SCRATCH PROPERTY OF POLYURETHANE NANOCOMPOSITES STUDIED BY NANOINDENTATION

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ABSTRACT

Nanoindentation technique has been used extensively to measure the nanomechanical properties of thin films. However, the determination of the surface mechanical properties such as scratch behavior using this technique is relatively new. In this work, the scratch property of polyurethane nanocomposites was studied and proposed. A series of polyurethane-graphite oxide (GO) and polyurethane carbon nanotubes (single-walled (SWNT) and multi-walled carbon nanotubes (MWNT)) were prepared by in situ polymerization. It is believed that the preparation of polymer/GO or polymer/CNTs nanocomposites with homogeneous dispersion of nanofillers in the matrices is a crucial step to developing high-performance polymer nanocomposites. The results pronounced that with incorporation of nanofillers (GO and CNTs) the scratch depth of polyurethane matrix was dramatically reduced. With only 4wt% of GO the PU nanocomposites had greater hardness and showed better scratch resistance. In addition, the scratch penetration was less for PU-SWCNT composites than for the PU-MWCNT composites and it demonstrated as the time to achieve the maximum depth increased.

Keywords: polyurethane nanocomposite, nanoindentation, scratch property.

INTRODUCTION

Polymers and nanocomposites have been widely used in microelectronic packaging, coatings, aerospace, automotive, food packaging and biomedical applications because of their adequate strength, lightness, versatility, ease to processing and low cost (Alaa *et al* 2015; Cai *et al* 2012; Yusoh *et al* 2010; Wong *et al* 2004). In recent years, the developments of polymeric materials as coating materials has been gain more and more attention. However, polymer matrices are very sensitive to scratching and subjected to low scratch and wear resistance, and are unacceptable for most coating applications.

There are common efforts of improving the scratch resistance of polymeric materials. The first solution found to reduce this scratch sensitivity was to deposit a mineral coating on the surface of the polymer. This procedure experienced however little success, at least partly due to the large difference between the elastic strains domains of the substrate and coating (Demerchi *et al* 2005). A second generation of coatings used polysiloxane and acrylic materials, where the scratch resistance is given by the hardness of the coat and the coatings have elastic strain domains in the range as the substrate (Demerchi *et al* 2005).

The new generation of protective coatings has employed nano-materials, in which an organic matrix is filled with nanosized particles of fillers or polymer nanocomposites (Demerchi *et al* 2005). The idea behind this strategy is to associate the large elastic domain of an elastomeric polymer with the hardness of the filler. As nanocomposites material, polymers are combined with hard nanofillers, in order to improve the materials properties of polymer. Polymer nanocomposites offer the advantage of favorable material properties and diminish their disadvantages.

Research on nanoscale scratching can help develop mechanical scratching into a promising nanofabrication process. Thus, whether it is aiming to improve the surface scratch resistance or to engineer polymer surfaces for more efficient nanofabrication process, knowledge on scratch and wear properties at the micro to nanoscale is crucial (Wong *et al* 2004).

It has been suggested by various authors that the surface properties of polymers might be different from those of the bulk due to differences in molecular dynamics (Brown and Russell, 1997; Kajiyama *et al* 1996). Conventional wear type tests, which focus on bulk properties, might not be appropriate for assessing the surface properties of polymer nanocomposites. In recent years, the rapidly expanding field of depth-sensing nanoindentation which uses a sharp tip sliding on the surface provides a quantitative method for studying the scratch and wear properties of the surface or subsurface region of polymeric materials (Dasari *et al* 2007). .

The advent of newly developed depth sensing devices which use a sharp tip sliding on the surface to stimulate a single asperity contact has made possible characterization techniques, such as nanoscratch, that are sensitive enough to examine the surface properties for small scale and light loads (Kim *et al* 2001). Unlike an indentation process where the normal load is uniformly distributed beneath the indenter, scratching involves a high-friction-induced sliding process (Dasari *et al* 2009). The indenter is fully supported by the specimen in the front and only partially by recovered material in the rear-half. The extent of recovery again depends on the stress-relaxation characteristics of the material in the contact zone.

Research on surface roughness and scratch behaviour of polymer nanocomposites is very limited. In order to develop good understanding on interfacial phenomena in nanostructure materials, knowledge in scratch and wear on a nanoscale in a lightly loaded situation is essential to providing a bridge between surface science and engineering. Thus, in order to investigate the effect of nanofillers in polyurethane nanocomposites, the nanoscratch test under certain scratching conditions was studied using the nanoindentation test. A typical profile depth of scratch test was recorded as shown in Figure-1. The profile depth is the penetrating depth of the tip into the material, influenced by the hardness of the scratched material. It is also indicates the resistance of the material to the tip penetration. However, in this work the nano-scratch hardness cannot be measured due to the nature of the polyurethane itself where the scratch morphology is totally invisible after the scratch test. Normally, the scratch deformation can be measured using the scratch hardness and calculated using equation 1 [Mathia and Lamy 1986]:

$$\text{Scratch hardness, } H_s = \frac{P}{A} = q \frac{4P}{\pi . d_s^2} \qquad (1)$$

where P is the applied normal load, A is the projected load supporting area, and d_s is the recovered scratch width. The parameter q is a measure of the material response, which is arbitrarily chosen as 1 (Mathia and Lamy, 1986).

In this work, the research focused on the scratch behaviour of polyurethane nanocomposites with different kinds of nanofillers. The depth profile was measured based on the constant load and the different scratch velocity and the results were correlate between the relative scratch resistance and the mechanical properties of the nanocomposites. Due to the problem to identify the scratch damage with the high depth recovery in PU, the scratch hardness was not measured. Thus, the study was only focused on the relative scratch depth using the depth profile of the nanoscratch and the relative scratch resistance.
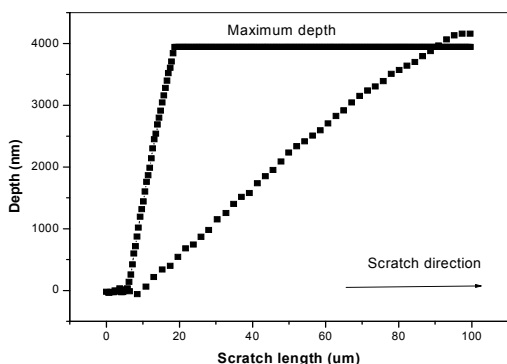
Figure-1. Typical scratch plot using indentation scratch test.

EXPERIMENTAL

Preparation of PU nanocomposites

Graphite oxide was prepared using the oxidation of expandable graphite (EG) and it was conducted following the procedure. 2.5g EG was mixed with 57.5 ml concentrated H_2SO_4 in ice bath (0C) for half an hour. 7.5g $KMnO_4$ was slowly added into the mixture in order to keep the temperature of the mixture below 20ºC. The mixture was then heated to 35ºC and kept stirring for 30 minutes. Dropwise addition of 115ml distilled water caused the temperature increase to 98ºC. The reaction was kept at this temperature for 15 minutes. Finally, the oxidation reaction was terminated by the addition of 350ml distilled water and 25 ml 30% H_2O_2 solution. Collection of the EGO by filtering and successive washing with 5% HCl aqueous solution was repeated by three times until there was no sulphate detected by $BaCl_2$ solution. The EGO was dried at 50ºC under vacuum for one week. The exfoliation of 100 mg EGO in 10 g DMF was achieved using ultrasonication with a power of 300 W for 30 minutes at room temperature. 6 g PPG-4000, 1.5 g PPG-6000, 0.8 g BDO, 3.89 g MDI and 0.11 g DBTL (catalyst) were stirred in DMF at 60ºC for 24 hours in a four-necked flask protected by N_2, by which PU/DMF solution was finally obtained with 40 wt% solid content. Afterward, the calculated amount of the GNOP/DMF dispersion was mixed with the PU/DMF solution at 80ºC for another 1 hour. The two-week drying at 50ºC was the last step for the preparation of the GNOP/PU composites.

Both MWNTs and SWNTs were provided by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. The as-grown MWNTs and SWNTs were produced by CCVD, in which CH_4 or C_2H_2 were converted into CNTs at 700 and 1000ºC in presence of a Ni-La2O3 catalyst. The diameter of MWNT and SWNT was at 8-15 nm, and 1-2 nm, respectively. The product were washed with concentrated HCl to remove the catalyst and the carrier of catalyst, and then were purified with concentrated HNO_3 to remove the amorphous carbon particles. In preparation of stable polyol-CNTs dispersions, 194 g of polyol, 4 g of MWNTs or SWNTs and 2 g of dispersion agent BYK 9077 were blended and stirred at 600 rpm for 4 hours at 80C. Then to prepare the PU-CNTs nanocomposites, 20g of polyol-CNT dispersion was blended with 0.89g of 1, 4-butanediol, 5.93 g of MDI and 0.03 g of Dabco-33LV at room temperature for 2 minutes and was vacuum-degassed for 3-5 minutes to remove the bubbles. Then the viscous prepolymer was poured into an O-ring metal mould and cured at 50ºC for 24 hrs and 80ºC for one week to obtain PU-CNT nanocomposites. The films were characterized by SEM and TEM observation.

Scratch test

The nanoscratch test involves moving a sample (on sample stub) while being in contact with the diamond tip as shown in Figure-2. All single-pass nanoscratch tests

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were performed over the square shaped sample surface with a thickness of ~1mm at ambient temperature and using the same nanoindentation equipment with a Berkovich pyramidal diamond indenter of a tip radius of 50nm and an included angle of 60ºC. In this test, the specimen was fixed on the sample stub and the scratch load and length were 5mN and 100μm at the various scratch rates and scratch velocities, respectively.
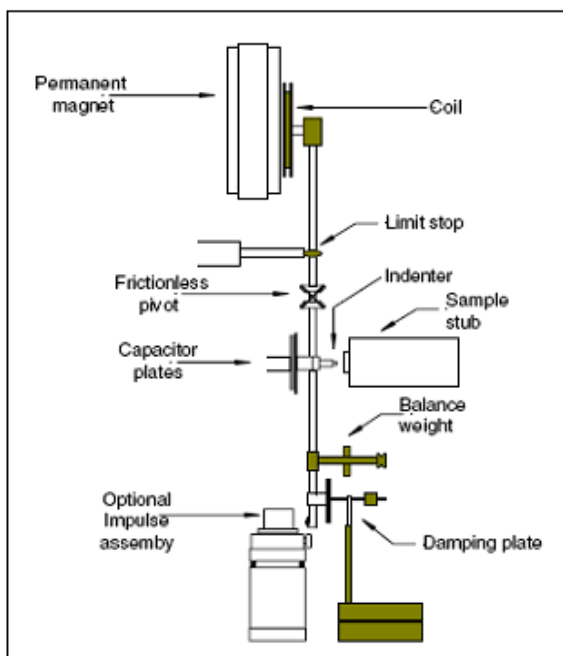

Figure-2. Schematic of nanoscractch test.

RESULTS AND DISCUSSIONS

Scratch depth profile

In the nanoscratch test, the scratch depth of the indenter in the sample was recorded along with the scratch length at a certain scratch rate, which reflects the ability of the surface coatings for the substrates. Figures 3 and 4 show the scratch depth profiles of the PU and its nanocomposites with 1wt% and 4wt% of GO against the scratch length. At a scratch rate of 3 μm/s (Figure-3), the curve of the PU reveals that the scratch depth completely achieved a maximum value just after 40 μm of the scratch length. However, incorporation with GO the maximum depth was delayed until 100 μm. Figure 3 (inlet) shows that at 40 μm of scratches, the scratch depth profiles of PU were reduced 37% for incorporation with 1wt% of GO (3501 nm to 2194 nm) and 51% for 4wt% of GO (to 1708 nm), respectively. Meanwhile, at a scratch rate of 5 um/s they seems to give a significant amount of scratch depth reduction as shown in Figure-4 (inlet). The incorporation of 1wt% of GO in the PU matrix resulted in nearly 21% (2666nm to 2099nm) reduction in scratch depths. For 4wt% of GO, such effect is apparent with a large reduction

in scratch depth with 73% from 2666nm to 712nm. It is clear that an increase in the concentration of GO, the scratch resistance was dramatically improved. The improvement in PU-GO nanocomposites at higher concentration could be attributed through the strong interaction between GO and the PU matrix due to the chemical crosslinker for isocyanate-terminated PU by GO (Cai *et al* 2009; Cai *et al* 2012). This phenomenon makes the PU/GO composites show strong potential in protecting metallic surface, such as airplanes and wind turbines.
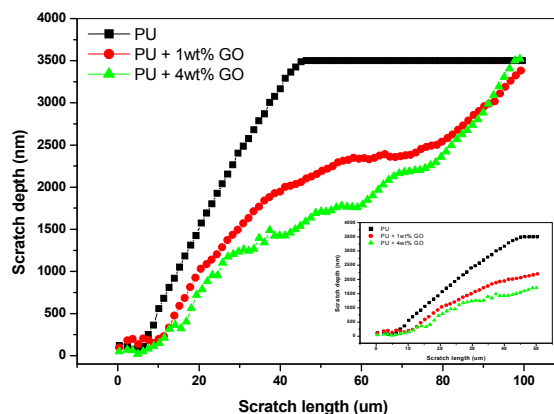

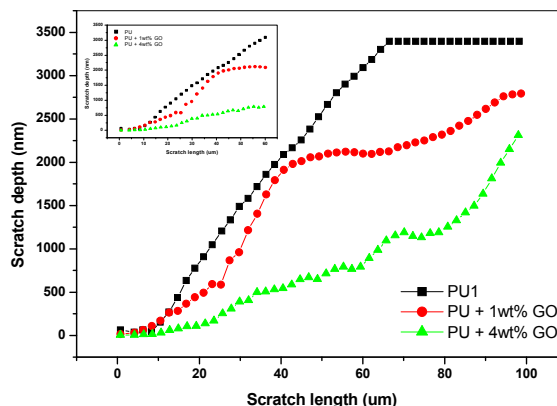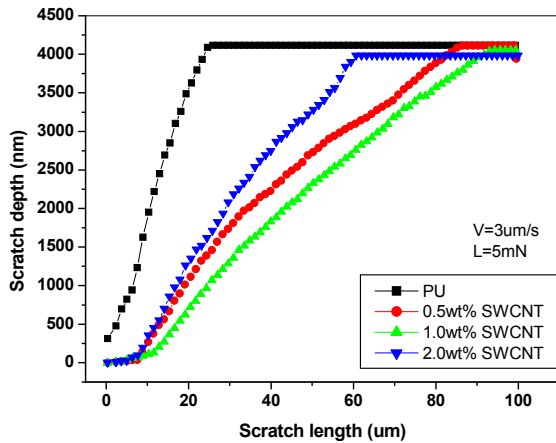**Figure-3.** Nanoscratch depth profiles for PU and its GO nanocomposites at 3μm/s.

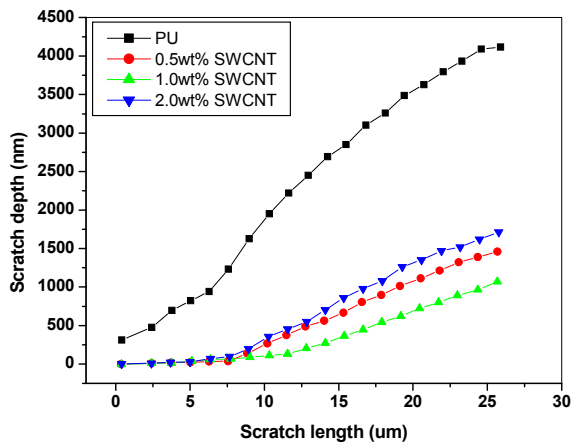**Figure-4.** Nanoscratch depth profiles for PU and its GO nanocomposites at 5μm/s.

In CNT, two different polyurethane CNT nanocomposites were studied. Typical scratch depth profiles for PU and different CNT loadings are given in Figures 5 (a and b) - 6 (a and b). As expected, the scratch penetration for the PU with SWCNTs exhibited greater resistance to nanoscratch as evident from the depth profiles at all percentages of nanotubes as compared to MWCNTs. It can be seen that the scratch depth dramatically reduced with increasing the loading level of

the nanotubes until 1wt%, as presented in Figures 5a, 5b, 6a and 6b. In contrast, with 2wt% of SWCNT, the scratch resistance was slightly lower as compared to 0.5wt% and 1wt% counterparts. For PU-SWCNT, the addition of 1wt% of nanotube at 3µm/s showed a strong impact on scratch resistance and it was lower nearly 3000nm of scratch depth as compared to pure PU after 25µm of scratching. Similar phenomena with PU-MWCNT, at 1wt% of MWCNT the scratch depth was lowered almost 2800nm as compared to pure PU. In addition, the scratch penetration was less for PU-SWCNT composites than for the PU-MWCNT composites and it demonstrated as the time to achieve the maximum depth increased. This is consistent with PU-SWCNT composites being highly filler dispersion compare to the PU-MWCNT. Thus the higher modulus/hardness/weight % of nanofiller composites results in lesser depth of penetration among the PU-CNT samples.
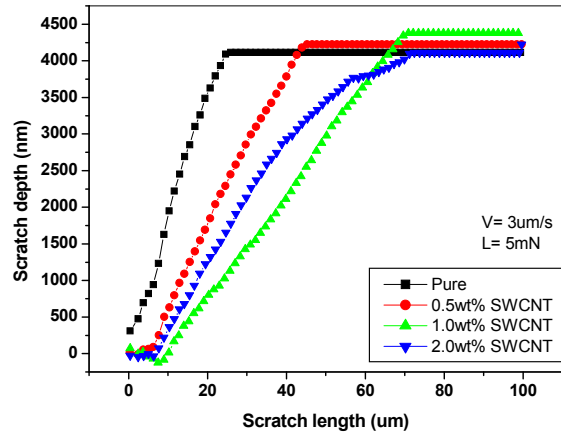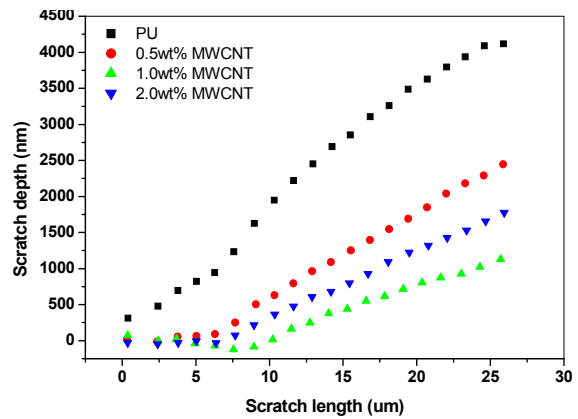

6(a)



6(b)

Figure-6. Nanoscratch depth profiles for PU and its MWCNT nanocomposites at 3µm/s. (a) After 100 µm and (b) After 25 µm of scratch length.

5(a)

5(b)

Figure-5. Nanoscratch depth profiles for PU and its SWCNT nanocomposites at 3µm/s. (a) After 100 µm and (b) After 25 µm of scratch length.

Relative scratch resistance

The relative scratch resistance as a function of GO concentration is shown in Figure-7. Introduction of GO into the PU matrix increased in the surface hardness and enhanced the scratch resistance. Figure-7 shows that with only 4wt% of GO the PU nanocomposites had greater hardness and showed better scratch resistance. Generally speaking, the main factor principally responsible for the enhancement effect of the addition of GO to polymer is the reduction in the phase separation of the PU matrix. The reduction of the phase separation caused by the GO is the function as a chemical cross-linker for isocyanate-terminated PU. The second factor is exfoliation of GO in the PU matrix. When the GO are completely and uniformly dispersed in a continuous polymer matrix, an exfoliated or delaminated structure was obtained demonstrated by TEM and SEM images in Figure-8 [Cai *et al.* 2009]. This structure makes the entire surface of GO available for the polymer and maximizes polymer-GO interactions.

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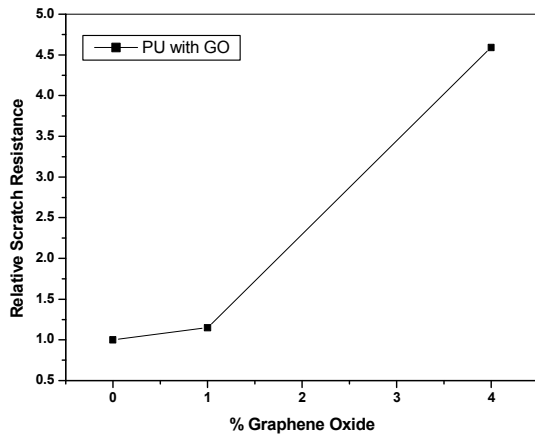
Figure-7. Relative scratch resistance as a function of GO concentration.

(a)   (b)

(c)
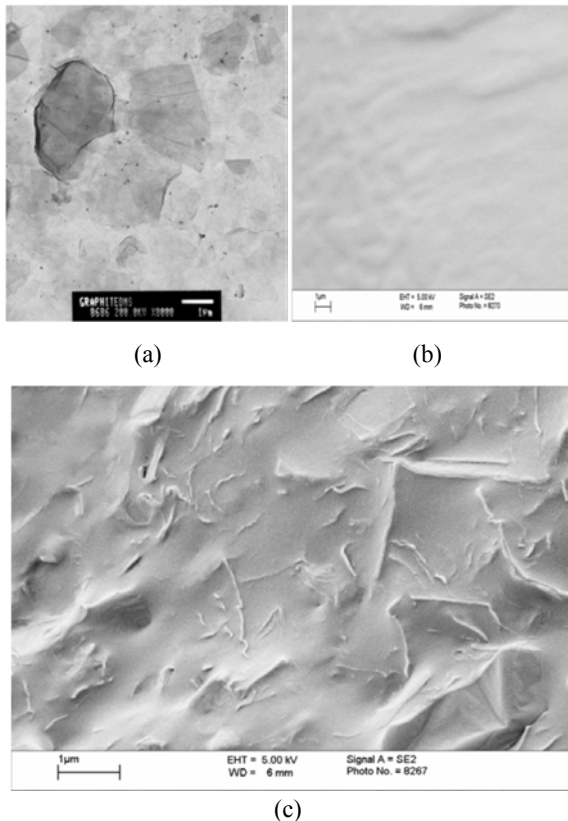
Figure-8. (a) TEM image of the GO/DMF dispersion; (b) SEM image of the PU; (c) SEM images of 4wt% GO/PU composite.

The relative scratch resistance as a function of CNT concentrations is shown in Figure-9. Introduction of CNT into the PU matrix increased in the surface hardness and enhanced the scratch resistance. Figure-9 shows that with only 1wt% of SWCNT in the PU the scratch

resistance increased by more than 1.6 fold as compared to pure PU. Meanwhile with 1wt% of MWNT, the relative scratch resistance moderately increased and it was approximately by 0.6 fold as compared to the pure PU. As shown in scratch depth profile observation, the concentration of CNT more than 1wt% exhibits only a moderate improvement to the scratch resistant. There could be three main factors principally responsible for the enhancement: chemical bonding as contributed by homogeneous dispersion of CNTs in the PU matrix, nano-mechanical interlocking and non-bond interaction due to van der Waals and electrostatic forces [Liao and Li 2001]. Therefore, the combination of above three factors contributes the strong interactions between CNTs and the PU matrix, thus strengthening the scratch performance of the composites. However, at high concentration, aggregation of CNTs occurs which could minimize the CNT and PU segment interactions.
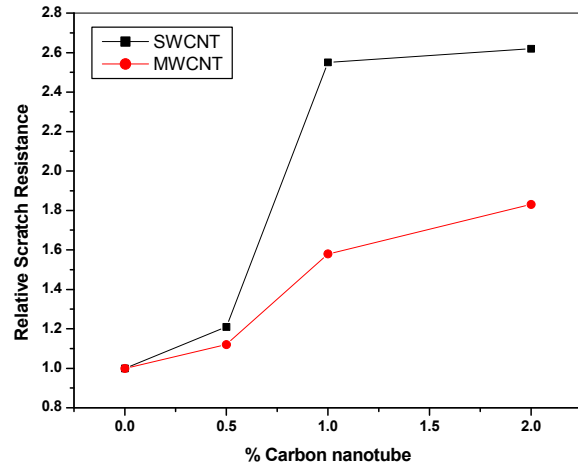
Figure-9. Relative scratch resistance as a function of SWCNT and MWCNT concentrations.

CONCLUSIONS

The scratch behaviour of polyurethane and its nanocomposites were studied. The scratch resistance exhibited a significant enhancement with incorporation of nanofillers by lowering the scratch depth as compared to the pure PU. With 4wt% of GO, the scratch penetration of the PU shows a large reduction in depth with 73% from 2666nm to 712nm. It is clear that the addition of GO, the scratch resistance of the PU was dramatically improved. For PU-CNT nanocomposites, as expected, the scratch penetration exhibited greater resistance to nanoscratch as evident from the depth profiles at all percentages of SWCNTs compared to MWCNTs. It can be seen that the scratch depth dramatically reduced with only 1wt% of the loading level of the SWCNTs. The main reason could be due to the friction response which greatly reduced at the higher velocity of scratch. The decrease in friction with increased velocity was suggested to be a reason to the

reduction of plastic build-up in front of the scratch tips and thus, the resistance to penetration definitely improved.

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