance measurements for electrical conductivity verification were performed using a TREK152-1 device to measure surface resistance in $\Omega/\square$ units.

2.2. Synthesis

2.2.1. Synthesis of PMMA

10 g of liquid methyl methacrylate (MMA) and 5 mg of azobisisobutyronitrile (AIBN) were placed in a 20 mL vial. The mixture was stirred at 500 rpm at 80 °C for 5 hours. After 5 hours of stirring, the resulting mixture was cooled to room temperature, and PMMA (7.72 g, yield 57%) was obtained by removing it from the vial.

2.2.2. Synthesis of 1.0~2.0 wt% MWCNT/PMMA

The procedure involved placing 9.8~9.9 g of liquid methyl methacrylate (MMA) and 0.1~0.2 g of solid multiwall carbon nanotubes (MWCNT) into a 20 mL vial, followed by stirring at room temperature 500 rpm for 10 minutes. AIBN was added to the vial (4.9~5.0 mg), and the temperature was raised to 80 °C. The mixture was then stirred at the same speed (500 rpm) for 5 hours at 80 °C. After the 5 hour stirring period, the resulting mixture was cooled to room temperature. Then, the vial was removed from the stirring plate, and the PMMA containing MWCNT was obtained from the vial after cooling to room temperature.
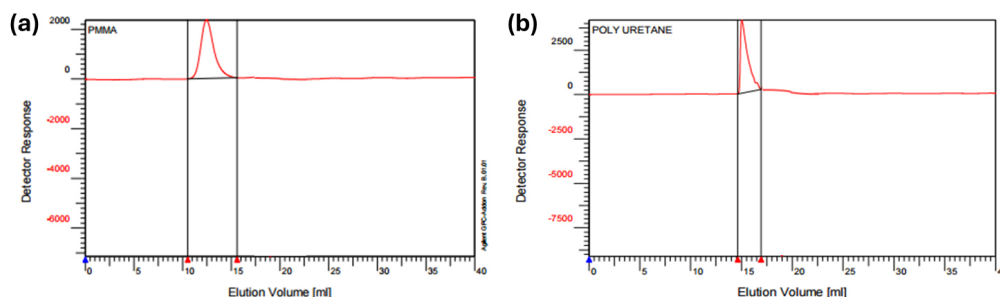
Figure 1. GPC data of synthesized (a) PMMA, (b) PU.

2.2.3. Synthesis of PU

The procedure involved placing 10 g of liquid polyethylene glycol 400 (PEG 400) and 4.35 g of toluene diisocyanate (TDI) into a 20 mL vial. The mixture was then stirred at 100 °C with a speed of 500 rpm for 8 hours. After the 8 hour stirring period, the resulting mixture was cooled to room temperature. Subsequently, PU (5.57 g, yield 47%) was obtained by removing it from the vial after cooling to room temperature.

2.2.4. Synthesis of 1.0~2.0 wt% MWCNT/PU

The process involved placing 9.8~9.9 g of liquid PEG 400 and 0.1~0.2 g of solid MWCNT into a 20 mL vial and stirring at room temperature 500 rpm for 10 minutes. Subsequently, 4.267~4.310 g of toluene TDI was added to the vial, and the temperature was raised to 100 °C. The mixture was then stirred at the same speed (500 rpm) for 8 hours at 100 °C. After the 8 hour stirring period, the resulting mixture was cooled to room temperature. Then, the vial was removed from the stir plate, and PU containing MWCNT was obtained from the vial after cooling to room temperature.

3. Results and discussion

3.1. Synthesis

Pure PMMA and PU are colorless, but as polymerization progresses, the MWCNT/PMMA and MWCNT/PU composites turn black due to the presence of MWCNT. With the addition of MWCNT, the reaction time slightly decreases compared to when pure PMMA and PU are synthesized. This is attributed to the influence of MWCNT on the polymerization process. In the case of PMMA, it has been reported that MWCNT affect the polymerization of methyl methacrylate (MMA) by activating the π-bonds on the surface of MWCNT through initiators like AIBN, thereby promoting free radical polymerization[22]. To determine the molecular weight of the MWCNT/PMMA and MWCNT/PU composites, gel permeation chromatography (GPC) was performed (Figure 1). The weight-average molecular weight (Mw) of the MWCNT/PMMA composite was found to be 235,000 g/mol, while for the composite PU, the Mw value was 5,700 g/mol. PU with its low molecular weight exhibits elastomeric properties, thus providing higher flexibility and resilience. On the other hand, PMMA with its high molecular weight enhances mechanical strength, demanding structural stability. In this study, both low and high molecular weight polymers

demonstrate improvement in conductivity, showcasing the potential applicability across a range of polymer molecular weights. This suggests that polymers with varying molecular weights can be utilized to achieve desired conductivity properties. This confirms the successful synthesis of the composite polymers.

3.2. Morphology

The surfaces of pure polymers and polymer surfaces coated with CNT were examined using a Field emission scanning electron microscope (FE-SEM) to confirm the uniformity of CNT distribution. As shown in Figure 2, pure PU showed a smoother surface compared to PMMA, whereas PMMA exhibited a rough surface layer. PMMA containing 2.0 wt% MWCNT showed well-deposited MWCNT on the surface of pure PMMA, while PU containing 2.0 wt% MWCNT exhibited a different form of MWCNT distribution compared to pure PU. This observation confirms that during polymerization, the deposition of MWCNT leads to the formation of a homogeneous *in-situ* polymer composite where the polymer and MWCNT are well blended together. This homogeneous property is expected to reduce conductivity variations when applied as antistatic trays, leading to more consistent conductivity properties.

3.3. Thermal analysis

To assess the thermal stability of MWCNT coated samples, thermogravimetric Analysis (TGA) was performed under a nitrogen atmosphere (Figure 3). It was observed that as the MWCNT content increased from 0 wt% to 2 wt%, the decomposition temperatures (T_d, corresponding to 5% weight loss) of PMMA increased from 197 °C to 224 °C and 226 °C, respectively. Similarly, PU showed an increasing trend in Td values from 289 °C to 297 °C. This indicates that the incorporation of carbon containing MWCNT into the polymers enhances the thermal stability of the respective composite materials. Differential Scanning Calorimetry (DSC) analysis revealed the glass transition temperature (T_g) of PMMA, which increased from 90 °C to 107 °C and 115 °C as the MWCNT content increased from 0 wt% to 2 wt%[23]. For PU, the melting temperature (T_m) was observed, showing a similar increasing trend in T_g values as seen in PMMA with increasing MWCNT content, from 158 °C to 171 °C and 187 °C[24] (Figure 4).

3.4. Electrical conductivity

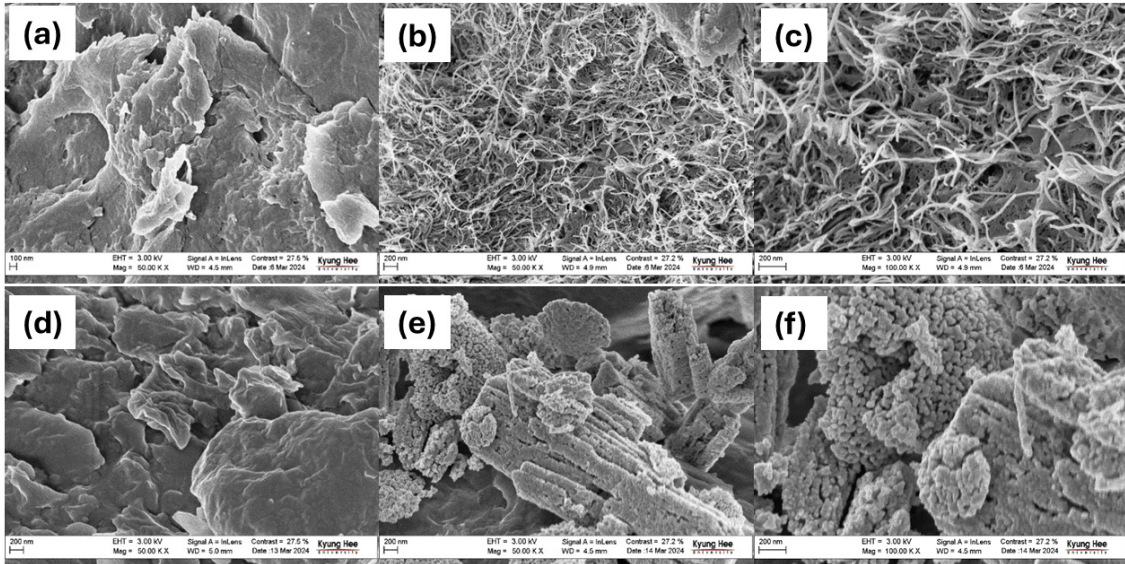To investigate the electrical characteristics of each composite with

Figure 2. Field electron scanning electron microscope (FE-SEM) images of multiwall carbon nanotubes (MWCNT): (a) PMMA, (b), (c) 2.0 wt% PMMA, (d) PU, (e), (f) 2.0 wt% PU [(a), (b), (d), (e): 50 magnification, (c), (f): 100 magnification].
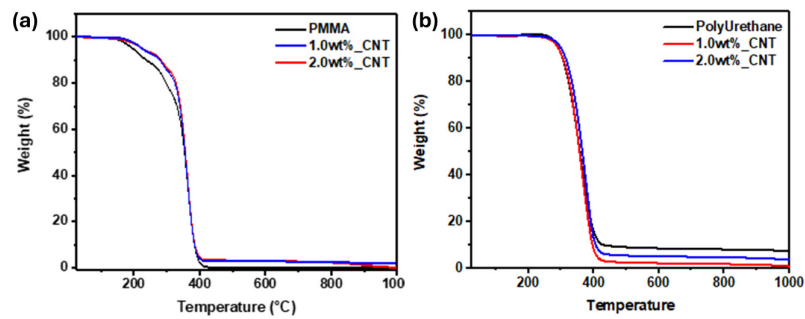

Figure 3. Thermo gravimetric analyzer (TGA) results of materials. (a) PMMA, MWCNT/PMMA, (b) PU, MWCNT/PU.
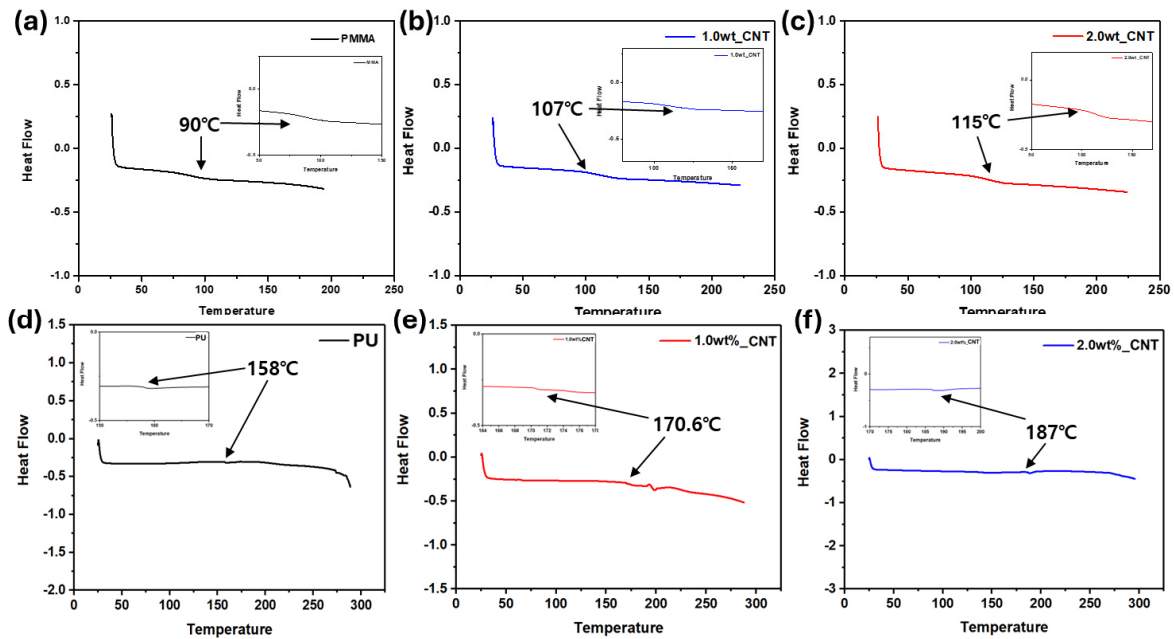

Figure 4. Differential scanning calorimetry (DSC) results of materials. (a) PMMA, (b) 1.0 wt% PMMA, (c) 2.0 wt% PMMA, (d) PU, (e) 1.0 wt% PU, (f) 2.0 wt% PU.

Table 1. Surface Resistivity of Different MWCNT/PMMA, MWCNT/PU Composites

Ω	Sample	Surface resistivity ($\Omega/\square$)	Sample	Surface resistivity ($\Omega/\square$)
1	CNT only	8.25×10^2	CNT only	8.25×10^2
2	PMMA only	$> 10^{13}$	PU only	$> 10^{13}$
3	PMMAMWCNT (1.0 wt%)	9.7×10^3	PU + MWCNT (1.0 wt%)	6.3×10^3
4	PMMA + MWCNT (1.2 wt%)	7.8×10^3	PU + MWCNT (1.2 wt%)	4.5×10^3
5	PMMA + MWCNT (1.4 wt%)	7.2×10^3	PU + MWCNT (1.4 wt%)	4.0×10^3
6	PMMA + MWCNT (1.6 wt%)	5.5×10^3	PU + MWCNT (1.6 wt%)	2.3×10^3
7	PMMA + MWCNT (1.8 wt%)	3.2×10^3	PU + MWCNT (1.8 wt%)	1.2×10^3
8	PMMA + MWCNT (2.0 wt%)	2.2×10^3	PU + MWCNT (2.0 wt%)	0.1×10^3
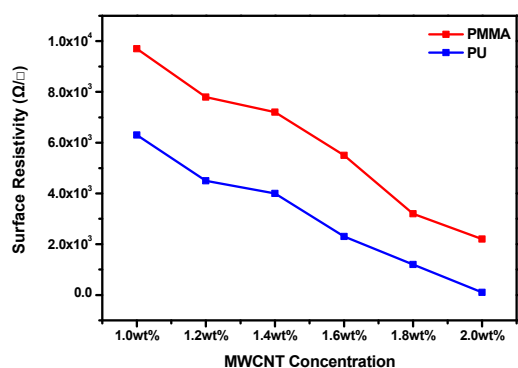
Figure 5. Surface resistivity of the different MWCNT/PMMA, MWCNT/PU composites.

varying weights of PMMA, PU, and MWCNT, surface resistance measurements were performed as shown in Table 1.

Both composites exhibit decreasing surface resistance values as the weight percentage of MWCNT increases. In the case of PMMA, after the addition of 1.0 wt% CNT, subsequent additions of 0.2 wt% MWCNT resulted in a gradual decrease in surface resistance, as shown in Figure 5. Similarly, PU also showed a decrease in surface resistance with increasing MWCNT weight percentage. The decrease in surface resistance values with increasing MWCNT weight percentage indicates an increase in conductivity corresponding to the increased MWCNT content. These trends suggest that as the MWCNT weight percentage increases, the conductivity also increases. The numerical results obtained from these experiments show excellent surface resistance levels below 10^5 $\Omega/\square$, which is indicative of a typical antistatic effect. This suggests that materials with stable surface resistance values have been successfully developed, demonstrating effective antistatic properties. The polymer composite incorporating MWCNT can be applied to semiconductor IC tray products.

4. Conclusion

This study investigated the surface, thermal, and electrical properties of MWCNT/PMMA and MWCNT/PU composite materials as a function of MWCNT content. The dispersion of MWCNT within the com-

posites was confirmed through FE-SEM measurements, revealing homogeneous composite materials forming *in-situ* polymer composites distinct from the surfaces of pure PMMA and PU. Thermal analysis showed an increase in thermal stability with increasing MWCNT weight ratio, indicating the influence of carbon-based MWCNT on thermal stability within the polymer matrix. Electrical conductivity, as assessed by surface resistance measurements, exhibited a decrease in surface resistance with increasing MWCNT content. This suggests an enhancement in electrical conductivity of the composites with increasing MWCNT content. Furthermore, the obtained surface resistance values were below the standard threshold of 10^5 $\Omega/\square$, indicating the potential for these composites to exhibit superior antistatic properties. Based on these research findings, it was possible to develop new antistatic materials for semiconductor IC trays using various conductive polymers incorporating carbon nanotubes.

References

1. J. W. Ha and K. H. Whang, Formulation of a thermally curable coating composition with anti-static function, *J. Korean Ind. Eng. Chem.*, **12**, 27-33 (2001).
2. S. H. Hong, M. H. Kim, C. K. Hong, D. S. Jung, and S. E. Shim, Encapsulation of multi-walled carbon nanotubes by poly (4-vinylpyridine) and its dispersion stability in various solvent media, *Synthetic Met.*, **158**, 900 (2008).
3. C. H. Yoon and H. S. Lee, Carbon nanotube composite, *Polym. Sci. Technol.*, **18**, 4 (2007).
4. S. Park, M. Cho, S. Lim, H. Choi, and M. Jhon, Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with poly(methyl methacrylate) prepared by in-situ bulk polymerization, *Macromol. Rapid Commun.*, **24**, 1070 (2003).
5. X. Xie and L. Gao, Characterization of a manganese dioxide/carbon

nanotube composite fabricated using an in situ coating method, *Carbon*, **45**, 2365 (2007).

6. R. B. Mathur, S. Pande, B. P. Singh, and T. L. Dhami, Electrical and mechanical properties of multi-walled carbon nanotubes reinforced PMMA and PS composites, *Polym. Compos.*, **29**, 717 (2008).

7. A. I. Oliva-Aviles, F. Aviles, and V. Sosa, Electrical and piezoresistive properties of multi-walled carbon nanotube/polymer composite films aligned by an electric field, *Carbon*, **49**, 2989 (2011).

8. J. Xiong, Z. Zheng, X. Qin, M. Li, H. Li, and X. Wang, The thermal and mechanical properties of a polyurethane/multi-walled carbon nanotube composite, *Carbon*, **44**, 2701 (2006).

9. T. Uchida and S. Kumar, Single wall carbon nanotube dispersion and exfoliation in polymers, *J. Appl. Polym. Sci.*, **98**, 985 (2005).

10. V. Datsyuka, M. Kalyvaa, K. Papagelisb, J. Partheniosa, D. Tasisb, A. Siokoua, I. Kallitsisa, and C. Galiotisa, Chemical oxidation of multiwalled carbon nanotubes, *Carbon*, **46**, 833 (2008).

11. S. Berber, Y. K. Kwon, and D. Tomanek, Unusually high thermal conductivity in carbon nanotubes, *Phys. Rev. Lett.*, **84**, 4613 (2000).

12. Y. Gao, Y. Wang, J. Shi, H. Bai, and B. Song, Functionalized multi-walled carbon nanotubes improve nonisothermal crystallization of poly (ethylene terephthalate), *Polym. Test.*, **27**, 179 (2008).

13. S. M. Yuen, C. C. M. Ma, Y. Y. Lin, and H. C. Kuan, Preparation, morphology and properties of acid and amine modified multiwalled carbon nanotube/polyimide composite, *Comp. Sci. Technol.*, **67**, 2564 (2007).

14. J. Ryszkowska, Quantitative image analysis of polyurethane/carbon nanotube composite micostructures, *Mater. Charact.*, **60**, 1127 (2009).

15. S. Park, K. Cho, and C. Choi, Effect of fluorine plasma treatment on PMMA and their application to passive optical waveguides, *J. Colloid Interf. Sci.*, **258**, 424 (2003).

16. M. J. Galante, P. A. Oyanguren, K. Andromaque, P. M. Frontini, and R. J. J. Williams, Blends of epoxy/anhydride thermosets with a high-molar-mass poly(methyl methacrylate), *Polym. Int.*, **48**, 642 (1999).

17. T. C. Chang, C. L. Liao, K. H. Wu, H. B. Chen, and J. C. Yang, Degradation of some poly(methylphenylsiloxane)-poly(methyl methacrylate) interpenetrating polymer networks, *Polym. Degrad. Stab.*, **66**, 127 (1999).

18. Y. T. Shin, M. G. Hong, J. J. Choi, W. K. Lee, G. B. Lee, B. W. Yoo, M. G. Lee, and K. C. Song, Preparation and properties of aminosilane terminated waterborne polyurethane, *Korean Chem. Eng. Res*, **48**, 434-439 (2010).

19. M. G. Hong, Y. T. Shin, J. J. Choi, W. K. Lee, G. B. Lee, B. W. Yoo, M. G. Lee, and K. C. Song, Preparation of silylated waterborne polyurethane/silica nanocomposites using colloidal silica, *Korean Chem. Eng. Res.*, **48**, 561-567 (2010).

20. G. Mittal, K. Y. Rhee, and S. J. Park, The effects of cryomilling CNTs on the thermal and electrical properties of CNT/PMMA composites, *Polymers*, **8**, 169 (2016).

21. M. Jeon, *Development of Compound Material for IC Tray Using Recycled Trays*, Korea Planning & Evaluation Institute of Industrial Technology, Daegu, Korea (2012), https://scienceon.kisti.re.kr/srch/selectPORSrchReport.do?cn=TRKO201200008209.

22. Z. Jia, Z. Wang, C. Xu, J. Liang, B. Wei, D. Wu, and S. Zhu, Study on poly (methyl methacrylate)/carbon nanotube composites, *Mater. Sci. Eng. A*, **271**, 395(1999).

23. Z. Li, S. Chen, S. Nambiar, Y. Sun, M. Zhang, W. Zheng, and J. T. W. Yeow, PMMA/MWCNT nanocomposite for proton radiation shielding applications, *Nanotechnology*, **27**, 234001 (2016).

24. Y. Kanbur and U. Tayfun, Investigating mechanical, thermal, and flammability properties of thermoplastic polyurethane/carbon nanotube composites, *J. Thermoplast. Compos. Mater.*, **31**, 1661-1675 (2018).

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