

THEORETICAL MODELING OF TRIBOLOGICAL BEHAVIOR OF NANOCLAY/EPOXY COMPOSITES

Chun Ki Lam*, Kin Tak Lau*

*Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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Abstract

In this paper, a comprehensive work on the micro-hardness and wear resistance of nanoclay/epoxy composites (NCs) is addressed through analytical and experimental approaches. It was found that the micro-hardness and wear resistance of NCs increased with increasing nanoclay content. The improvement of mechanical properties of NCs by increasing nanoclay content was explained by the degree of agglomeration of nanoclay clusters inside NCs through SEM and XRD investigations. Mathematical models were proposed for the determination of hardness and wear resistance of NCs in different nanoclay contents from the relationship between the diameter of nanoclay clusters and inter-cluster distance.

1 Introduction

In everyday engineering applications, an excellent wear resistance of engineering materials is a critical requirement for surface coating applications in severe working environment. Furthermore, the maintenance cost can be kept as low as possible as for an engineering component to possess a high wear resistance. Wear resistance is a critical requirement of engineering materials for surface coating applications and some structural components which are exposed to a harsh working environment. It is absolutely essential for an engineering component to possess a high wear resistance in order to keep the maintenance cost low. In the past decade, many researches have been conducted on the applications of various types of nanocomposite coatings for different engineering components [1-3]. Novel nanocomposites are more desirable than micro-composite surface coating materials as the former shows a more remarkable wear resistance. It is due to the increase of surface contact area which allows

more interlinking between the nanoparticles and the matrix. Hence, the mechanical properties of the nanocomposites can also be greatly enhanced. Conventional nanocomposites surface coatings, such as diamond-like carbon-based nanoparticles in Ni matrix, are fabricated by cutting the hard micro-particles into nano-sized particles and electrodepositing them on the metal surfaces. Nevertheless, the applicability of the novel nanocomposite surface coatings are only limited to metal surfaces as the coatings have to be applied by electroplating or electrodepositing methods. Therefore, the application is only restricted to conducting engineering product surfaces. Furthermore, the cost for manufacturing the coatings is relatively high due to the refinement of the superhard materials to nanoparticles such as diamond and silicon carbides. Thus, for large engineering products, such as automobiles and aircraft, the expenditure for such high wear resistant coatings would be incredibly high and not economically viable. Finally, the densities for superhard nanoparticles are usually high and thus increase the weight of the coatings. This actually is not a feasible solution for the weight sensitive engineering technologies. Recently, researchers have showed that polymer nanocomposites can provide high mechanical and tribological performance with wide applicability in both conducting and insulating surfaces of engineering products without adding much extra loading to the main engineering bodies. TiO₂ [4], SEBS [5] and carbon nanotubes [6] were being used as nanofillers in epoxy, polystyrene and other polymers for nanocomposite coatings.

Layered montmorillonite (MMT) or nanoclays (SiO₂) are newly invented nanofillers in polymers for extraordinary improvements in mechanical behaviors of polymer matrix. Fig. 1 shows three typical forms of MMT inside polymer matrix.

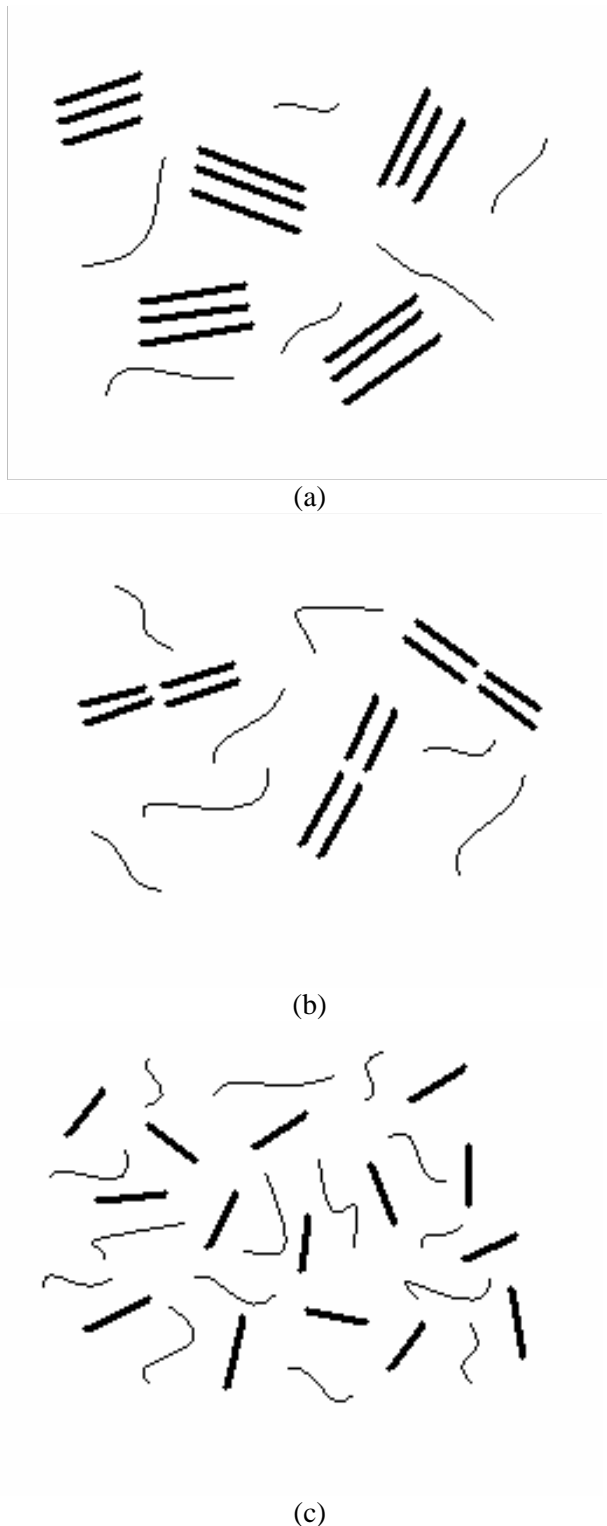


Fig. 1. Three typical forms of MMT inside polymer matrix. (a) intercalated; (b) flocculated and (c) exfoliated

MMT is composed by stacks of nanoclay platelets. They can provide significant improvement to the

mechanical properties of polymer matrix due to their high aspect ratio of the nanoclay platelets and thus provide large contacting interfaces for the interaction between the nanoclays and the matrix. Many researchers have begun to study the abrasive durability of nanoclay-based polymer composites in order to replace the traditional superhard nanoparticles-based surface coatings [7-9]. Nevertheless, fully exfoliated nanoclay/epoxy composites (NCs) can only exist in laboratory studies by absolute controlled experimental conditions. Lam et al. [10-11] has studied the effects of nanoclay clusters in NCs and the results showed that there was an optimum nanoclay wt. % inside NCs in order to possess the highest mechanical reinforcement. It was found that the maximum hardness can be achieved for the nanoclay content at 4 wt%. Further increasing the amount of nanoclays resulted in decreasing the hardness of the NCs. The nanoclay clusters behaved like the novel superhard nanoparticles in conventional surface coatings. As a result, intercalated nanoclay clusters should be investigated for surface coatings that can cope with most engineering manufacturing processes instead of testing the applicability of fully exfoliated nanoclay platelets inside controlled laboratory conditions. To the best knowledge of the authors, the wear resistance of intercalated NCs has not yet been studied to date.

In this study, up to 4 wt% of nanoclays mixed with an epoxy matrix to form NC samples were fabricated. Scanning Electron Microscopy (SEM) and X-ray spectroscopy (XRD) examination was used to verify the degree of intercalation of nanoclays inside the samples. Vickers micro-hardness test was conducted to test their hardness and twin SiC sliding wheels test was employed to visualize the wear resistance of the NC samples.

2 Experimental Investigations

2.1 Materials

Nanoclays (SiO₂ Nanolin DK1 series from the Zhejiang Fenghong Nanoclay Chemical Technology Company) were used as nano-reinforcements for this study. The mean diameter, density and montmorillonite content of the nanoclays were 25 nm, 0.45 g/cm³ and 95%-98% of SiO₂, respectively. The epoxy resin and hardener selected for this study were Araldite[®] GY 251 bisphenol-A liquid epoxy resin and Hardener HY 956 aliphatic amine from

Ciba Speciality Chemicals respectively. They were mixed in a ratio of 5 to 1 parts by weight.

2.2 Sample Preparation

NC samples were fabricated by using mechanical mixing process with different amounts of nanoclay, 0 wt.% (NC-0), 1 wt.% (NC-1), 2 wt.% (NC-2) and 4 wt.% (NC-4). The predetermined amounts of nanoclays were dispersed in epoxy resin. The mixtures were hand stirred for 10 minutes until the epoxy resin and the nanoclays were well mixed at room temperature. Ultrasound sonication was employed to further disperse the nanoclays in the resin. The sonication time was fixed at 20 minutes for all the samples in order to ensure their maximized mechanical performance [11]. Hardener was added into sonicated mixtures by hand stirring and followed by vacuuming for 24 hours at room temperature for curing. The abrasive testing samples were prepared by curing them in same grade of surface-treated circular polypropylene discs with 4-inches in diameter.

2.3 Measurements

X-ray diffraction (XRD) of NC samples were conducted on a Philips PW 1830 X-ray Generator (Cu K_{α} , $\lambda = 0.154$ nm) in order to visualize the degree of aggregation of the nanoclay clusters. Scanning Electron Microscopy (SEM) of the fractured surfaces of NC samples was conducted on a Leica Stereoscan 440 SEM.

Micro-hardness test of NC samples was conducted by using the micro-hardness tester (FM-7E) of the Future-Test Corporation from Tokyo, Japan. Each NC sample was indented ten times at different locations under the same indenting conditions and the average value was taken as a representing micro-hardness of the specified NC samples.

Wear resistance of the NC samples was obtained from an abrasive test performed on the circular NC samples with 4-inches in diameter in a 5131 Abraser of Taber Industries, North Tonawanda, N. Y., USA. The sliders were two circular-disked like silicon carbide abrasive wheels manufactured by Taber Industries. The wear resistances of the NC samples were compared by the wear index (WI) calculated by,

$$WI = \frac{1000(W_s - W_f)}{R} \quad (1)$$

where W_s (measured in grams) is the initial weight of the NC sample before testing, W_f (measured in grams) is the final weight of the NC sample after testing and R is the number of testing cycles.

3 Results and Discussions

3.1 X-ray Diffraction

The XRD spectrums of the NC samples with different wt. % of nanoclays are shown in Fig. 2.

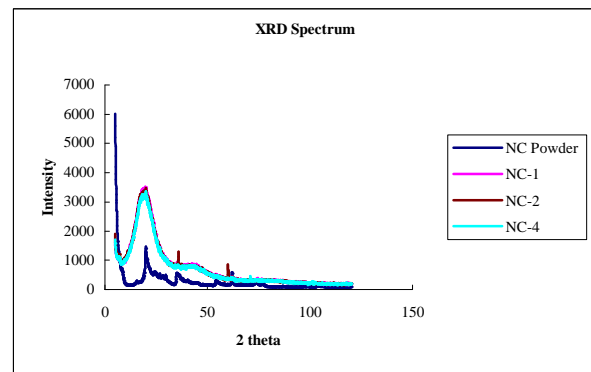


Fig. 2. XRD spectrum of different wt. % of NCs

Only one common peak at $2\theta = 18.8^\circ$ with maximum intensity exists in the NC samples when comparing with pure nanoclay powders. By using the Bragg's formula, $2d\sin\theta = n\lambda$, the interplanar distance between nanoclay platelets was 0.239 nm approximately. For a fully exfoliated NC sample, the angle 2θ in the XRD spectrum should be as small as possible in order to achieve the largest interplanar separation between the nanoclay platelets. Hence, there should be no obvious peaks in the XRD spectrums of totally exfoliated NC samples. Therefore, all of the nanoclay platelets of the NC samples in the experiments were intercalated.

3.2 Scanning Electron Microscopy

The SEM of the fractured surface of the NC sample with 4 wt.% of nanoclays is shown in Fig. 3. Nanoclay clusters were readily found and hence the nanoclays inside the NC samples existed in the form of intercalated nanoclay clusters.

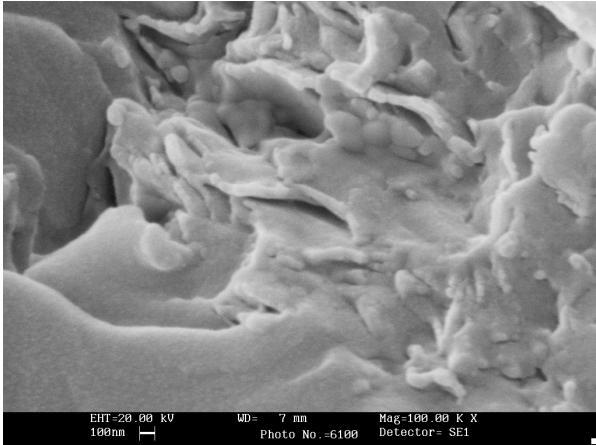


Fig. 3. SEM of the fractured surface of NCs at 4 wt.% of nanoclays

3.3 Micro-Hardness

Fig. 4 shows the average hardness of different NC samples.

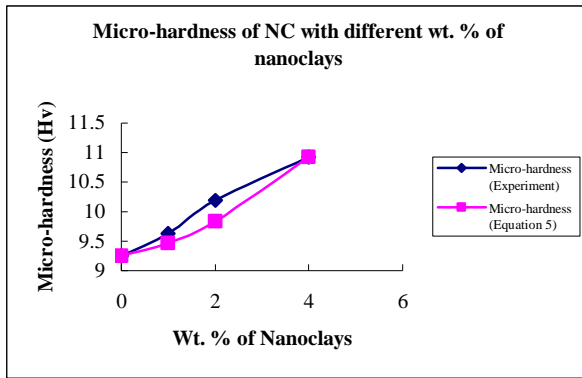


Fig. 4. Micro-hardness of different wt. % of NCs

By adding nanoclays into epoxy resin, the micro-hardness of the NCs increased proportionally with the nanoclay contents up to 4 wt.%. By Zhang et al. [8], the correlations between the inter-particle distances, diameters of the nanoparticles and wt.% of the nanoparticles in nanocomposites can be explained by Eq. (2),

$$\tau = d \left[\sqrt[3]{\left(\frac{\pi}{6\phi_p}\right)} - 1 \right] \quad (2)$$

where τ is the inter-particle distance, d is the particle diameter and ϕ_p is the filler content.

In the theoretical modeling of NCs, τ , d and ϕ_p represent the inter-cluster distance, the diameter of the nanoclay clusters and the nanoclay content respectively.

As the micro-hardness of the NCs increases in proportion to the content of nanoclays, the diameter of the nanoclay clusters increases while the inter-cluster distance between them decreases accordingly [10], the micro-hardness of the NCs can be modeled as,

$$H = H_i + k_H \left(\frac{\phi_p d}{\tau} \right) \quad (3)$$

where H is the micro-hardness of the NCs, k_H is the micro-hardness proportional constant and H_i is the micro-hardness of pure epoxy. Thus, Eq. (2) can then be rewritten as,

$$\frac{d}{\tau} = \frac{1}{\left[\sqrt[3]{\left(\frac{\pi}{6\phi_p}\right)} - 1 \right]} \quad (4)$$

Substituting Eq. (4) into Eq. (3), the micro-hardness of the NCs can be determined by,

$$H = H_i + \frac{k_H \phi_p}{\left[\sqrt[3]{\left(\frac{\pi}{6\phi_p}\right)} - 1 \right]}, \text{ and} \quad (5)$$

$$H = H_i + k_H \left[\frac{1.817 \sqrt[4]{\phi_p}}{\left(\sqrt[3]{\pi} - 1.817 \sqrt[3]{\phi_p} \right)} \right]$$

3.4 Wear Resistance

Fig. 5 shows the test results of the wear resistance of the NC samples.

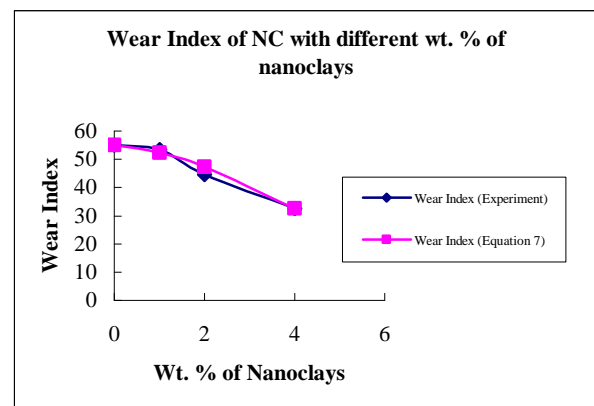


Fig. 5 Wear index of different wt. % of NCs

The higher the wear index, the lower the wear resistance and vice versa. Therefore, NC-4 has the highest wear resistance. As the wear resistance of the NCs increases in proportion to the nanoclay content, the wear resistance of the NCs can be correlated to the diameters of the nanoclay clusters and the inter-cluster distance from the argument as stated in Eq. (3) by,

$$W = W_i - k_w \left(\frac{\phi_p d}{\tau} \right) \quad (6)$$

where W is the wear resistance of the NCs, k_w is the wear resistance proportional constant and W_i is the wear resistance of pure epoxy.

Substituting Eqs. (4) into (6), the micro-hardness of the NCs can be determined by,

$$W = W_i - \frac{k_w \phi_p}{\left[\left(\sqrt[3]{\frac{\pi}{6\phi_p}} - 1 \right) \right]}, \text{ and} \quad (7)$$

$$W = W_i - k_w \left[\frac{1.817 \sqrt[4]{\phi_p}}{\sqrt[3]{\pi - 1.817 \sqrt[3]{\phi_p}}} \right]$$

The mathematical predictions of micro-hardness and wear resistance of the NCs were based on the empirical data with the nanoclay contents from 0-4 wt.% and the condition of fully intercalation of nanoclay platelets inside nanoclay clusters was assumed. In Figs. 4 and 5, the mathematical predictions of micro-hardness and wear index of the NCs are compared to the experimental results respectively. It shows that these mathematical models of the NCs are valid for the micro-hardness and wear index estimation once the nanoclay content is known.

4 Conclusion

In this paper, the micro-hardness and wear resistance of the NCs with the nanoclay content up to 4 wt.% were investigated. Both properties increased with increasing the content of nanoclays. The improvement in the wear resistance of the NCs compared to a pure epoxy can provide an adequate compatibility among novel nanocomposites for surface coatings. A mathematics correlation of micro-hardness and wear resistance of the NCs with

the diameters of intercalated nanoclay clusters and inter-cluster distance is proposed in this paper. This can aid the understanding of the infrastructure inside the NCs for everyday engineering applications. The intercalation of nanoclays in NC surface coatings on engineering products were accurately modeled instead of only considering ideally exfoliated NCs in many laboratory studies.

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