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Nay Win Khun, Poh Yueh Loong, Erjia Liu and Lin Li*

Enhancing electrical and tribological properties of poly(methyl methacrylate) matrix nanocomposite films by co-incorporation of multiwalled carbon nanotubes and silicon dioxide microparticles

Abstract: Multiwalled carbon nanotubes (MWCNTs) and silicon dioxide microparticles (SiO_2 -MPs) were co-incorporated in poly(methyl methacrylate) (PMMA) matrices to form PMMA/MWCNT- SiO_2 -MP nanocomposite films. The SiO_2 -MP content in the nanocomposite films was varied at a fixed MWCNT content of 4 wt% to investigate the effect of SiO_2 -MP content on the electrical and tribological properties of the PMMA/MWCNT- SiO_2 -MP nanocomposite films. The co-incorporation of MWCNTs and SiO_2 -MPs dramatically lowered the electrical resistance of the nanocomposite films compared to that of the PMMA film, while higher fractions of SiO_2 -MPs more effectively promoted the decrease in the electrical resistance of the nanocomposite films by improving the conductive networks formed by the MWCNTs in the PMMA matrices. Although the friction of the nanocomposite films significantly increased with increased SiO_2 -MP content due to the promoted mechanical interlocking between the surface asperities of two mating surfaces, the wear of the nanocomposite films was much less severe than that of the PMMA film during ball-on-disc tribological tests.

Keywords: electrical resistance; friction; PMMA/MWCNT- SiO_2 -MP nanocomposite film; wear.

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1 Introduction

Polymer-based composites are used in a wide range of applications, because the specific development of polymer

matrix composites, even with a small amount of fillers, obtains new materials with new structural and functional properties superior to those of pure polymers [1, 2]. Nowadays, polymer matrix composites are finding more and more electronic applications with the rapid growth of the electronic industry [3]. Conductive polymer matrix composites have been made with thermoplastic and thermoset materials filled with carbon or metal fillers and their electrical conductivities depend on the conductivity, shape and size of their fillers as well as their processing methods [4].

Carbon nanotubes (CNTs) are considered one of the most attractive fillers for the fabrication of polymer matrix composites due to their unique properties such as excellent electrical conductivity, high thermal stability, high aspect ratio, high elastic modulus and high tensile strength [5]. However, the high surface energy, high aspect ratio and strong Van der Waals interaction of CNTs greatly induce their agglomeration themselves [5, 6]. As a result, it is very difficult to produce polymer matrix composites with very high electrical conductivity by adding CNTs [5]. Therefore, the fabrication of conductive polymer matrix composites co-incorporated with multiwalled CNTs (MWCNTs) and silicon dioxide microparticles (SiO_2 -MPs) is particularly interesting, because the co-incorporation of MWCNTs and SiO_2 -MPs would be able to enhance the electrical networks formed by MWCNTs within the polymer matrix, which has not been reported yet. In addition, a high wear resistance of conductive polymer matrix composites is necessary for electronic devices made from them, in which worn composites can lead to an early failure of the devices [7–9]. Since the electrical conductivity and wear resistance of polymer matrix composites can be altered by the type, shape, dispersion and content of their fillers, a good understanding of a correlation between co-incorporation of MWCNTs and SiO_2 -MPs in polymer matrix composites and their electrical and tribological properties is important for their successful applications.

In this study, SiO_2 -MPs were chosen to investigate whether an addition of non-electrical conductive SiO_2 -MPs would improve conductive networks formed by MWCNTs

*Corresponding author: Lin Li, School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore, e-mail: milli@ntu.edu.sg
Nay Win Khun, Poh Yueh Loong and Erjia Liu: School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

in poly(methyl methacrylate) (PMMA) matrix or not. In addition, SiO_2 -MPs were used instead of SiO_2 nanoparticles because the MPs would more effectively narrow down spaces between MWCNTs to make the MWCNTs closer to one another than the nanoparticles.

The PMMA/MWCNT- SiO_2 -MP nanocomposite films were prepared with different MWCNT contents of 4–10 wt% and different SiO_2 -MP contents of 2–10 wt% to optimize an MWCNT content. Among the nanocomposite films, the films with 4 wt% MWCNTs exhibited the most significant decrease in electrical resistance with increased SiO_2 -MP content from 2 to 10 wt%. Therefore, the SiO_2 -MP content in the nanocomposite films was varied from 2 to 10 wt% while the optimized MWCNT content of 4 wt% was fixed. The effects of SiO_2 -MP content on the electrical and tribological properties of the PMMA/MWCNT- SiO_2 -MP nanocomposite films were systematically investigated.

2 Materials and methods

2.1 Materials

PMMA powder was purchased from Sigma-Aldrich Pte Ltd (Singapore) with an average molecular weight of 120,000 and used as a matrix. MWCNTs were purchased from Baytubes (Bayer Material Science, Pittsburgh, PA, USA) with diameter and length of about 8–15 nm and 10–50 μm , respectively. SiO_2 -MPs were purchased from HCS Scientific & Chemical Pte Ltd (Singapore) with particle size of 3–4 μm .

2.2 Sample preparation

The PMMA powder was first gently poured into acetone in a beaker and fully dissolved with the aid of an ultrasonic bath. The MWCNTs and SiO_2 -MPs at different concentrations were gently poured into the PMMA/acetone mixture and the mixture was then ultrasonicated again for 30 min to evenly disperse the MWCNTs and SiO_2 -MPs. After that, the dispersed mixture was poured into a Petri dish that was then placed into a zip-lock bag with holes created on the top of the dish only in order to slow down the evaporation of the acetone in the dish. The zip-lock bag with the Petri dish inside was placed into a fume hood at room temperature ($\text{RT} \sim 22\text{--}24^\circ\text{C}$) for about 48 h to completely evaporate the acetone and cure a PMMA/MWCNT- SiO_2 -MPs nanocomposite film in the dish. The nanocomposite film formed was carefully removed from the dish and kept in a fresh zip-lock bag to be ready for measurements of its electrical and tribological properties.

2.3 Characterizations

The electrical resistance of the films was measured using a digital multimeter (Agilent, Santa Clara, CA, USA) and averaged with 10 measurements per sample.

The surface features of the films were observed using scanning electron microscopy (JEOL-JSM-5600LV, JEOL Ltd, Tokyo, Japan) and surface profilometry (Talyscan 150, Taylor Hobson Ltd, Leicester, UK) with a diamond stylus of 4 μm in diameter. Three measurements on each film were carried out to get an average root-mean-squared surface roughness (R_q).

A steel ball-on-disc micro-tribometer (CSM, CSM Instruments, Switzerland) was used to evaluate the tribological properties of the films. The sample was rotated against a 100Cr6 steel ball of 6 mm in diameter in a circular path of 2 mm in diameter for about 3000 laps at a sliding speed of 1 cm/s under a normal load of 1 N at RT. Prior to the tribological test, the films were very carefully prepared on laboratory glass plates using an epoxy glue and left at RT for about a week. Three measurements/sample were carried out to get an average friction coefficient. Surface profilometry was used to measure the width and depth of wear tracks.

3 Results and discussion

Figure 1 shows the electrical resistance of the PMMA/MWCNT- SiO_2 -MP nanocomposite films as a function of SiO_2 -MP content. The insulating property of the pure PMMA film makes its electrical resistance out of the measurement range. However, the co-incorporation of

Figure 1: Electrical resistance of poly(methyl methacrylate) (PMMA)/multiwalled carbon nanotube silicon dioxide microparticles (MWCNT- SiO_2 -MP) nanocomposite films as a function of SiO_2 -MP content.

Figure 2: Scanning electron microscopy (SEM) micrographs showing dispersions of multiwalled carbon nanotubes (MWCNTs) and silicon dioxide microparticles (SiO_2 -MPs) in poly(methyl methacrylate) (PMMA)/MWCNT- SiO_2 -MP nanocomposite films co-incorporated with (A and C) 4 wt% MWCNTs and 2 wt% SiO_2 -MPs and (B and D) 4 wt% MWCNTs and 10 wt% SiO_2 -MPs at different magnifications.

4 wt% MWCNTs and 2 wt% SiO_2 -MPs in the PMMA matrix dramatically decreases the electrical resistance to about 152.71 k Ω . It is clear that the dramatically reduced electrical resistance of the nanocomposite film mainly results from the incorporation of MWCNTs, because the MWCNTs are the only electrical conductive materials in the nanocomposite film [5]. The electrical resistance of the nanocomposite films further decreases from about 131.17 k Ω to 23.43 k Ω with increased SiO_2 -MP content from 4 wt% to 10 wt% at a fixed MWCNT content of 4 wt% as found in Figure 1, which clearly implies that the increased SiO_2 -MP content apparently decreases the electrical resistance of the nanocomposite films by enhancing a conductive network of MWCNTs within the PMMA matrix.

Figure 2 shows the dispersion of fillers in the PMMA/MWCNT- SiO_2 -MP nanocomposite films as a function of SiO_2 -MP content. Comparison of Figure 2A and B clearly indicates that the increased SiO_2 -MP content to 10 wt% at the fixed MWCNT content of 4 wt% significantly improves the uniform dispersion of the fillers in the PMMA matrix. As shown in Figure 2C and D, the MWCNTs are dispersed among the SiO_2 -MPs as the increased SiO_2 -MPs narrow

down the spaces between the MWCNTs. It can be seen that the incorporation of SiO_2 -MPs together with MWCNTs can indeed occupy spaces in the PMMA matrix, thereby decreasing the spaces between the MWCNTs and making the MWCNTs closer to one another, which then enhances

Figure 3: Root mean squared surface roughness, R_q , of poly(methyl methacrylate) (PMMA)/multiwalled carbon nanotube silicon dioxide microparticle (MWCNT- SiO_2 -MP) nanocomposite films as a function of SiO_2 -MP content.

Figure 4: Surface topographies of (A) poly(methyl methacrylate) (PMMA) film and PMMA/multiwalled carbon nanotube silicon dioxide microparticle (MWCNT-SiO₂-MP) nanocomposite films co-incorporated with (B) 4 wt% MWCNTs and 2 wt% SiO₂-MPs and (C) 4 wt% MWCNTs and 10 wt% SiO₂-MPs.

electrical conductive paths in the PMMA matrix [10]. As a result, the increased SiO₂-MP content further enhances the electrical conductive paths in the PMMA matrix by occupying more spaces between the MWCNTs. Therefore,

the increased SiO₂-MP content to 10 wt% leads to the significantly decreased electrical resistance of the nanocomposite films by enhancing the electrical connections between the MWCNTs (Figure 1).

The surfaces of the PMMA/MWCNT-SiO₂-MP nanocomposite films were measured prior to the tribological test since the surface features of the films have a significant influence on their tribological properties. Figure 3 illustrates the R_q value of the PMMA/MWCNT-SiO₂-MP nanocomposite films as a function of SiO₂-MP content. The R_q value of the PMMA film is about $0.23 \pm 0.04 \mu\text{m}$. The co-incorporation of 4 wt% MWCNTs and 2 wt% SiO₂-MPs in the PMMA matrix significantly increases the R_q value to about $5.15 \mu\text{m}$ as a result of the incorporation of the fillers and their aggregation. At the fixed MWCNT content of 4 wt%, the increased SiO₂-MP content from 4 wt% to 10 wt% increases the R_q value of the nanocomposite films from about $6.85 \mu\text{m}$ to $8.71 \mu\text{m}$, probably due to the promoted aggregation of the fillers.

Figure 4 shows the surface topographies of the PMMA film and PMMA/MWCNT-SiO₂-MP nanocomposite films. In Figure 4A, the PMMA film has a relatively smooth surface topography. However, the nanocomposite film co-incorporated with 4 wt% MWCNTs and 2 wt% SiO₂-MPs has a rougher surface topography attributed to the protruded filler aggregates above the surface (Figure 4B). When the nanocomposite film is co-incorporated with the fixed MWCNT content of 4 wt% and the higher SiO₂-MP content of 10 wt%, the surface topography of the nanocomposite film becomes even rougher as a result of the promoted aggregation of the fillers (Figure 4C). It is clear that the increased SiO₂-MP content significantly increases the surface roughness of the nanocomposite films via the promoted aggregation of the fillers.

The tribological properties of the PMMA/MWCNT-SiO₂-MP nanocomposite films were investigated by sliding them against a 100Cr6 steel ball for about 3000 laps at a sliding speed of 1 cm/s under a normal load of 1 N. Figure 5A presents the friction coefficients of the PMMA film and PMMA/MWCNT-SiO₂-MP nanocomposite films. The friction coefficient of the PMMA film is about 0.539. As found in Figure 5A, the friction coefficient of the nanocomposite film co-incorporated with 4 wt% MWCNTs and 2 wt% SiO₂-MPs is about 0.591 that is higher than that of the PMMA film, indicating that the co-incorporation of MWCNTs and SiO₂-MPs increases the friction of the nanocomposite film. The incorporation of MWCNTs should reduce the friction of the nanocomposite film due to the solid lubricating effect of the MWCNTs [6, 11–17]. However, the increased friction of the nanocomposite film (Figure 5A) clearly shows that the solid lubricating effect of the MWCNTs on the friction of the nanocomposite film is not significant in this study. In addition, the surface wear can release filler aggregates to the interface between the steel ball and nanocomposite film during the sliding and reduce the friction of the

Figure 5: Friction coefficients of poly(methyl methacrylate) (PMMA)/multiwalled carbon nanotube silicon dioxide microparticle (MWCNT-SiO₂-MP) nanocomposite films, slid against a 100Cr6 steel ball of 6 mm in diameter in a circular path of 2 mm in diameter for about 3000 laps at a sliding speed of 1 cm/s under a normal load of 1 N, as functions of (A) SiO₂-MP content and (B) the number of laps.

nanocomposite film via the free-rolling of the aggregates [6, 11–17]. The increased friction of the nanocomposite film associated with the co-incorporation of MWCNTs and SiO₂-MPs clearly indicates that the fillers do not have the free-rolling effect on the friction of the nanocomposite film.

The effect of surface roughness on the friction of the PMMA/MWCNT-SiO₂-MP nanocomposite film should be taken into consideration, since a rougher surface can induce a higher friction via mechanical interlocking between the surface asperities of two mating surfaces [18–22]. It is clear that the apparently protruded asperities above the surface of the nanocomposite film with the co-incorporation of MWCNTs and SiO₂-MPs (Figure 4B) are responsible for the higher friction of the nanocomposite film due to the stronger mechanical interlocking between the surface asperities of the steel ball and nanocomposite film. Therefore, the co-incorporation of 4 wt% MWCNTs and 2 wt% SiO₂-MPs gives rise to the higher friction coefficient of the nanocomposite film than that of the PMMA film, as the increased SiO₂-MP content to 10 wt% at the

Figure 6: Surface topographies of worn (A) poly(methyl methacrylate) (PMMA) film and PMMA/multiwalled carbon nanotube silicon dioxide microparticle (MWCNT-SiO₂-MP) nanocomposite films co-incorporated with (B) 4 wt% MWCNTs and 2 wt% SiO₂-MPs and (C) 4 wt% MWCNTs and 10 wt% SiO₂-MPs.

fixed MWCNT content of 4 wt% significantly increases the friction coefficient of the nanocomposite films to about 0.728 (Figure 5A) as a result of the significantly increased surface roughness of the nanocomposite films (Figure 3). It can be deduced that the surface roughness of the nanocomposite films mainly contributes to their friction.

In Figure 5B, the PMMA film and PMMA/MWCNT-SiO₂-MP nanocomposite films exhibit a relatively stable friction during the entire sliding as a result of their stable wear as the friction coefficient of the nanocomposite films with respect to the number of laps apparently increases with increased SiO₂-MP content. It is clear that the increased SiO₂-MP content significantly increases the friction of the nanocomposite films throughout the wear test.

Figure 6 shows the surface topographies of the worn PMMA film and PMMA/MWCNT-SiO₂-MP nanocomposite films. In Figure 6A, the sliding of the steel ball on the PMMA film generates a significant wear track with measurable wear width and depth of about $407.67 \pm 13.98 \mu\text{m}$ and $4.5 \pm 0.45 \mu\text{m}$, respectively. However, the co-incorporation of 4 wt% MWCNTs and 2 wt% SiO₂-MPs in the PMMA matrix apparently improves the wear resistance of the nanocomposite film so that a significant wear track is not found on the nanocomposite film as shown in

Figure 6B. In addition, the nanocomposite film co-incorporated with 4 wt% MWCNTs and 10 wt% SiO₂-MPs also does not exhibit a significant wear track on its surface (Figure 6C). Although the repeated sliding of the steel ball does not generate any significant wear tracks on the nanocomposite films, the worn surface asperities of the nanocomposite films are apparently found in Figure 6B and C. It is clear that the co-incorporation of MWCNTs and SiO₂-MPs significantly increases the friction (Figure 5), but dramatically decreases the wear of the nanocomposite films (Figure 6).

Figure 7A and B clearly confirm that the repeated sliding of the steel ball on the PMMA film generates a significant wear on the surface. Abrasive lines on the wear track of the PMMA film (Figure 7B) is indicative of the abrasive wear of the PMMA film [16, 17]. The surface wear of the PMMA film generates wear debris during the sliding and the repeated sliding of the steel ball compacts the debris to form localized tribolayers on the wear track. Therefore, the tribolayers are apparently found on the wear track of the PMMA film as shown in Figure 7A and B. Although the repeated sliding of the steel ball on the nanocomposite film co-incorporated with 4 wt% MWCNTs and 10 wt% SiO₂-MPs does not generate any measurable

Figure 7: Scanning electron microscopy (SEM) micrographs showing surface morphologies of worn (A and B) poly(methyl methacrylate) (PMMA) film and (C and D) PMMA/multiwalled carbon nanotube silicon dioxide microparticle (MWCNT-SiO₂-MP) nanocomposite film co-incorporated with 4 wt% MWCNTs and 10 wt% SiO₂-MPs at different magnifications.

wear track on the surface, the protruded surface asperities are apparently worn out as found in Figure 7C and D. The scanning electron microscopy observation clearly shows that the nanocomposite films have much higher wear resistance than the PMMA film.

4 Conclusions

In this study, the MWCNTs and SiO₂-MPs were co-incorporated in the PMMA matrices to form PMMA/MWCNT-SiO₂-MP nanocomposite films. The SiO₂-MP content in the nanocomposite films was varied at a fixed MWCNT content of 4 wt% to investigate the electrical and tribological properties of the nanocomposite films. The co-incorporation of MWCNTs and SiO₂-MPs resulted in the dramatically lower electrical resistance of the nanocomposite films than that of the PMMA film. In addition, the increased SiO₂-MP content further decreased the electrical resistance of the nanocomposite films by improving the electrical conductive paths within the PMMA matrices. The wear resistance of the nanocomposite films was examined using a

ball-on-disc micro-tribometer. The friction coefficient of the nanocomposite films significantly increased with increased SiO₂-MP content, because the increased surface roughness of the nanocomposite films promoted the mechanical interlocking between the surface asperities of two mating surfaces. Although the repeated sliding of the steel ball on the PMMA film generated a measurable wear track on the surface, the nanocomposite films did not exhibit any measurable wear tracks on the surfaces, indicating that the co-incorporation of MWCNTs and SiO₂-MPs resulted in a significant improvement in the wear resistance of the nanocomposite films. It could be concluded that the co-incorporation of MWCNTs and SiO₂-MPs in the PMMA matrices effectively reduced the electrical resistance and improved the wear resistance of the PMMA/MWCNT-SiO₂-MP nanocomposite films.

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