Study the Effect of Bi-Layers on the Friction and Impact Resistance of PMMA/Nano-composite Hard Coatings

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Abstract
A comparison work of mechanical and surface behavior of one hard coating layer and bi- layers (soft /hard layer) precipitation on poly (methyl methacrylate) substrates was studied.TiO_2 was treated with appropriate coupling agent typically 3-aminopropyltrimethoxysillane (APTMS) to enhance it's compatibility and dispersibility with polymer matrix. TiO_2/ PMMA nanocomposite was chosen as a upper layer for double layers coatings and polysilicon rubber as a soft base sublayer was presented with thickness 200 μm to show impact of a soft subbase layer on the mechanical and surface properties. The results showed that the existence of soft base layer caused decreases the coefficient of friction and enhance the impact resistance for bilayer as a compare monolayer coating.

Keywords: PMMA, nanocomposite coating, soft layer, coefficient of friction.

INTRODUCTION

Polymers have a critical impact in materials and mechanical designing, not just for their straightforwardness in assembling and low unit cost, additionally for their conceivably fantastic tribological execution in engineered structures [1]. Polymers can be applied as coatings on harder substrates by several different techniques such as adhesive bonding, vacuum deposition, electrochemical methods and pressure casting .The thickness of the polymer coating produced can vary from a few micrometers to several millimeters[2]. In any case, those coatings were not fulfilled for the prerequisites to upgrade abrasion and scratch strength, and the mechanisms of the surface harm development on covering layer have still not completely saw yet [3]. So, most of the polymeric coatings that used in tribological applications are modified by suitable fillers to decrease the friction coefficient and wear resistance, to enhance their resistance and their modulus of elasticity. These fillers are intended to bring a elastic contribution into a completely plastic behavior or to build the flexible part in a elastic plastic behavior of the covering[4]. Poly(methylmethacrylate), is an important engineering polymer, which has application in numerous parts, for example,

flying machine coating, signs, lighting, design, and transportation. PMMA could be additionally helpful in amalgamation dentures, drug gadgets, sustenance taking care of hardware, throat lights, and lenses because it's non-toxic material[5].

A. Rubin et al, they studied the impact of nanostructured design of an rubber strengthened piece copolymer PMMA on both surface and volume mechanical properties and they demonstrated that yielding of the contact shows up at higher strain on PMMA–PBA–PMMA than on PMMA or CI30 and that harms are lower. Nanostructuration design is in this manner the way to keep away on transparency [6]. P. Chouwatat et al, they studied the impact of delicate base layer in light of scratch properties for hard acrylic coatings and they demonstrated that the presentation of the soft base layer could hinder the cracks produced on the covering surface, and they recommended that the scarify properties of coatings acrylic were essentially enhanced by presenting the soft base layer[3].

When two parts are in contact under a normal load and a relative motion between the bodies' starts, some friction force arises. The ratio between the friction force (F_t) and the applied normal load to the moving tip is called the apparent friction coefficient μ_{app} (equation 1)[7].

$$\mu_{app.} = \frac{F_t}{F_n} \qquad (1)$$

Friction coefficient may be split into two components, the adhesion coefficient ($\mu_{ad.}$) and the surface deformation coefficient ($\mu_{def.}$).

$$\mu_{app.} = \mu_{def.} + \mu_{ad.} \qquad (2)$$

And the deformation coefficient:

$$\mu_{def.} = \mu_{plastic} + \mu_{elastic} \qquad (3)$$

Deformation coefficient can be represented by the ratio between surface shear stress and the mean contact pressure:

$$\mu_{ad.} = \frac{A\tau}{AP_m} = \frac{\tau}{P_m} \qquad (4)$$

Where A is the contact area, τ is the shear stress and p_m mean contact pressure[8].

In sliding contacts with polymers, both ploughing of the surfaces by hard particles or counterface asperities and the adhesion between the surfaces in contact participate in the overall friction force. Three basic types of deformation properties and failure modes may occur, elastic or viscoelastic with tearing failure, plastic or viscous flow with necking failure and brittle failure accompanied by fracture. These failure modes are typical for elastomers, ductile polymers and glassy polymers respectively[9][10].

Thus, in this study, single and double coatings on the plastic substrate were readied. The upper layer made of PMMA/TiO$_2$ nanocomposite while the soft base layer with same thickness was rubber layer coating. To investigate the effect of the soft base layer on the impact resistance and friction behavior, mechanical and surface tests were conducted. This tests methods can give the significant data about surface harm move and quantitatively assess the surface properties of coating materials. In addition, crack formation was deliberately seen by optical microscopic to comprehend the harm mechanism..

MATERIAL AND METHODS

A commercial PMMA was considered as a matrix material in this study. TiO$_2$ (Kronos 2310) was also used as an additional filler. The composites were prepared by solution mixing process, and 3-Aminopropyltrimethoxysillane as a coupling agent. Tetrahydrofuran (THF) [purity 99.9%] was used as an organic solvent.
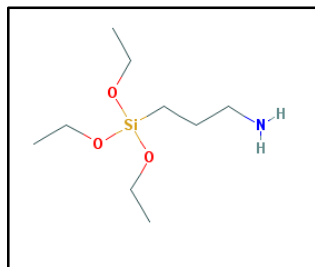

Figure 1: 3-Aminopropyltrimethoxysillane

Surface modification of TiO$_2$ nanoparticle

In order to improve the dispersibilty and compatibility of TiO$_2$ with PMMA matrix, 0.5 g of TiO$_2$ Nano-powder was scattered in 50 ml deionized water by ultrasonication technique for ten min. Then, the sillane coupling agent 3-aminopropyltrimethoxysillane (APTMS) were included the scattering. The blend was continued refluxing at various reaction conditions. From that point forward, scattered particles were isolated from solvent by centrifuge (ten min at 6,000 rpm) trailed by washing with ethanol and water on the other hand for no less than 2 cycles to evacuate over the top sillanes. Once the procedure was done, the improved particles were dried in an oven at 100 ∘C for four hours.

Nanocomposites coating preparation

To prepare polymer nanocomposite coating we employed solution mixing (dispersion – dispersion – precipitates) process[4]. Solution mixing is the most common method to prepare polymer/ TiO$_2$ nanocomposites. It consists of mixing TiO$_2$ fillers and the polymer in an appropriate dissolvent before dissipating the dissolvent to make a composite film. This technique depends on a productive dispersion of TiO2 fillers. The decision of dissolvent is for the most part made in light of the solubility of the polymer. Solution process begins by dispersing the fillers in a solvent, typically Acetone with verity weight percent (0.5, 1, 2 wt. %). This solution is mixed with a solution of PMMA dissolved in the same solvent. The nanocomposite is then recovered via precipitation in cooled distilled water, drying under vacuum 4h at 70ºC temperature to yield a solid flaky nanocomposite. The same procedure was employed to prepare a control sample (pure PMMA).

Samples preparation

The substrate which used for coating is a sheet of PMMA commercial type. The first layer was a soft layer we used a polysilicon rubber with thickness (≈ 200 μm) and after drying it for 24 h at room temperature the second hard layer was applied.

To prepare hard layers with thickness (≈ 200 μm), the composite powders were dissolved in dry tetrahydrofuran THF (1 g /5 mL) and sheared by magnetic stirrer. All coated samples were dried at ambient temperature for 24 h to make the surface of the coating layer more stable and then at 70 °C under vacuum for 8 h. The neat PMMA control samples were prepared in the same manner (Figure 2) and (Figure 3).
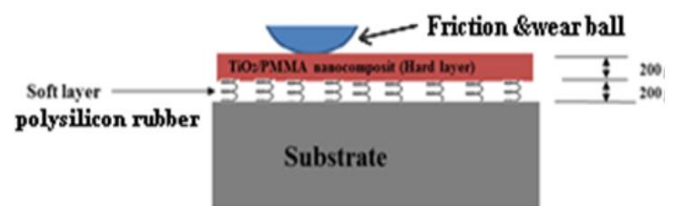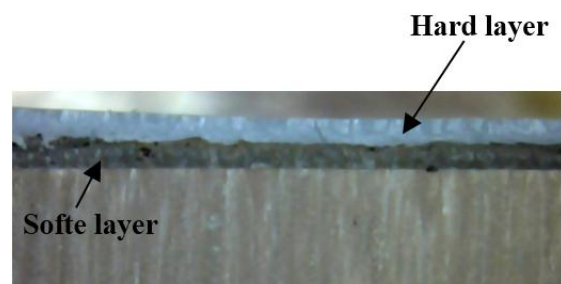

Figure 2: A schematic of the double layer coating

Figure 3: Optical microscope for double layers coating

Characterization

FTIR

The FTIR spectra were measured with a Bruker Optics Vertex 70. The samples were dispersed as neat powder and compressed in KBr. The spectra were recorded from 400 to 4000 cm^{-1}.

Pin on disc friction test

Tribological testing was performed in the pin-on-disk. Tribometer test device model MT/ MICROTEST system, in College of materials Engineering/ Babylon University. Consisting of an arm to which a ball or pin holder is attached, an accessory that turns (rotating disc) of about 115 mm diameter, A set of weights is included with the system to apply normal forces until 80N. The rotating disc is driven by an electrical motor and can turn up to 700 rpm. The friction coefficient is determined from the measures of the force of friction signal by the instrumented arm (deflection of the arm that holds the pin or ball holder). These measuring values, as the path, rotational angle, number of turns, time of test, etc, are measured and stored through the computer control system, According to (ASTM G99) the balls specimen used in this work are made from steel material that had hardness approximately (HV:830) and Alumina material that had Hardness approximately(HV: 1500) with dimensions of (6 mm) ,roughness 0.1 μm fixed to the upper arm using the ball holder. The disk specimens were made with diameter 50 mm and 4mm thickness.

Impact strength

Impact test was performed according to ASTM D-256-87 by using CEAST resil impact German, gant (HAMBURG) company (model WP 400 charpy type instrument). all specimens were fixed in a cantilever position, then the pendulum arm strokes, the energy absorbed by the specimens in joule unit. The calculation of Impact strength can be done by the following equation: [11]

$$Gc = \frac{Uc}{A} \qquad (5)$$

Gc: Impact strength of material (J/m^2), **Uc**: Impact energy (J), and **A,**: cross sectional area of specimen (mm^2).

RESULTS AND DISCUSSION

FTIR

The initial reactants and the product were analyzed by FTIR. (Figure. 4) shows the FTIR spectra of the bare TiO$_2$ nanoparticles and TiO$_2$ treated with 3-aminopropyltrimethoxysillane (APTM). There is a shift in the peak at 3432 cm^{-1} due to an increase in the bonding length.

As presented in (Figure 4) FTIR spectra of treated TiO$_2$ show characteristic bands groups around 1618cm^{-1} and 1489cm^{-1}, these peaks are not present in the untreated TiO$_2$ spectra, and appear on the APTMS modified TiO$_2$. The reason for the formation of the new chemical bond is the (O$_2$) in the TiO$_2$ may be played as a reduction agent for (H$_2$) to form the new bond between TiO$_2$ and APTM with water molecule. The spectra of the new bond in the range (1590- 1650 cm^{-1}) bending.
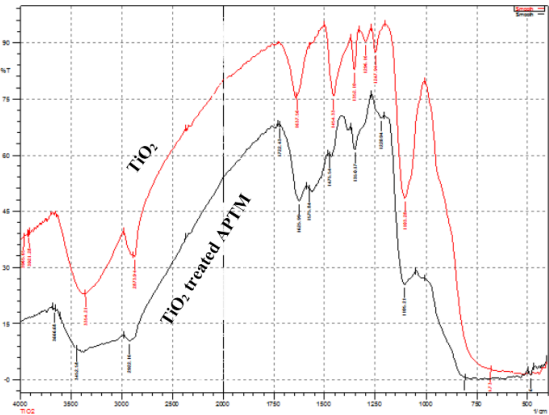

Figure 3: FTIR spectrum of TiO$_2$ and TiO$_2$ treated APTM

Micro hardness

The Vickers hardness number (Hv) was computed utilizing the relation:

$$Hv = 1.854 \times L/d^2 \text{ kg/mm}^2 \qquad (6)$$

Where L is the load in kg, and d is the length of corner to corner of indentation in mm. A few indentation were made for each load and the average hardness number was registered. Amid indentation, the specimens were kept entirely horizontal level and unbending. For PMMA-TiO2 nanocomposites covering (Hard layer), it is obvious from the (Figure5) that the Hv esteem increments with expanding the weight percent of TiO2, which demonstrate the role of nano-filler in improving the mechanical properties of hard layer.
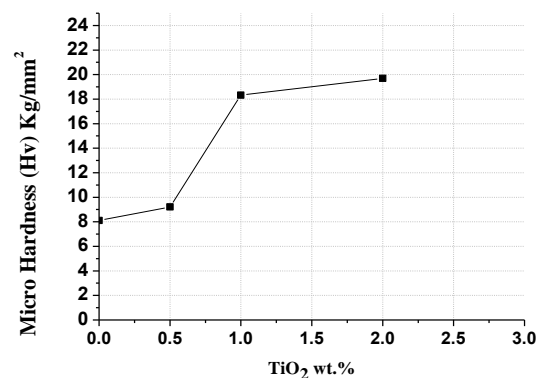

Figure 4: Effect of increasing TiO$_2$ wt% on the Hardness of hard layer.

Impact strength

The Results showed that addition of 1 wt. % TiO_2 to PMMA can improve the impact resistance by 35%, indicating the beneficial effect of well-dispersed TiO_2 on the resins' impact toughness. In the other hand, the case of duplex layer coating the results showed a significant enhancement in impact strength for all composite coatings about (28 %) which indicated the roll of the soft base layer in absorbing the shock energy (Figure 6).
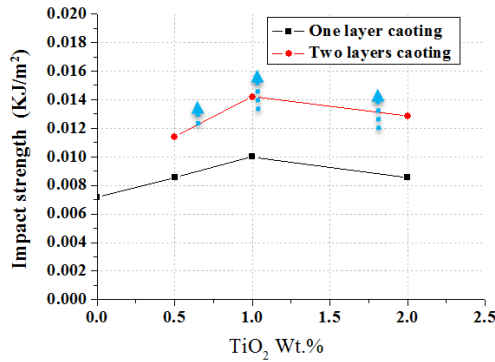

Figure 5: Impact Strength vs. TiO_2 wt. % for one and two layer coating

Coefficient of friction

The Friction tests were conducted at normal loads 1 N and performed at room temperature with under dry (un-lubricated) conditions, and the samples were tests at sliding velocities 50 rpm, by steel ball. The results of surface friction tests showed that the friction coefficient of the TiO_2/PMMA composite is reduced decreasing trend with the increase in TiO_2 content. At the same sliding condition, the 2 wt. % TiO_2 filled composite shows lower friction coefficient were the coefficient of friction decreased from 0.45 for pristine PMMA to 0.2 for TiO_2/PMMA nanocomposite coating (Figure 7). This behavior attributed to the fact that the TiO_2 have a self-lubricant nature which can help to decrease the interfacial shear.
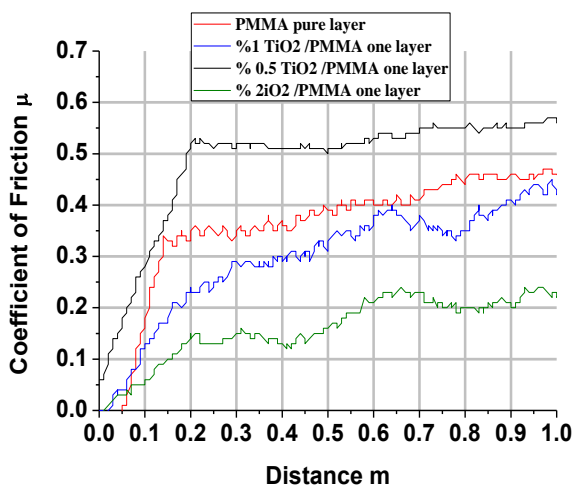

Figure 6: Effect weight percent of TiO_2 on the coefficient of friction

The presences of the soft base layer can significantly reduce the coefficient of friction 40% and 38.5 for double layer coating rubber /(PMMA- 1%TiO_2) and rubber/(PMMA -2% TiO_2) respectively, and this may be due to the elastic effect of base layer which increase the elastic component in the elastic – plastic behavior.
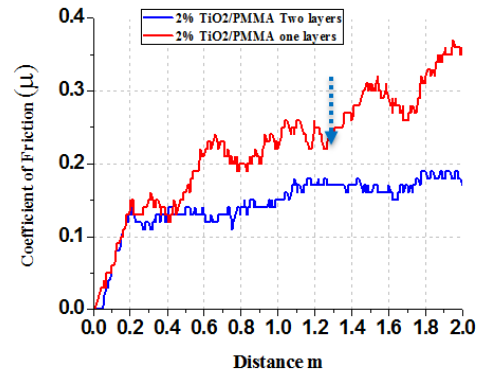

Figure 7: The role of soft base layer on decreasing coefficient of friction for nanocomposite coating

Morphology of the worn surface

Figure. 9 shows the optical micrscopic images of the shear deformations at the wear tracks sliding for the worn surface morphologies of single hard layer coating and double layer coating against steel ball. The result images showed that the present of soft base layer have a great impact on the improvement of wear resistance.

There is a relationship between elastic recovery and frictional behavior of polymer surfaces. With presence soft base layer, the surfaces exhibited a higher recovery and lower coefficient of friction. This is because a more elastic surface with a higher recovery property has lower real contact area, and thus lower adhesion compared to the plastic surface with plastic deformation/ plowing and material removal.
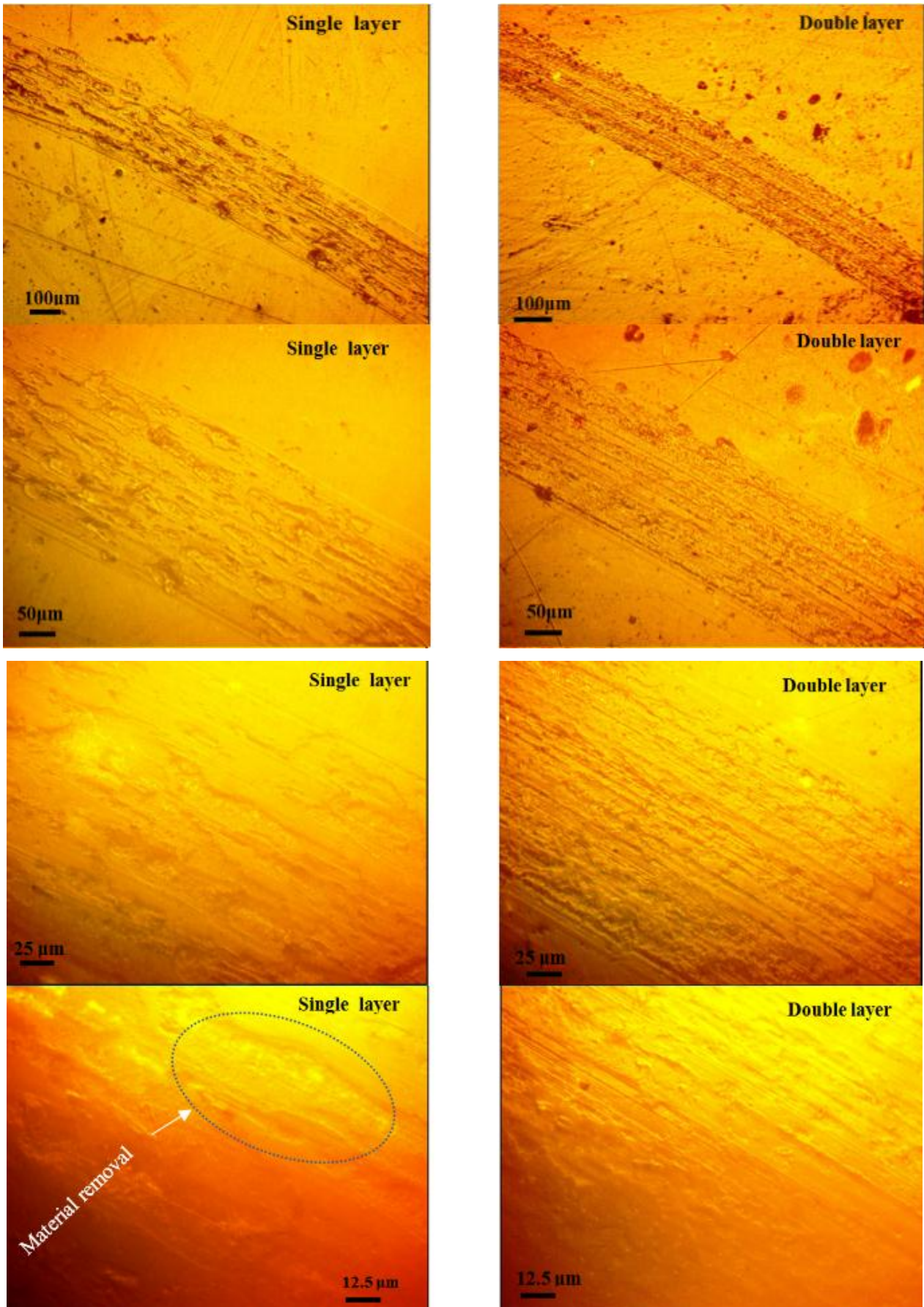
Figure 8: Optical microscope images of the wear track for single layer and double layers coating

CONCLUSION

The influence of soft base layer on friction and impact resistance for acrylic nanocomposite hard coatings was explored. The impact strength and friction resistance significantly enhanced after introduce the soft base layer. The presentation of soft base layer could enhance the impact strength and friction resistance for the coating surface.

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