

NANOMECHANICAL PROPERTIES OF HYBRID NANOCOATINGS

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ABSTRACT

This research focuses on the development of coatings and inorganic nanoparticles containing nanocoatings. Four different coatings were formulated based on specified chemical structures. The chemical formulations were varied systematically to achieve a polymer coating, a hybrid polymer-ceramer coating, a ceramer coating and a quasi ceramic coating. Compositions containing epoxy polymer and/or silicone polymers were chosen for this study.

Five different types of inorganic nanoparticles were chosen based on their nanostructures. Three different concentrations—0.1, 0.3 and 0.5 wt. %—of each type of nanoparticle were incorporated into coating formulations. Polished aluminum substrates were coated with 4 coatings and 60 nanocoatings. The coatings and nanocoatings were hardened and characterized using FTIR spectroscopy operating in reflectance mode.

The surface topography and scratched coating morphology of the coatings were investigated with the help of atomic force microscopy. The pristine polymer coating showed smooth surface morphology, while the hybrid, ceramer and quasi-ceramic coatings showed surface roughness in the nanometer regime.

The coatings and nanocoatings were tested for their nano-mechanical properties using the nanoindentation technique. The hardness modulus values were determined and correlated with the structure of the coatings and nanocoatings. The effect of nanoparticles on the hardness and modulus values of coatings was investigated. It was found that hardness increased with the addition of nanoparticles but inconsistent modulus values were seen in the nanocoatings.

The coatings and nanocoatings were analyzed using the nanoscratch technique. The effect of nanoparticles on fracture and delamination was studied. The SEM analysis was conducted on the scratched coating to understand the failure mode in the material. It was discovered that scratch resistance increased with the increase in nanoparticle. However, the nanocoatings showed increased brittleness over the pristine coatings.

The visco-elastic behavior of the coatings and nanocoatings was studied at five different test frequencies. The storage and loss modulus values were recorded for pristine coatings and nanocoatings. The variations in visco-elastic properties on the incorporation of the nanoparticles in coatings were investigated and correlated with the associated molecular structures. It was found that the storage modulus remained unaffected, while the loss modulus varied with test frequencies. Both the storage and loss modulus of the coatings varied marginally with the addition of nanoparticles.

Keywords: Silicones, ceramer, quasi-ceramic, FTIR spectroscopy, nanocoatings, nanoindentation, nanoscratch, viscoelastic.

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Chapter 1

INTRODUCTION

Corrosion is an electrochemical process that returns metals into their inert oxide state. Considerable costs—350 billion dollars annually in the United States alone—are spent in an effort to prevent corrosion [1]. Other industrialized nations have similar corrosion costs on a per capita basis [2]. Corrosion is more prominent in regions close to the ocean because the saline environment induces an electrochemical process on the metal surface. There are several reports documenting the loss of human life due to issues related to corrosion. Scientists and engineers are working together to develop new metals, alloys and materials that have better corrosion resistance in aggressive environmental conditions. However, the preservation of existing infrastructures is still of great concern and can be accomplished by shielding bare surfaces from the corrosive environment.

Historically, metals have been protected using thick polymer paints, varnishes and coatings—all of which delaminate after extended exposure in moist environments, making the removal of degraded coatings and re-application of new coatings necessary on regular basis. The removal of these coatings is time consuming and their disposal often creates environmental concerns. In addition, the majority of such coatings are based on expensive petroleum products that are in short supply. Alternative surface treatments or coating technologies are necessary.

1.1 Motivation

The most basic problem that material industries currently face is coating delamination. Porous organic coatings allow the permeation of ionic solutions to metal coating interface. The metal corrodes, causing the corrosion product to delaminate coating from the surface. To improve coating's adhesion, coating's porosity needs to be controlled. The adhesive strength of conventional, thick organic coatings can be evaluated using several techniques such as peel and scratch tests. Thin inorganic or quasi-inorganic coatings, however, that reacts and bonded to metal surfaces are difficult to test using conventional techniques. The mechanical properties of such coatings can be tested using the nanoindentation technique.

1.2 Goal of this research effort

The aim of this research is to develop materials with varying epoxy and silicone concentrations and compare the effects of incorporating nanoparticles in the resultant modified polymer coatings. The pure epoxy polymer, epoxy-silicone hybrid and silicone coating have been formulated. The coating formulations were charged with three different concentrations of five different nanoparticles. The coatings and nanocoatings were applied on 6061-Al-T6 specimens and cured for 30 days. The coatings and nanocoatings were subjected to the following analyses:

- The chemical structures of the coatings and nanocoatings were confirmed using FTIR spectroscopic analysis.
- The surface topography was studied using atomic force microscopy.

- The nano-mechanical properties were evaluated using nanoindentation and nano-scratch techniques.
- The visco-elastic behavior of the coatings and nanocoatings was examined with nanoindentation mediated dynamic mechanical analysis.

1.3 Organization of the Thesis

The first chapter introduces the subject to the readers. In the chapters that follow, the research is described in detail. The background information related to this research and relevant, non-comprehensive literature review are given in Chapter 2. The materials, manufacturing and methodology adopted to conduct this research are outlined in Chapter 3. The characterization of coatings and nanocoatings using FTIR spectroscopy is described in Chapter 4. The nano-mechanical analysis of coatings and nanocoatings is given in Chapter 5. Finally, the conclusions are given in Chapter 6.

Chapter 2

LITERATURE REVIEW

2.0 INTRODUCTION

The strength of conventional polymers can be evaluated using a universal testing machine operating in tensile or compressive mode. The thin coatings or films that cannot be removed from the substrate can be tested using the nanoindentation technique.

The basic nano-mechanical properties obtained from the nanoindentation tests are the elastic modulus and indentation hardness of the material. Several test methods are available that can determine fracture toughness, creep, storage and loss modulus, yield stress, as well as interfacial and surface adhesion. Similarly, the tribological behavior of surfaces, such as scratch or mar resistance, friction coefficients, and wear performance can be obtained [3].

2.1 Theory

This section briefly describes the theoretical concepts associated with the instrumented nanoindentation technique (IIT). Standard IIT equipment (Fig. 2.1) consists of three basic components: an actuator to apply force, an indenter mounted to a rigid column through which the force is applied on the sample and a sensor that measures the displacement of the indenter [4].

IIT equipment can generate required forces electromagnetically using either coils and magnets or capacitors that have fixed and moving plates. In some cases, the piezoelectric actuators can be used to generate small forces. The indenters used in IIT are

selected according to the type of information that is being collected. The indenter may have pyramidal, spherical, cube corner or conical geometry. A pyramidal shaped Berkovich indenter is most common in acquiring the nano-mechanical data. The displacement in IIT can be recorded using capacitive sensors.

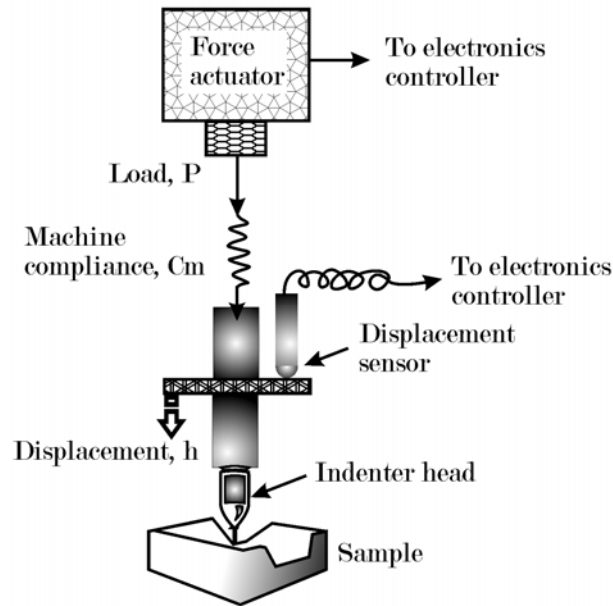


Fig. 2.1. A typical nanoindenter setup for the mechanical properties measurement of coatings

2.1.1 Nanoindentation Curve

A wide variety of coated substrates can be tested using the IIT. Properties of the coatings are normally influenced by the underlying substrates. However, the nano-mechanical properties of the coated material are least affected by the substrate when determined from the 10% of the thickness of the coating [5, 6]. In a typical nanoindentation experiment, the indenter makes contact with the material surface and then penetrates to a particular depth or load. A nanoindentation curve is plotted for load as a function of displacement of the indenter and shows a loading and unloading pattern (Fig. 2.2). Any inconsistency observed in the curve indicates cracking, delamination or

another failure in the coating. Fig. 2.3 shows the unloading process and parameters associated with the contact geometry. The depth of penetration is considered to be displacement into the sample. The hardness and modulus values are determined as discussed in section 2.1.2.

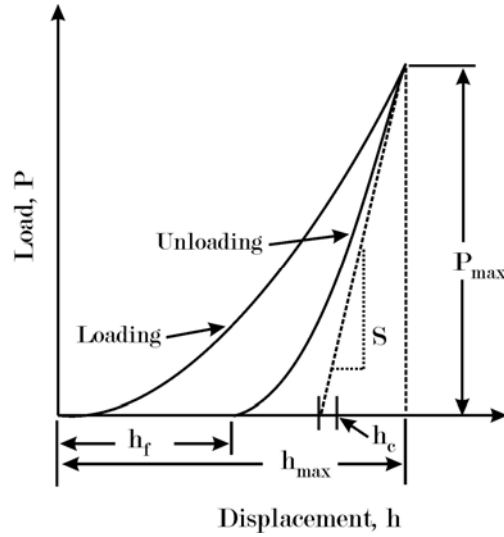


Fig. 2.2. Typical nanoindentation loading and unloading curve¹.

2.1.2 Hardness and Young's Modulus Analysis

The load and displacement curve can be used to determine the hardness and elastic modulus of the material [7]. The hardness H of the material is determined by dividing maximum load $P_{\max}$ by the projected contact area A of the indenter at maximum load as shown in equation 2.1.

$$H = \frac{P_{\max}}{A} \quad (2.1)$$

For ideal indenter geometry, the projected contact area A can be determined from the contact depth h_c at maximum load $P_{\max}$ such as in equation 2.2.

¹ This figure is reproduced with minor modifications. The image first appeared in Ref. [7] Oliver WC, Pharr GM. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. Journal of Materials Research. 1992;7:1564-83.

$$A = c_0 h_c^2 \quad (2.2)$$

The value of c_0 depends on the type of indenter tip. For example, the value of c_0 is 24.5 for the Berkovich pyramidal diamond tip. In the load vs. displacement curve, the contact depth h_c is different from maximum indentation depth $h_{\max}$ at the maximum load due to the elastic deformation of the area around the indenter head. The contact depth is given in equation 2.3.

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S} \quad (2.3)$$

Where, S represents stiffness that can be calculated from the slope of the unloading curve at the maximum load. The value of ε is 0.75 for the pyramidal indenter.

The calibration of indenter shape is critical in determining the hardness of the material. Fused quartz silica is used for the calibration of indenter tip because the mechanical properties of the fused quartz are known. The stiffness $S_{\max}$ is obtained from load-depth curves and assuming that the elastic modulus of the fused quartz is constant, the projected contact area A can be obtained as a function of stiffness $S_{\max}$ as given in equation 2.4.

$$A = \left(\frac{\pi}{4} \right) \left(\frac{S_{\max}}{E_r} \right)^2 \quad (2.4)$$

Where E_r is the reduced modulus, which represents the elastic deformation occurring both in sample and indenter. The value E_r can be calculated from equation 2.5.

$$\frac{1}{E_r} = \frac{1 - \nu_s^2}{E_s} + \frac{1 - \nu_i^2}{E_i} \quad (2.5)$$

Where E_s is the elastic modulus of the fused quartz silica, E_i is the elastic modulus of the indenter, ν_s is the Poisson's ratio of the fused quartz silica and ν_i is the Poisson's ratio of the indenter. The projected area A calculated using equation 2.4 can be plotted as a function of the contact depth h_c . The area function $A(h_c)$ so obtained is a fifth order polynomial that can be represented as equation 2.6.

$$A = c_0 h_c^2 + c_1 h_c + c_2 h_c^{1/2} + c_3 h_c^{1/4} + c_4 h_c^{1/6} + c_5 h_c^{1/8} \quad (2.6)$$

Where $c_0, c_1, c_2, c_3, c_4, c_5$ are constant and can be determined by curve fitting of the measured area function $A(h_c)$.

The elastic modulus E of the material can be determined using equation 2.7 and 2.8. The ν in equation 2.8 is the Poisson's ratio of the test material.

$$E_r = \frac{dp}{dh} \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} = S \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} \quad (2.7)$$

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \quad (2.8)$$

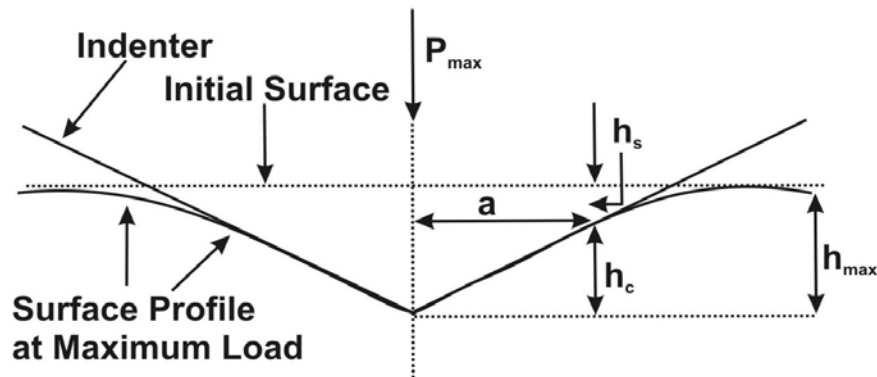


Fig. 2.3. Schematic of an ideal conical indenter at maximum load².

² This figure is reproduced after Ref. [7] *ibid*.

2.1.3 Scratch Tests

The coating performance depends on its ability to resist marks and scratches. Several techniques and test methods have been proposed by researchers but none of them is as precise as the nanoscale scratch testing, which uses an instrumented nanoindenter. The scratch test helps determine the mechanism that causes the deformation of materials as well as the delamination of coatings.

In a typical scratch experiment, a ramp load is applied to an indenter head in the normal direction as it simultaneously moves on the sample surface in a lateral direction. The instrument controls the normal force and lateral displacement of the indenter, while the lateral force and normal displacement are recorded as a function of time. Critical information such as the coefficient of friction, cross profile topography, residual deformation and pile-up of material during the scratch can be obtained as a function of scratch distance.

2.1.4 Dynamic Mechanical Properties

The stress-strain relationship of the materials displaying linear visco-elastic properties under sinusoidal loading is shown in equation 2.9 [8]:

$$\sigma = \varepsilon_o E' \sin \omega t + \varepsilon_o E'' \cos \omega t \quad (2.9)$$

Where σ is the stress, ε_o is the strain amplitude, ω is the angular frequency and t is the time elapsed. Rearranging equation 2.9 we get equations 2.10 and 2.11:

$$E' = \frac{\sigma_o}{\varepsilon_o} \cos \phi \quad (2.10)$$

and

$$E'' = \frac{\sigma_o}{\varepsilon_o} \sin \phi \quad (2.11)$$

Where σ_o is the stress amplitude, ϕ is the phase lag between the stress and strain and E' and E'' are storage and loss modulus respectively. The term E' represents the capacity of material to store energy, a component that is in phase with the applied load or displacement. The term E'' represents the capacity of material to dissipate energy, a component that is 90° out of phase with the applied load or displacement. The ratio E''/E' represents $\tan\phi$, also called loss factor, and is used to measure the damping characteristic of a linear visco-elastic material.

In order to determine the value of E' and E'' from a dynamic nanoindentation experiment, the equipment supplies a controlled load to the indenter head that sets the force amplitude, while the displacement amplitude and phase angle are measured [9]. At each test site, the indenter head contacts the material's surface. The indenter vibrates at a frequency and the resulting response is measured. The instrument's contribution to the total recorded response is then subtracted to determine the response from the material.

2.2 Background and Literature Survey

The nano-mechanical properties of coatings can be influenced by the coating substrate, so it is wise to consider the indentation data when the indenter penetration depth is approximately 10% of the coating thickness. When a coating is subjected to an indentation experiment, several different types of damage may occur as the load on the indenter increases. For example, the coating may delaminate due to a loss of contact between the coating and its substrate, and brittle coatings may fracture. These failures can

be used to determine the fracture strength, toughness as well as residual stresses of both the coating network and its interface with the substrate.

2.2.1 Studies on Epoxy Based Coatings

The epoxy resin based coatings have been used for a long time on wide variety of substrates. These coatings have a tendency to adhere to the substrate through mechanically created anchoring sites. The large polymeric chains in such coating composition allow formulators to accommodate desired pigments and fillers. However, such polymer coatings consist of defect sites such as pinholes, holidays and cavities that allow the diffusion of moisture which in turn lead to premature failure of the material. Considerable research has been conducted on such coatings. In the proceeding paragraphs we described the studies conducted on an epoxy coating using IIT.

Shi et al. [10] added 1 wt. % nanoparticles of Zn, SiO₂, Fe₂O₃ and halloysite clay in a commercial epoxy resin. The authors noticed that the epoxy coating containing SiO₂ nanoparticles displayed significant enhancement in Young's modulus measuring up to approximately 2.5 GPa compared to 250 MPa in pristine epoxy coating. However, the other modified nanoparticle coatings did not show enhancement in the stiffness value. Similarly, approximately 30 % of an increment in Young's modulus was obtained for nano-Zn modified epoxy coating while the nano-Fe₂O₃ and nanoclay modified coatings showed a 25% to 30% decrease in Young's modulus value compared to that of the unmodified epoxy coating.

Woo et al. [11] investigated the residual mechanical properties of epoxy-organoclay nanocomposites after they were exposed to moisture and UV light. They recorded an increase of up to 8% in flexural modulus upon adding 5 wt. % organo-clay,

but the flexural modulus decreased gradually with an increase in exposure time to moisture. Similarly, the tensile modulus increased with the incorporation of clay, but the strength and failure strain decreased due to clay aggregates, voids and different cure kinetics affected by the presence of organoclay. Also, tensile strength decreased after 250 h of UV light exposure. Their micro-hardness experiment suggests that hardness increased with embrittlement, but after UV light exposure, the nanoindentation modulus decreased systematically.

Davies et al. [12] studied the nano-mechanical behavior of epoxy adhesive joints of different thicknesses bonded with aluminum substrates. They used the nanoindentation technique to understand different aspects associated with the joint interphase such as modulus of the joints and substrate/adhesive. They found that the modulus value drops from 70 GPa corresponding to the aluminum substrate to 2 GPa corresponding to the adhesive layer. They concluded that nanoindentation studies were insufficient to monitor the presence of the interface region between the adhesive and substrate.

Li et al. [13] analyzed epoxy resin containing various percentages of coiled carbon nanotubes and single-walled carbon nanotubes using the nanoindentation technique. They found that the H and E values of nanocomposites increased with the increase in nanotube concentration. They found that the hardness and elastic modulus remained constant for different concentration of carbon nanotubes, indicating a uniform dispersion of carbon nanotubes in nanocomposite.

Kardar et al. [14] synthesized an epoxy acrylate resin containing different multifunctional acrylate monomers cured under UV radiation. A suspension of nano-alumina in tripropyleneglycoldiacrylate was also added to the formulation. The resulting

nanocomposites were investigated using nanoindentation and nanoscratch techniques. They found that nanocomposites containing nano-alumina displayed less hardness and increased elastic behavior compared to that of pristine resin.

2.2.2 Studies on Hybrid Silicone Coatings

Hybrid materials that contain higher organic branching points for crosslinking reactions displayed higher H values than do linear polymers [15]. Reduced modulus and reduced hardness varied through the different layers of the coating [16]. High value of reduced modulus and reduced hardness values were recorded at the surface due to a condensed morphology, lower values were recorded in the bulk due to a porous structure, and values increased again at the coating-metal interface due to a denser structure [16, 17].

In hybrid coatings, compositions with higher organic content cause segregation in the network, resulting in high-silica regimes surrounded by hydrocarbon-rich regimes. These coating networks displayed distinctly different mechanical properties than did the pristine silica network. A silica-rich coating based on tetraethoxysilane (TEOS) display near elastic behavior while a hybrid glycidoxypopyltrimethoxysilane (GTMS) coating displayed increased penetration on loading and almost complete recovery during unloading. The TEOS coating showed the smallest amount of creep due to a densely packed, rigid silica network while the creep was higher for the GTMS coating due to the viscoelastic flow and relaxation processes associated with the long chain hydrocarbon-rich domains. Young's modulus also decreased with the increase in organic portion in the backbone of the coating structure. In fact, the modulus of GTMS was 25 times less than that of TEOS [18].

The nano-mechanical properties were determined on quasi-ceramic high-silicone content coatings (QC) that were aged for three months on three different aluminium alloy substrates. H and M values were determined as a function of displacement into the coatings. The average hardness values for the QC-coated 2024Al, 6061Al and 7075Al were 0.42 GPa, 0.41 GPa and 0.47 GPa, respectively while the average modulus values were 4.40 GPa, 4.51 GPa and 5.45 GPa, respectively. The loading-and-unloading curves demonstrate the elastic recovery of the coatings with negligible plastic deformation. The average hardness of uncoated alloys 2024Al, 6061Al, and 7075Al were 1.87 GPa, 1.47 GPa and 2.37 GPa, respectively, while the average modulus values were 77 GPa, 76 GPa and 78 GPa, respectively. The slight variation in the mechanical properties of the QC coatings on different surfaces suggests that the coating may have been influenced to a small degree by the substrate mechanical properties or by the solubilised alloying elements from the substrate alloy [19].

In a nano-mechanical scratch test, cracks grew in a silicone ceramer (CR) coating on a 6061Al substrate due to the propagation of the indenter head. The coating cracks were perpendicular to the direction traversed by the indenter head. The length of the cracks increased in proportion to the force on the indenter and to the penetration of the nanoindenter through the thickness of the coating. Delamination and peeling occurred when the load on the indentation head exceeded the force required to hold the molecular segments in the coating. The results indicate that the degree of plastic deformation in the coating was limited, which is characteristic of the highly cross-linked coating [20].

Coatings applied on substrates can display lower mechanical properties with elevated-temperature curing if ions from the substrate diffuse and accumulate in the

coating, modifying its structure. Residual stress values suggest that the coatings are put under stress when the substrate restricts coating contraction due to shrinkage.

Additionally, the higher coefficient of thermal expansion of the coating compared to that of the substrate contributes to more residual tensile stresses after cooling. Coatings containing photo-curable groups have shown compressive residual stresses with UV light curing, suggesting that the effect of shrinkage due to drying is much less than with UV curing [21].

Mirabedini et al. [22] studied the silicone elastomer coatings containing TiO_2 . They investigated the effect of TiO_2 on the modulus, hardness, tensile strength and abrasion resistance of resultant silicone elastomer coating. They also studied the effect of TiO_2 on the adhesion strength of the coating that acted as a top layer. The results were correlated with the mechanical properties of silicone elastomer coating. They found that the incorporation of TiO_2 pigment affected the mechanical properties of the resultant coating. The changes in the properties were a function of the volume fraction of the incorporated pigment. The increase in pigment loading resulted in an increase in the elastic modulus, hardness, tensile strength and abrasion resistance, as well as the energy required to break the coating; however, it resulted in a decrease in the elongation at fracture. An increase of approximately 15 % was observed in mechanical properties except the hardness increment was only marginal. The adhesion strength of the coating also increased with the increase in pigment concentration to 10 wt.% due to an increase in cohesive strength as a result of an increase in tensile strength and modulus values. However, the adhesive strength of the coating reduced when the concentration of TiO_2

increased beyond 10 wt.%, probably because of the agglomeration of the pigment at a higher loading.

Tanglumlert et al. [23] prepared a hard coating suspension to improve the scratch resistance of polymethylmethacrylate surface. A coating solution was formulated by reacting silatrane with 3-glycidoxypropyltrimethoxysilane in the presence of an acid catalyst. They found that the scratch resistance of the coated surface increased with the increase in alkoxysilane content in the coating. They also discovered that the curing time and curing temperature affected the scratch resistance and adhesion properties of the coating layer.

Antanacio et al. [24] measured mechanical properties and adhesive strength of hybrid sol-gel coating. They found that an increase in the chain length of the organic modifier resulted in an increase in the hardness and elastic modulus of the final film. Cracking characteristics of the coating dropped due to the increase in flexible linkage as a result of an organic modifier. The toughness value of organically modified coating decreased due to a lower Young's modulus, while the adhesion improved. They proposed that the organosilane in the coating composition contributed to the dissipation of the energy required for cracking due to a large cohesive zone and the ability of the film to deform visco-elastically at high strains.

Etienne-Calas et al. [21, 25] studied two different organic-inorganic coatings on silicone and glass substrates. They prepared the coatings through a sol-gel procedure and deposited them on substrates using the spin coating technique. The first coating composition was formulated using methyltrimethoxysilane, colloidal silica and tetraethylorthosilicate, while the second composition was based on

3-(trimethoxysilyl) propyl-methacrylate. At lower loads, they determined coating hardness and modulus values from indentation curves. At higher load values, propagation of cracks were used to determine the coating toughness, residual stress and interface toughness, while energy analysis was used to study chipping and delamination in the coating. They found that mechanical properties of the coatings were influenced by the rapid diffusion of the sodium ions into the coating from the glass substrate.

Esfandeh et al. [26] reported a study on the adhesion behavior of several silicone modified epoxy coatings. A three layered coating assembly of approximately 200 μm were applied on a 1050 aluminum alloy. The effect of different silanes on the adhesive strength of the coating was studied using a pull-off test and a scanning electron microscope. Based on their observations of gel time, failure mode and adhesive strength, they concluded that the coating assembly consisting of 50/50 silicone-epoxy ratio in the intermediate layer displayed the best results among the compositions. Scanning electron micrographs and immersion experiments in sea water confirmed the excellent adhesion of the layered coating on the aluminum surface.

Kohl et al. [27, 28] tested two sets of duplex coatings each with the same top coat but different bond coats over steel panels. Nanoindentation and scratch tests were performed on the coating of thickness between 65 μm and 485 μm . The authors found that the top coat layer had an indentation modulus of 2.7 MPa and irrecoverable energy of 11%. Similarly, one bond coat displayed an indentation modulus of 3.9 MPa with 9% irrecoverable energy, while the other bond coat showed an indentation modulus of 155 MPa with 54% percent irrecoverable energy. Fracture mechanics and inelastic deformations of the coatings were also studied. Critical tensile stress that was required for

tearing off the coating was used to develop a theoretical model that predicted the critical value of load when the failure occurred.

Kozuka et al. [29] studied the changes in residual stress on alkoxide-derived silica and titania films coated on the glass substrates. They found that residual tensile stress increased with the increase in the curing temperature of the coating. They also found that the cracking tendency of the coating decreased as the thickness increased and the heating rate decreased. Interestingly, they also found that adding an organic polymer to the coating composition helped create a crack free coating.

Kim et al. [30] prepared the coating compositions by reacting vinyl terminated polydimethylsiloxane with tetrakis(dimethylsiloxy)silane in the presence of a platinum-divinyltetramethylsiloxane complex. They used a statistical experimental design to study the effect of different chemical constituents on resultant shear stress in the coatings. They found that the modulus of the coating varied with the thickness of the coating and that the shear rate depended on the modulus of the coating.

Chen et al. [31] studied AlOOH boehmite nanorods incorporated GPTS sol-gel coating. The nanorod concentration up to 40 wt% was utilized in the coating composition and was applied over a glass substrate. They recorded lower modulus and hardness values in the nanocoatings than in a commercially available coating composition containing boehmite nanoparticles. E and H values for nanorod filled coating were 8.86 GPa and 0.83 GPa, while those of nanoparticles filled coating were 9.88 GPa and 0.98 GPa. However, the coating composition containing nanorods with an aspect ratio of approximately 20 displayed significant improvement in the crack toughness, which was achieved by incorporating nanorods with a high aspect ratio. Their orientation in the

composite coating also contributed to the anisotropic toughness. The enhanced toughness was also attributed to the formation of chemical bonds between boehmite nanorods and the coating.

Hu et al. [32] studied hybrid coatings synthesized by the hydrolytic condensation of (3-methacryloxypropyl) trimethoxysilane or vinyltrimethoxysilane, with 5–30 wt% TEOS, in the presence of formic acid. The coating of thickness between 600 and 800 nm was applied on glass substrate by the dip coating technique. The authors used IIT to find the H and E values of the coatings. They found that coating compositions based on (3-methacryloxypropyl) trimethoxysilane and 20–30 wt% TEOS exhibited a 0.5 GPa hardness value and a 0.07 GPa brittle index.

Sakai et al. [33] used a microindentation load relaxation technique to study the linear visco-elastic stress relaxation phenomenon in sol-gel-derived phenylsilsesquioxane film coated on a soda-lime glass plate. They applied thick coatings of approximately 20 μm to eliminate the effect of the substrate on the measured relaxation properties. Moreover, a stepwise penetration was used on the coating with the depth of about 1.4 μm , followed by the load relaxation measurement as a function of time. The effects of coating processing parameters on the rheological transitions of the coatings were studied. The authors found that the evolution of silicone clusters and chain networks during the sol-gel processing stage significantly affects the rheological transitions in the coating.

Innocenzi et al. [34] prepared hybrid organic-inorganic materials from acid catalyzed sols of TEOS, 3-glycidoxypropyltrimethoxysilane, as well as titanium or zirconium alkoxides and measured the mechanical properties using Knoop microindentation and a 3 point bending test method. The modulus values calculated for

the samples heated to 125 °C for 120 h was found between 3 and 5 and 1 and 2 GPa for the samples synthesized with titanium butoxide or zirconium butoxide, respectively. However, modulus values increased with an increase in heat treatment time. The fracture toughness value was in the range of 0.4–0.5 MPa.m^{1/2} for samples treated for 168 h at 125 °C.

Amerio et al. [35] formulated hybrid coating by a dual curing process that combined sol-gel reaction with UV light induced polymerization. They reacted bisphenol-A ethoxylate dimethylacrylate as an organic binder, methacryloxypropyl-trimethoxysilane as coupling agent and TEOS as crosslinker. The preformed silica nanoparticles were used in the formulation in place of TEOS for comparison. The coating curing procedure that employed UV light and sol-gel curing demonstrated high scratch resistance, while the composition containing pre-formed nano silica showed poor scratch resistance, severe cracking and large plastic deformations.

Douce et al. [36] performed nanoindentation experiments on silicone coatings containing various surface modified silica nanoparticles of different sizes ranging from 15 nm to 60 nm. The authors found that Young's modulus of the coatings increased with the increase in silica nano-fillers. However, the scratch resistance of the coating decreased with the addition of nano-fillers, probably due to a weak interaction between inorganic fillers and the coating network.

Chapter 3

MATERIALS & MANUFACTURING METHODOLOGY

3.1 Introduction

The mechanical properties of a material are investigated based on the length and properties of the molecular segments. Fig. 3.1 shows a schematic of polymer and monomer entities utilized in this research. The first polymer coating formulation (i.e., PL) was prepared with cured epoxy resin using a commercial amide. In the second coating formulation (i.e., HY), a silicone composition was coupled with an epoxy polymer. The third coating formulation (i.e., CR) was a silicone epoxy group. The fourth coating formulation (i.e., QC) was made of pure silicone without an epoxy polymer or linkage. The coating formulations were developed with increasing silicone content or decreasing epoxy content. However, the same concentrations of nanoparticles were added to each coating composition to analyze the effect on the nano-mechanical properties of the cured coatings.

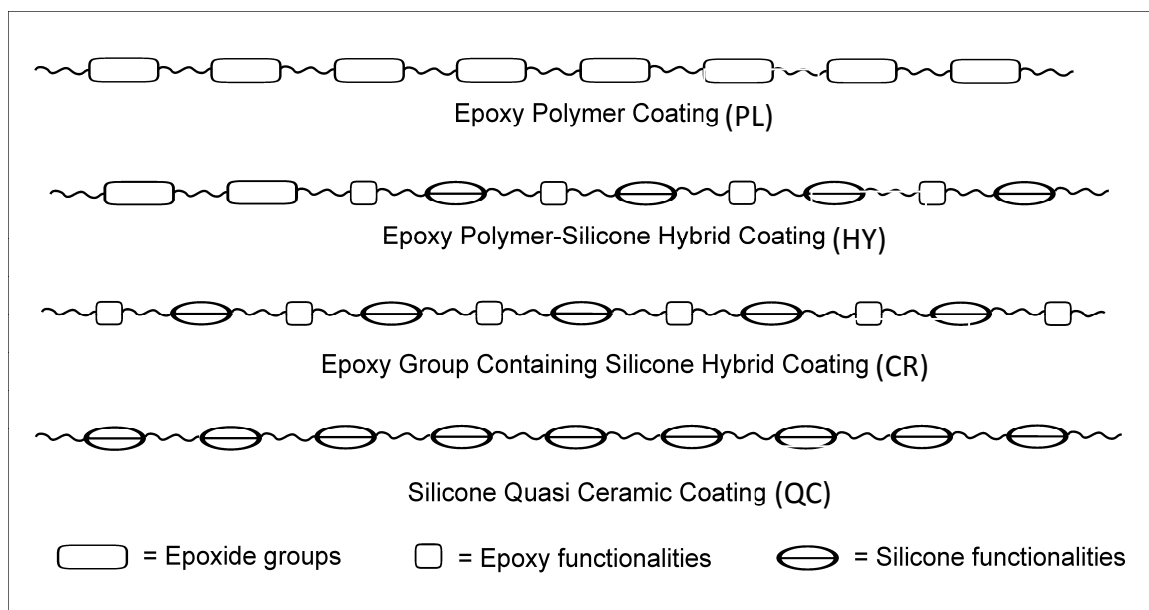


Fig. 3.1. Schematic of coating compositions formulated for in this study.

3.1.1 Epoxy and Silicone Based Coating Technologies

The adhesive strength of the coating depends on the amount of functionalities present in the material. High functional material tends to form a densely crosslinked network that often cracks. The epoxy polymer coating consists of high functionalities that allow the material to form strong adhesive bonds. However, hydrocarbon based epoxy coatings are porous in nature and allow the in-diffusion of electrolytes to the metal coating interface. The in-diffused electrolyte hydrolyzes the bonds of the adhesive and leads to the delamination of the coating.

Silicones, on the other hand, possess the unique characteristic of repelling water and acting as a coupling agent for other materials. They also tend to form thin coatings with their substrates via a covalent bond. Unfortunately, silicone coatings also crack due to their high crosslink density in the hardened material. Adding hydrocarbon to the coating formulation solves the cracking problem. In addition, a compound containing a methyl group can be introduced in the formulation to impart increased resistance to water.

3.1.2 Nanoparticles in Coating Technology

Silicone coatings used for corrosion protection are thin and can be easily scratched. Such a defect serves as a point of corrosion initiation through the coating. The hardness and scratch resistance of silicone coatings, however, can be improved by adding abrasion resistant inorganic fillers. The size and shape of the fillers depends on the thickness of the coating and field of application. The nanoparticles are generally used in the formulation of new generation coatings because these impart high abrasion resistance and hardness.

3.2 Materials Used

This section describes the chemicals and experimental methods used in the research and development of the coatings and nanocoatings.

3.2.1 Monomers and Polymers

The following chemicals were procured for the synthesis of the polymer, hybrid, ceramer and quasi-ceramic coatings: methyltriacetoxysilane (purity 95%); methyltrimethoxysilane (purity 98%); tetramethoxysilane (purity 97%); γ -glycidoxypropyltrimethoxysilane (purity 98%); tetraethoxysilane (purity 95%); 3-aminopropyltrimethoxysilane (purity 97%), purchased from Gelest; titanium ethoxide (purity 99%); dibutyltindilaurate catalyst (purity 95%), purchased from Alfa-Aesar; 1, 6-hexanediamine; isopropanol (ACS grade); diethylether (ACS grade), purchased from Sigma Aldrich, USA; 90% denaturated ethanol containing 5% methanol and 5% isopropanol, purchased from Alfa Aesar, USA; and sodium bicarbonate, purchased from Merck. All of the chemicals were analytical grade as quoted by the manufacturer. Ultrapure water of 18 M Ω •cm resistivity was used in this study.

The polymer utilized in coating formulation was DER 331[®] epoxy from Dow chemicals that was hardened with Ancamide[®] 2353 purchased from Air products.

3.2.2 Nanoparticles

The nanoparticles or ingredients used for the in-situ generation of nanoparticles were purchased in their pure form and used without further purification. It was important to keep the synthesis steps to a minimum to make the procedure cost effective and easy to adopt. The following nanoparticles were used in this study:

- (a). Titanium dioxide (TiO_2) anatase, purchased from Alfa Aesar. The material was a solid white powder as shown in Fig. 3.2. With SEM and transmission electron microscopy (TEM), the particles appeared needle in shape with an average thickness of 10 nm.
- (b). Titanium dioxide (in-situ generated) using titanium ethoxide ($\text{Ti}(\text{OH})_4$), was purchased from Alfa Aesar. The material was yellow liquid as shown in Fig. 3.3. With SEM and TEM, the generated nanoparticles appeared to be nano-spherical in shape with an average diameter of 80 nm.
- (c). Silicon dioxide (SiO_2) nanoparticles coated with a proprietary polymer and purchased from Energy Strategy Associates under the name Nan-O-Sil[®]. The material was solid white colored powder as shown in Fig. 3.4. With SEM and TEM, the particles appeared like nano-spheres with an average diameter of 90 nm.
- (d). Montmorillonite nanoclay (MMT), purchased from Across. The material was solid pale yellow colored powder as shown in Fig. 3.5. With SEM and TEM, the particles appeared like nano-sheets with an average thickness of 20 nm.
- (e). Silicon carbide (SiC) whiskers were purchased from Advanced Composite Materials. The material was dark grey powder as shown in Fig. 3.6. With SEM and TEM, the particles appeared like nano-sheets with an average thickness of 50 nm.

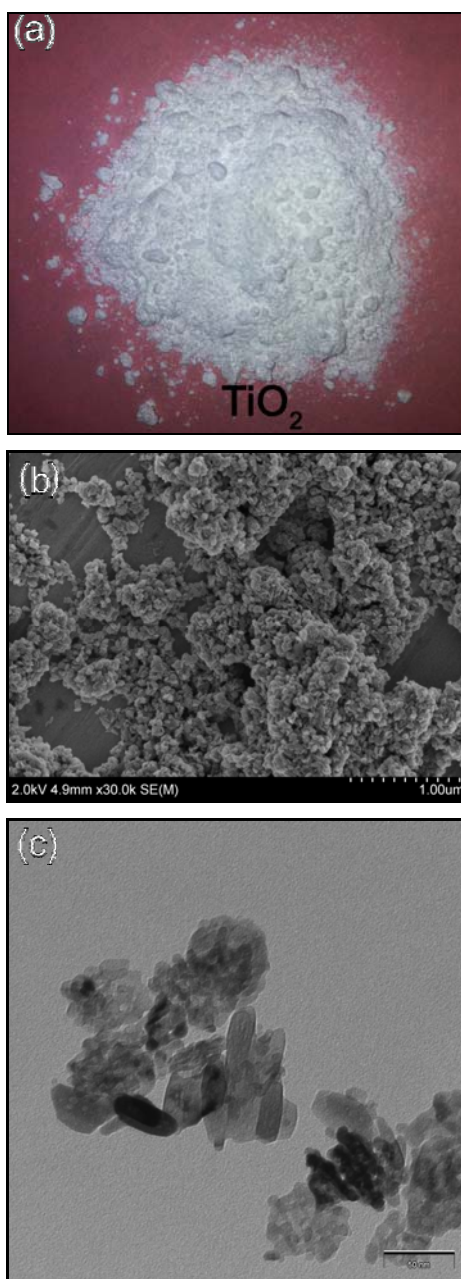


Fig. 3.2. Images of TiO₂ nanoparticles. (a) Optical image (b) SEM image (c) TEM image showing needle-like crystals.

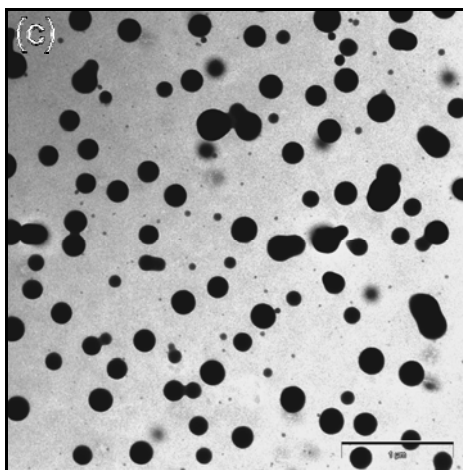
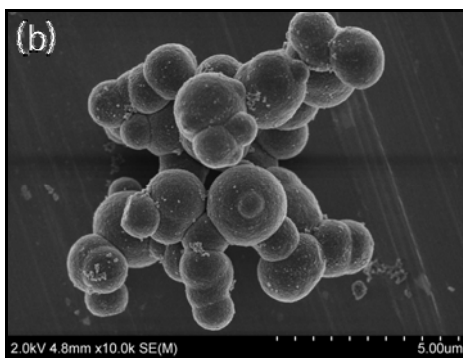


Fig. 3.3. Images of TiO₂ nanoparticles generated from Ti(OH)₄. (a) Optical image. (b) SEM image. (c) TEM image showing nano-spherical appearance.

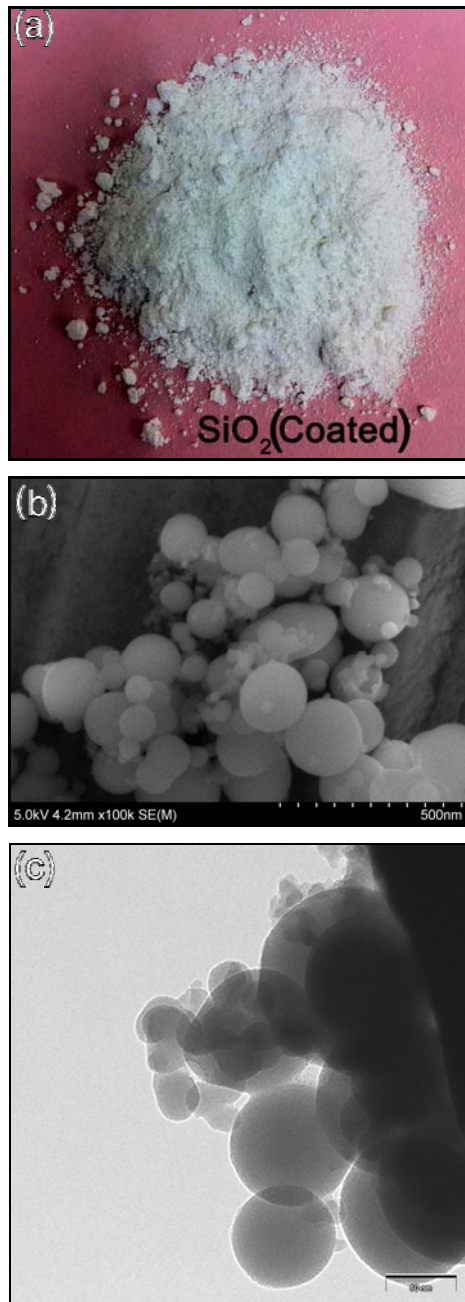


Fig. 3.4. Images of polymer coated SiO₂ nanoparticles. (a) Optical image. (b) SEM image. (c) TEM image showing nano-spherical appearance.

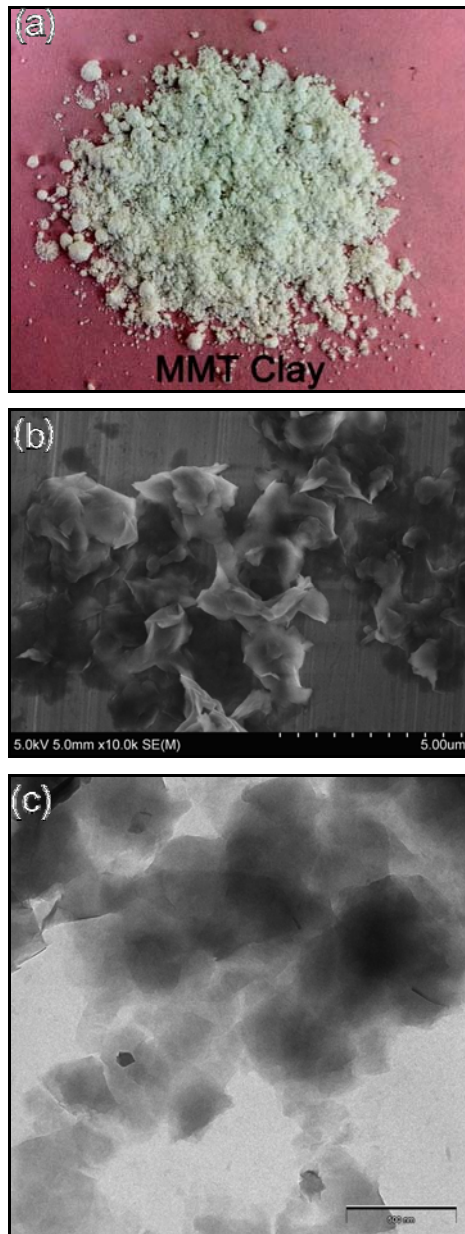


Fig. 3.5. Images of montmorillonite nanoparticles. (a) Optical image. (b) SEM image. (c) TEM image showing thin film morphology.

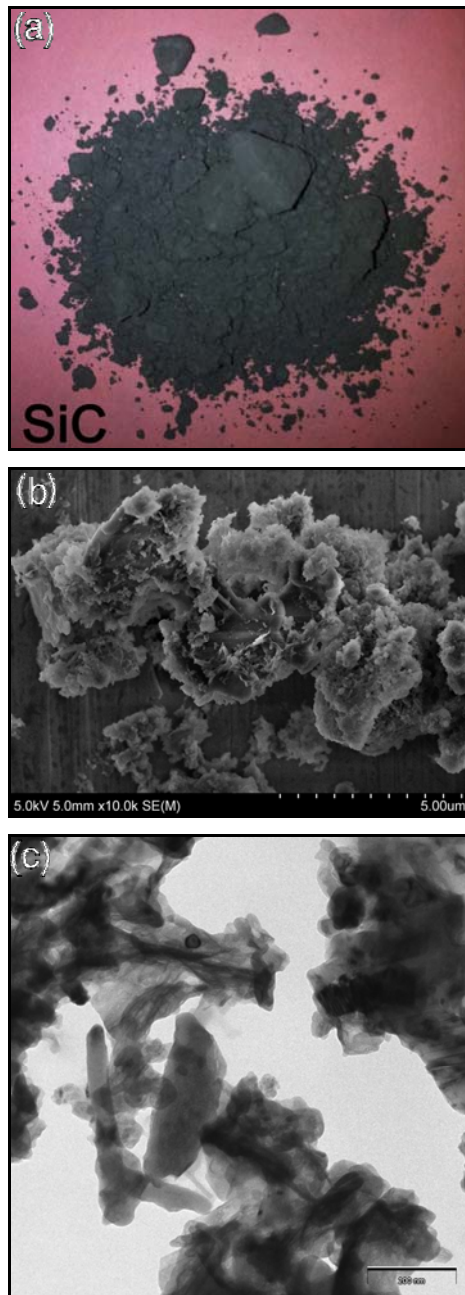


Fig. 3.6. Images of SiC nanowhiskers. (a) Optical image. (b) SEM image. (c) TEM image showing thin nano-whisker morphology.

3.3 Characterization Method Used

In this section different analytical techniques used to characterize materials in the formulation of coating are described.

3.3.1 FTIR Spectroscopic Investigations

The FTIR spectroscopy on solid coatings applied over aluminium metal was conducted using a Thermo Electron Nicolet Nexus 760 instrument integrated with a Continuum microscope. The spectra were recorded in reflectance mode and analysed using Thermo Electron's Omnic and Series software. A blank background spectrum was collected prior to collecting a spectrum of the sample. A minimum of 60 scans of the specimen were employed for each spectrum.

3.3.2 Microscopic Investigations

The coating morphology and scratched surface were analysed with a Hitachi S-3400N, Scanning Electron Microscopy (SEM). The LEO 912 Energy-Filtering Transmission Electron Microscope was used to study the appearance of nanoparticles. The samples were coated to prevent charging during the analyses. The atomic force microscopic (AFM) technique was used to study the surface morphology of the coatings hardened over a polished aluminum surface. The Veeco Multimode –II and Innova SPM equipments were used in contact mode to capture the surface topography. The 3D images were created using TrueMap software from TrueGage Surface Metrology.

3.3.3 Nano-mechanical Analysis

The nano-mechanical analysis was conducted on MTS Nanoindenter XP (Fig. 3.7) with a Berkovich diamond tip. The test samples were mounted with a thermoplastic

polymer resin onto an aluminium stub. Their hardness (H) and modulus (E) was measured using the continuous stiffness measurement option. Fused silica was used as a standard calibration sample. During the scratch tests, the platform holding the specimen was moved to create the scratch, while the indentation head controlled the load applied to the indenter. All the tests were performed in ambient conditions with temperature approximately 25 °C.

The nanoindentation, nanoscratch and dynamic mechanical properties were acquired with the help of TestWork 4 software from MTS instruments. The TestWork software exported the raw data files to the MS Excel software. The Excel data sheets were then imported on Analyst software from the MTS instrument for the data reduction. The Analyst-Excel files were finally used to plot the curves using Origin 7.5 software.



Fig. 3.7. Nanoindenter XP from MTS instruments used to record the nano-mechanical properties of the coatings and nanocoatings.

(a). Nanoindentation Experimental Procedure³

The coating specimens of 1x1 cm² were bonded to circular aluminum stubs using a thermoplastic resin. The stubs were then mounted on the Nanoindenter XP

³ The experimental testing steps as defined in MTS/Agilent instrument manuals.

nanopositioning tray and tested using an “XP basic hardness, modulus and tip calibration” test method. A Berkovich tip was used to perform 6 to 12 tests on each sample in different regions to achieve a good representation of nano-mechanical properties of the coating. The passion’s ratio used for the epoxy rich coating (i.e., PL) was 0.350, while for the silicone rich coatings (i.e., HY, CR & QC) it was 0.175 [37, 38].

In this test method, the CSM oscillation frequency and amplitude are set to Harmonic Frequency Target and Harmonic Displacement Target. The phase shift between the excitation oscillation and the displacement oscillation is zeroed. The indenter tip begins approaching the surface from a distance above the surface of the equivalent of the Surface Approach Distance. The approach velocity is determined by the Surface Approach Velocity. When the indenter determines that it has contacted the test surface, according to the criteria determined by the Surface Approach Sensitivity, the indenter penetrates the surface at a rate determined by the Strain Rate Target. When the surface penetration reaches the Depth Limit, the load on the indenter is held constant for ten seconds. The indenter is then partially withdrawn from the sample at a rate equal to the maximum loading rate. When the load on the sample reaches 10% of the maximum load on the sample, the load on the sample is held constant for 100 seconds. The indenter is then completely withdrawn from the sample and the sample is moved into position for the next test.

(b). Nanoscratch Experimental Procedure

The nanoscratch tests were conducted using an MTS Nanoindenter[®] XP with a Berkovich diamond tip. Test samples of 1x1 cm² were mounted with a thermoplastic resin on an aluminum stub. During the scratch tests, the platform holding the specimen

was moved to create the scratch, and the indentation head controlled the load applied to the indenter. Experimental parameters were chosen as follows: scratch speed, 10 $\mu\text{m/s}$; scratch length, 1000–3000 μm ; maximum lateral force, 250 mN (all orientations); maximum lateral force resolution, 2 μN ; maximum normal force, 500 mN; noise level, 300 μN (without contact); lateral force scratch orientation and Berkovich face forward. At least five tests were performed at each test site using continuous stiffness option.

During the test, the indenter tip begins approaching the surface from a distance above the surface the equivalent of the Surface Approach Distance. The approach velocity is determined by the Surface Approach Velocity. When the indenter determines that it has contacted the test surface, according to the criteria Surface Approach Sensitivity, the test begins. A test consists of several line scans or "profiles" along the scratch vector before and after the main "scratch." The velocity during all table movements is set by Scratch Velocity for the scratch segment and Profile Velocity during the profiling. The length and direction of the scratch are set by the Scratch Length and Scratch Angle, respectively. After the surface has been scratched, another short scan is performed that is $0.2 \times \text{Scratch Length}$. If the input Perform Cross Profile is set to 1, then a profile across the width of the scratch is also performed. The cross profile is performed at the location on the scratch where Load Applied on Sample reached the Cross Profile Location.

(c). Visco-Elastic Experimental Procedure

Visco-elastic tests were conducted using an MTS Nanoindenter[®] XP with a Berkovich diamond tip. Test samples of size $1 \times 1 \text{ cm}^2$ were mounted with a thermoplastic resin on an aluminum stub. At least six tests were performed using the single frequency

test method at each test site for each frequency and the average values of storage and loss modulus were recorded.

In a typical nanoindentation based, visco-elastic experiment, the system senses the contact of the indenter tip to the sample surface and pushes the indenter farther into the test material to a depth determined by Pre-test Compression. The dimensions specified by the Pre-test Compression are larger than the sum of displacement required for full contact and the oscillation amplitude of the material. The instrument then provides minimum (1 Hz) and maximum (45 Hz) vibration frequencies to the indenter. The number of frequencies varies as per the requirement. Poisson's ratio is provided for the calculation of complex modulus; however, the calculations are less sensitive to this value.

3.4 Development of Coatings and Nanocoatings

In this section, the steps involved in the development of various coatings and nanocoating compositions are described.

3.4.1 Development of Epoxy Based Polymeric (PL) Coating and Nanocoatings

The PL coating was developed as per the procedure reported elsewhere [39]. The calculated quantity of epoxy polymer DER 331 (100 gm) was mixed with Ancamide[®] hardener (60 gm) in 100 ml of methyl ethyl ketone. The entire content was mixed for 30 min in an ultrasonic bath before using as a PL coating precursor.

In order to prepare the nanocoatings, the calculated quantities (i.e., 0.1, 0.3, 0.5 wt% of solid content) of five nanoparticles described in section 3.2.2 were sonicated in 1 ml isopropanol for at least 24 h or maximum 7 days. A 10 ml of PL coating precursor solution was added to the suspension of each nanoparticle and sonicated for 5 h. These

nanoparticle coating suspensions were applied on polished aluminum specimens (Fig. 3.8).

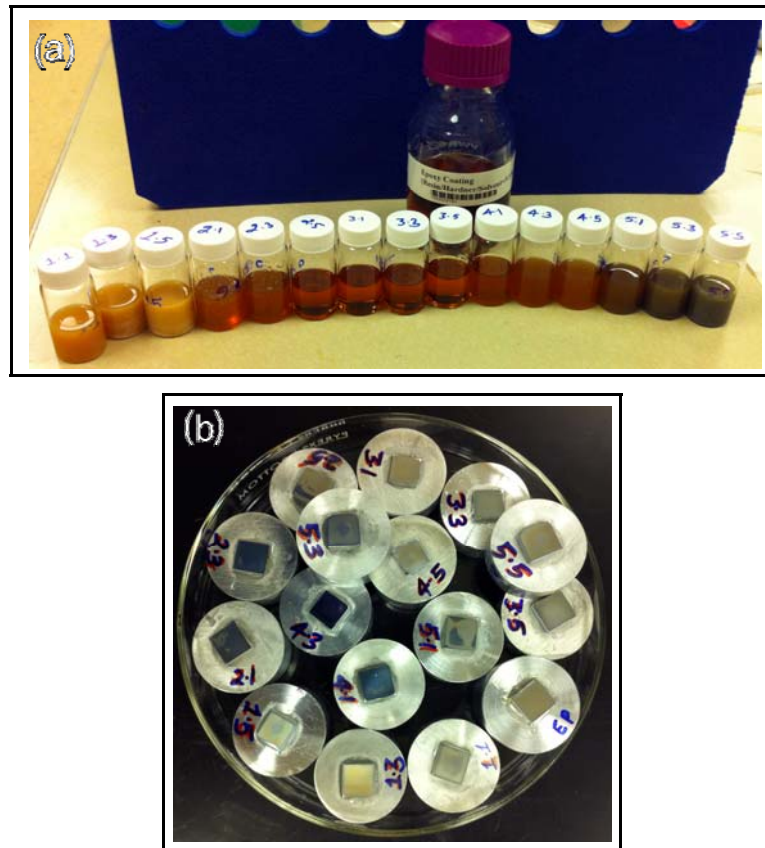


Fig. 3.8. Epoxy based polymer (PL) coating and nanocoatings. The PL nanocoatings were designated as #1-5 (showed in Table 3.1).

3.4.2 Development of Polymer-Ceramer Hybrid (HY) Coating and Nanocoatings

The HY coating was developed following the procedure given as follows. To prepare silicone composition a calculated quantity of γ -glycidoxypropyltrimethoxysilane (44.20 ml) was reacted with tetraethoxysilane (11.0 ml) in isopropanol (60 ml). In a second reactor, a calculated quantity of 3-aminopropyltrimethoxysilane (8.6 ml) were treated with 1, 6-hexanediamine (1.2 gm) in isopropanol (40 ml). The two components obtained above were reacted together in a third reactor and charged with dibutyltindilaurate catalyst and traces of water (1.0 ml). In a fourth reactor epoxy DER 331 (3.5 gm) was mixed with Ancamide[®] (3.0 gm) in 20 ml isopropanol. The epoxy-Ancamide mixture was then added to the silicone composition obtained in the third reactor and sonicated for 30 min. The epoxy-Ancamide[®] mixture was 10 wt% of the solid content in silicone composition obtained in the third reactor. The entire content of the fourth reactor was left in an ambient condition for 30 min before using it as a HY coating precursor.

In order to prepare nanocoatings, the calculated quantities (i.e., 0.1, 0.3, 0.5 wt% of solid content) of five nanoparticles described in section 3.2.2 were sonicated in 1 ml isopropanol for at least 24 h or maximum 7 days. A 10 ml of HY coating precursor solution was added to the suspension of each nanoparticle and sonicated for 5 h. These nanoparticle coating suspensions were applied on the polished aluminum specimens (Fig. 3.9).

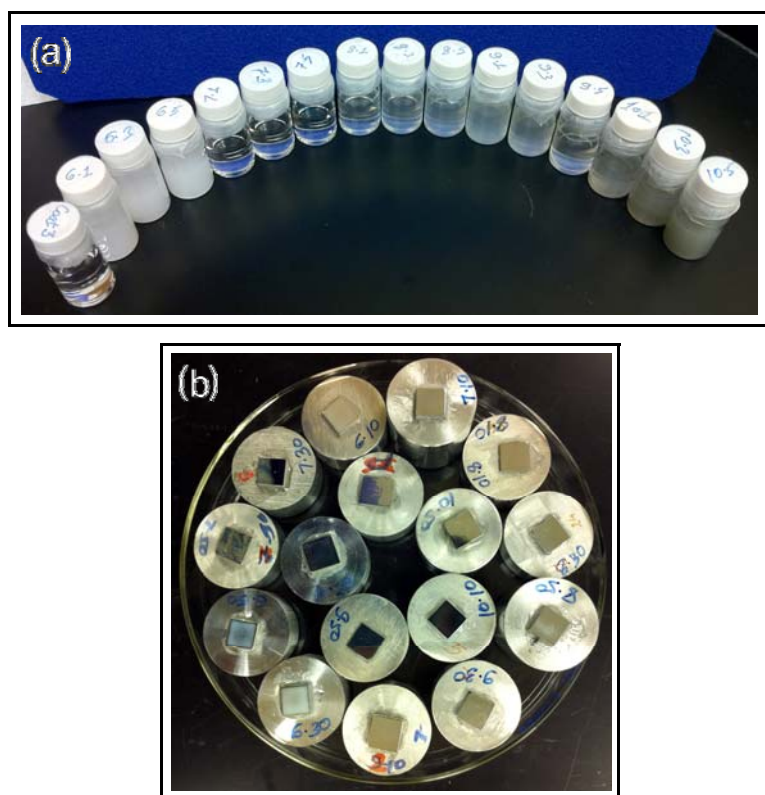


Fig. 3.9. The HY coating and nanocoatings. The HY nanocoatings were designated as #6-10 (showed in Table 3.1).

3.4.3 Development of Ceramer (CR) Coating and Nanocoatings

The CR coating was developed following the procedure described elsewhere [40]. To prepare silicone composition a calculated quantity of γ -glycidoxypentyltrimethoxysilane (44.20 ml) was reacted with tetraethoxysilane (11.0 ml) in isopropanol (60 ml). In second reactor, a calculated quantity of 3-aminopentyltrimethoxysilane (8.6 ml) were treated with 1, 6-hexanediamine (1.2 gm) in isopropanol (40 ml). The two components obtained above were reacted together in the third reactor and charged with dibutyltin dilaurate catalyst and traces of water (1.0 ml) that resulted in a ceramer coating precursor. The entire solution was left for 30 min in ambient conditions before using it as a CR coating precursor.

In order to prepare nanocoatings, the calculated quantities (i.e., 0.1, 0.3, 0.5 wt% of solid content) of five nanoparticles described in section 3.2.2 were sonicated in 1 ml isopropanol for at least 24 h or maximum 7 days. A 10 ml of CR coating precursor solution was added to the suspension of each nanoparticle and sonicated for 5 h. These nanoparticle coating suspensions were applied on polished aluminum specimens (Fig. 3.10).

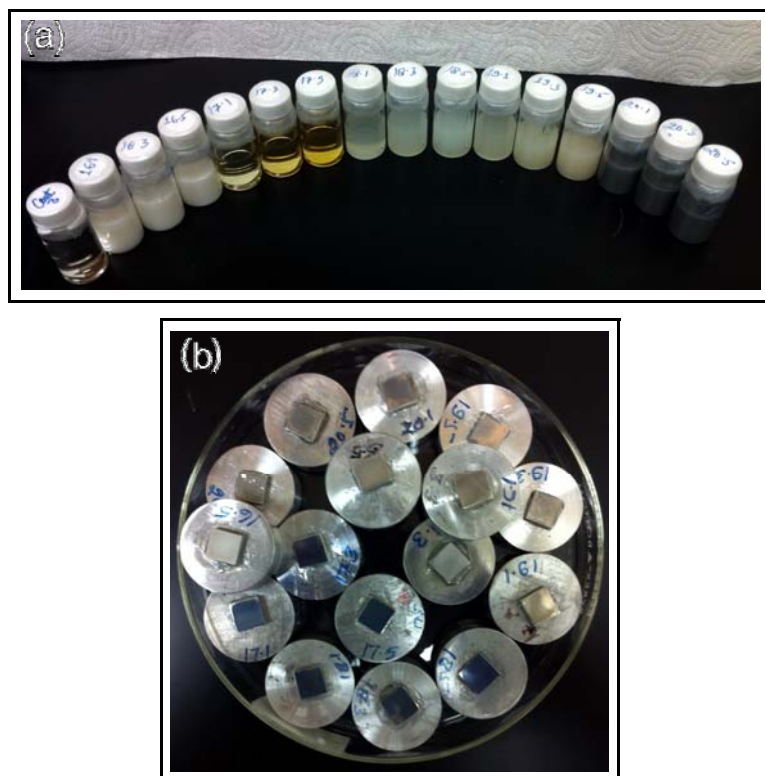


Fig. 3.10. The CR coating and nanocoatings. The CR nanocoatings were designated as #16-20 (showed in Table 3.1).

3.4.4 Development of Quasi-Ceramic (QC) Coating and Nanocoatings

The QC coating was prepared by following a method described elsewhere [41]. A proprietary mixture of silanes was prepared by reacting calculated quantities of methyltriacetoxysilane, methyltrimethoxysilane and tetramethoxysilane to a reactor vessel followed by sonication and an addition of isopropanol. In a second reactor, a calculated quantity of sodium bicarbonate was dissolved in a known volume of water. The water was constantly stirred while sodium salt was added and then stirred again every 2 h. The content of second reactor was added to the content of reactor one and then sonicated for 30 min. In the third reactor, a calculated quantity of titaniummethoxide was added to a known amount of isopropanol and sonicated for 15 min. The content from reactor three was added to the content obtained after mixing the solutions from reactor one and reactor two. A known quantity of isopropanol, diethylether and dibutyltindilaurate were mixed separately in a reaction vessel and added to the solution obtained in the above steps. The entire solution was left for 30 min in ambient conditions before using it as QC coating precursor.

In order to prepare nanocoatings, the calculated quantities (i.e., 0.1, 0.3, 0.5 wt% of solid content) of five nanoparticles described in section 3.2.2 were sonicated in 1 ml isopropanol for at least 24 h or maximum 7 days. A 10 ml of QC coating precursor solution was added to the suspension of each nanoparticle and sonicated for 5 h. These nanoparticles coating suspensions were applied on polished aluminum specimens (Fig. 3.11).

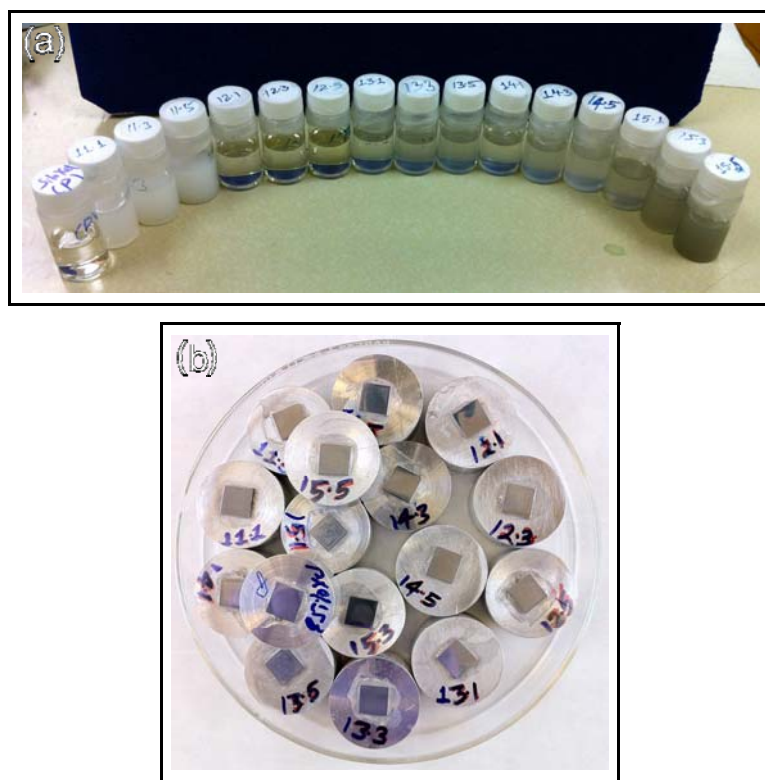


Fig. 3.11. The QC and nanocoatings. The QC nanocoatings were designated as #11-15 (showed in Table 3.1).

Table 3.1: Sample designations used for coatings and nanocoatings.

NP →	TiO₂			Ti(OH)₄			SiO₂			MMT			SiC			Neat
Coat ↓	0.1 (%)	0.3 (%)	0.5 (%)	0.1 (%)	0.3 (%)	0.5 (%)	0.1 (%)	0.3 (%)	0.5 (%)	0.1 (%)	0.3 (%)	0.5 (%)	0.1 (%)	0.3 (%)	0.5 (%)	
PL	1.1	1.3	1.5	2.1	2.3	2.5	3.1	3.3	3.5	4.1	4.3	4.5	5.1	5.3	5.5	PL
HY	6.1	6.3	6.5	7.1	7.3	7.5	8.1	8.3	8.5	9.1	9.3	9.5	10.1	10.3	10.5	HY
CR	16.1	16.3	16.5	17.1	17.3	17.5	18.1	18.3	18.5	19.1	19.3	19.5	20.1	20.3	20.5	CR
QC	11.1	11.3	11.5	12.1	12.3	12.5	13.1	13.3	13.5	14.1	14.3	14.5	15.1	15.3	15.5	QC

3.4.5 Specimen Preparation and Coating Application

The Al6061-T6 specimens were cut into 1x1 cm² and adhere to circular aluminum stubs using thermoplastic polymer. The specimens were then polished using 0.05 µm aluminum oxide agglomerate solution and dried until required during coating process. The sonicated solutions of coatings were applied on the polished aluminum specimens and dried in ambient conditions (~25 °C) for 48 hr followed by heating at 37 °C for 48 hr. The coated specimens were left in ambient condition for 30 days before testing their nano-mechanical properties.

Chapter 4

CHARACTERIZATION

4.0 Introduction

In this section the characterization of the coating and nanocoating are described based on their molecular chain length and nanoparticles in the final coating structure.

4.1 Characterization of Nanocoatings Using FTIR Spectroscopy

The FTIR spectroscopy is a useful tool in determining the presence of organic and inorganic constituents in a material. The mode and mechanism of reaction can be estimated using this technique. The FTIR instrument can be operated in several modes such as transmission, reflection, absorbance or total attenuated reflection mode.

4.1.1 Effect of Molecular Chain Lengths

Fig. 4.1a shows the FTIR spectrum of a pristine PL coating. The spectrum is typical for epoxy polymer materials. The peaks appearing between $600\text{--}800\text{ cm}^{-1}$ are due to bands from amide in Ancamide[®] hardener [42]. Similarly, amide bands appear between $1300\text{--}1520\text{ cm}^{-1}$, $1600\text{--}1900\text{ cm}^{-1}$ and at approximately 3100 cm^{-1} . The hydrocarbon peaks from epoxy resin can be seen between $900\text{--}1000\text{ cm}^{-1}$ and $2875\text{--}3000\text{ cm}^{-1}$, while an aromatic C=C band occurs at 1600 cm^{-1} [43]. A broad hump between $3100\text{--}3700\text{ cm}^{-1}$ is due to the contribution from amide and hydrogen-bonded hydroxyl stretching.

Fig. 4.1b shows FTIR spectrum of a pristine HY coating. This coating composition consists of 10 wt% (of solid content) epoxy resin and diamine as the

hardener. The remaining 90 wt% solid content is silicone. The peaks appearing between 600–820 cm^{-1} are due to hydrocarbons in the coating structure. A sharp peak at 945 cm^{-1} is due to a Si-OH group, while a shoulder at 915 cm^{-1} and sharp peak at 995 cm^{-1} are due to epoxy linkages. Sharp peaks between 1000–1200 cm^{-1} are due to the contributions from Si-O-Si linkages and hydrocarbons in the epoxy resin [44]. The amine peak can be seen at 1592 cm^{-1} and C=C appears at 1643 cm^{-1} . The symmetric and asymmetric hydrocarbon ($-\text{CH}_3$) can be seen between 2800–3000 cm^{-1} . The broad hump between 3000–3600 cm^{-1} is due to the contributions from amine and hydrogen-bonded hydroxyl stretching.

Fig. 4.1c shows the FTIR spectrum of a pristine CR coating. The peak appearing between 600–725 cm^{-1} are due to stretching of hydrocarbon ($-\text{CH}$) portion in the silicone. A shoulder appearing at approximately 920 cm^{-1} is due to epoxy linkage in the coating, while the sharp peak at 946 cm^{-1} is due to a Si-OH group from unreacted silanols. The two sharp peaks appearing between 1000–1250 cm^{-1} are due to Si-O-Si backbone stretching. Another peak appearing at 1442 cm^{-1} is due to hydrocarbon, while a peak appearing at 1593 cm^{-1} is due to amine linkages [45]. The symmetric and asymmetric –CH stretching can be seen at 2873 and 2940 cm^{-1} . A hump concentrating at 3278 cm^{-1} is due to hydrogen-bonded reactive groups.

Fig. 4.1 d shows the FTIR spectrum of pristine QC coating. The two sharp peaks appearing at 725 cm^{-1} and 921 cm^{-1} are due to a Si-OH group from unreacted silanols. Another set of peaks between 1010–1070 cm^{-1} are due to SiOSi vibrations from the backbone. The four peaks appearing between 1170–1600 cm^{-1} are due to the hydrocarbon portion in the coating composition [46]. A sharp peak at 2969 cm^{-1} is due to symmetric

-CH_3 stretching, while a weak hump between $3000\text{--}3500\text{ cm}^{-1}$ is due to hydrogen-bonded hydroxyl groups.

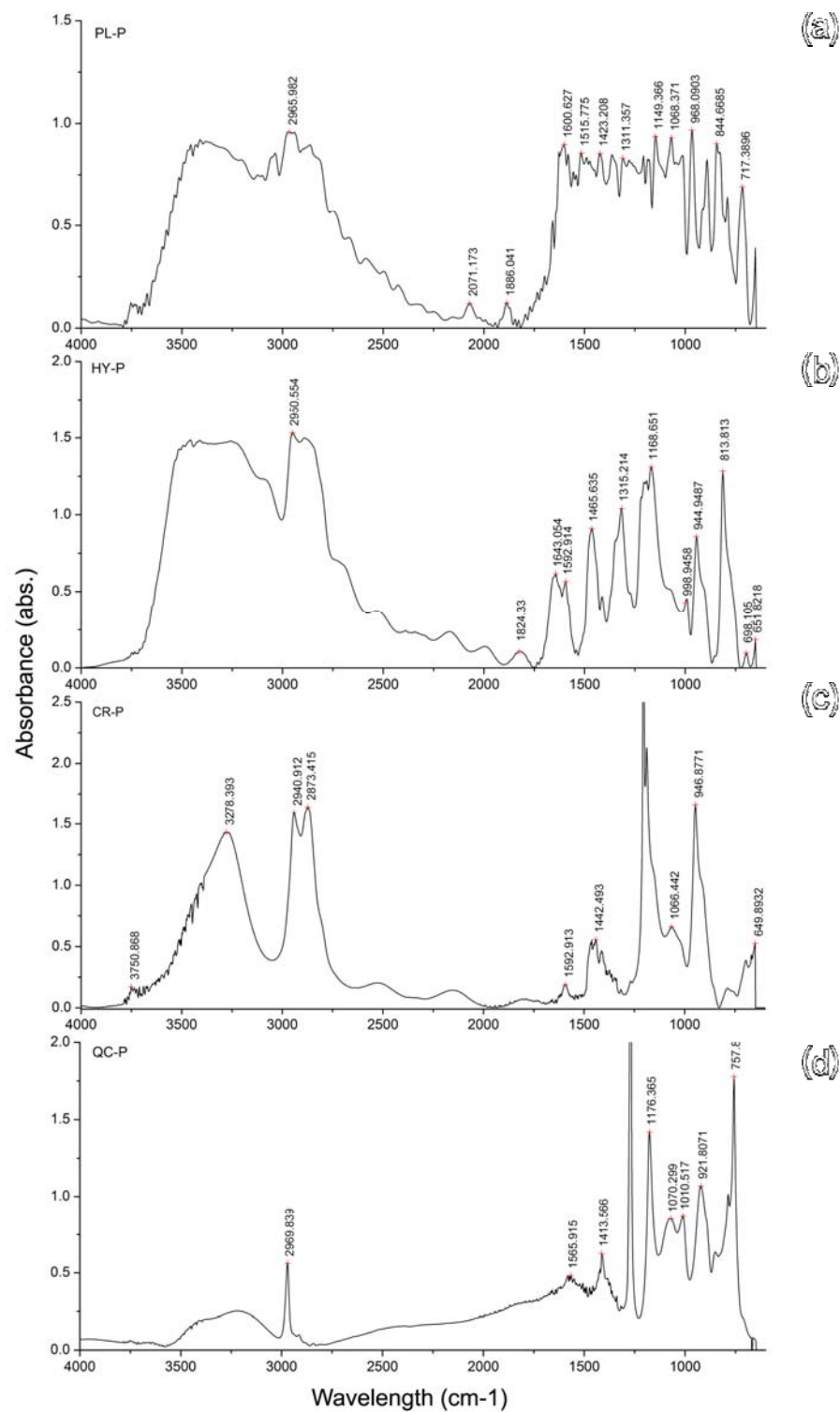


Fig. 4.1. FTIR spectral analysis of different coatings.

4.1.2 Effect of Nanoparticle Incorporation

Fig. 4.2 shows a FTIR spectral analysis of PL coating and five different nanocoatings (containing 0.1 wt. % nanoparticle concentration). The spectral assignment of PL-1.1 was similar to the pristine coating except the positions of the peaks were probably shifted as a result of a change in the refractive index due to the presence of TiO_2 nanoparticles. There was an increase in the absorbance intensity at approximately 3200 cm^{-1} due to presence of hydrogen-bonded TiO_2 particles. In the case of PL-2.1, when $\text{Ti}(\text{OH})_4$ was used to generate TiO_2 type nanoparticles the band appearing at 921 cm^{-1} clearly indicate the presence of TiOSi bond, while a band appearing at 3278 cm^{-1} indicates hydrogen bonding involving TiOH and SiOH groups [47].

The composition of PL-3.1 containing nanosilica has a spectrum with less resolved peak intensities. The silica particle appears to diffuse the IR radiation, thereby reducing the intensity of the IR beam reaching back to the detector.

The spectrum of PL-4.1 containing MMT nanosilica is similar to that of the pristine coating. However, there is a shift in the peak position in PL-4.1 compared to the peaks in the spectra of the pristine composition. The shift is due to the interaction between epoxy amide functionality and silica based nanoclay. The presence of MMT can be seen from a weak peak at 697 cm^{-1} and a strong vibration at approximately 1040 cm^{-1} [48].

In the case of PL-5.1 nanocomposites, the peaks appearing between $1000\text{--}1200\text{ cm}^{-1}$ gain intensity and broaden due to the presence of SiC in the matrix network [49]. Another sharp peak appearing at approximately 3405 and 3274 cm^{-1} is due to the hydrogen-bonded silicon group.

Apart from distinct features appearing in the FTIR spectrum of nanocomposites, hydrocarbon, and hydroxyl group stretching are similar to the pristine epoxy-amide coating.

The Fig. 4.3 shows FTIR spectra of pristine HY coating and nanocoatings. This coating composition consists of 10 wt% epoxy resin made of primarily hydrocarbon. The FTIR spectrum is therefore saturated with hydrocarbon peaks that overshadow peaks appearing from other groups in a similar regime. The peak assignment for HY-P coating is discussed in section 4.1.1.

In the case of the nanocoating composition of HY-6.1, peak positions are similar to pristine HY-P coating except an additional peak appears at 972 cm^{-1} , possibly due to the interaction of TiO_2 nanoparticles with the silicone and epoxy network. The additional peak at approximately 3200 cm^{-1} is probably due to hydrogen-bonded TiO_2 nanoparticles.

In the case of HY-7.1 nanocoating containing $\text{Ti}(\text{OH})_4$, the sharp strong peak that appears at 918 cm^{-1} is due to a SiOTi linkage, while a weak peak appearing at 786 cm^{-1} is possibly due to TiOTi bonding [50].

In the case of HY-8.1 nanocoating containing functionalized nanosilica, the peak positions were similar to those of the pristine HY-P coating except the peak at approximately 1100 cm^{-1} seems super saturated due to an excess of silicon in the coating [51]. Similarly, a peak at 3085 cm^{-1} suggests the presence of functionalized SiO_2 in the nanocoating network [52].

In the case of HY-9.1 nanocoating containing MMT nanoclay, no new peaks could be identified to verify the presence of nanoparticles in the nanocoating network.

However, the shift in peak positions suggests the presence of nanoclay in the hybrid nanocoating structure.

In the case of HY-10.1 nanocoating containing SiC whiskers, the peak position were shifted compared to that of the pristine coating, suggesting the presence of nanoparticles in the coating. Moreover, an additional sharp peak at 867 cm^{-1} indicates the presence of SiC in the nanocoating.

Fig. 4.4 shows the FTIR spectra from CR coatings and nanocoatings. In the case of CR-16.1 nanocoating containing TiO_2 nanoparticles, the vibrations were similar to those in pristine CR-P coatings. Moreover, the peak shoulder appearing at 920 cm^{-1} corresponds to the presence of TiO_2 in the nanocoating.

In the case of CR-17.1 nanocoating containing $\text{Ti}(\text{OH})_4$ the display spectrum is similar to that in pristine coating with an additional shoulder peak at approximately 920 cm^{-1} , confirming the presence of SiOTi linkage in the nanocoating network [53].

In the case of CR-18.1 nanocoating containing nanosilica, the peak positions are similar to those of the pristine CR-P coating except an additional peak appearing at approximately 2800 cm^{-1} . This peak may be due to the polymer coating on silica nanoparticles. Another peak appearing at 3164 cm^{-1} is probably due to the hydrogen-bonded hydroxyl groups.

In the case of CR-19.1 nanocoating containing MMT nanoclay, no major peaks were found that could differentiate nanocoating from pristine coating. A peak at approximately 660 cm^{-1} is in the spectrum that could be attributed to the presence of MMT in the structure.

In the case of CR-20.1 nanocoating containing SiC nanowhiskers, weak peaks exist in the region close to 2800 cm^{-1} possibly due to carbon in SiC, while a peak at 3072 cm^{-1} is due to the hydrogen bonding in the material.

Fig. 4.5 shows FTIR spectra of QC coating and nanocoatings. Because the amount of hydrocarbon is less compared to that of other coating compositions, the incorporation of foreign ingredients could be easily identified. In the case of QC-11.1 nanocoating containing TiO_2 nanoparticles, most of the peak positions are similar to those of the pristine QC coating except two peaks appearing at 929 cm^{-1} and 1014 cm^{-1} , suggesting the presence of TiO_2 nanoparticles in the nanocoating network.

In the case of QC-12.1 nanocoating containing $\text{Ti}(\text{OH})_4$, the peak position at 921 cm^{-1} clearly suggests the presence of SiOTi bonding. Another peak at 1010 cm^{-1} could be due to a TiOTi network in the coating. A hump at approximately 3100 cm^{-1} is due to the hydrogen bonding associated with hydroxyl group in the coating structure.

In the case of QC-13.1 nanocoating containing functionalized SiO_2 nanoparticles, no new peaks could be identified due to similar bonding within materials. The $-\text{CH}$ stretching at 2971 cm^{-1} decreased in intensity compared to pristine QC-P coating, suggesting the increase in silicon content in the coating structure.

In the case of QC-14.1 nanocoating containing MMT nanoclay, two new peaks were identified at 881 cm^{-1} and 983 cm^{-1} that were not present in pristine coating composition, suggesting the presence of silicon-based nanoclay in the nanocoating network. Moreover, an additional hump appearing at approximately 3200 cm^{-1} suggests the presence of hydrogen-bonded clay nanoparticles.

In case of QC-15.1 nanocoating containing SiC nanowhiskers, an additional peak were identified at approximately 920 cm^{-1} and 1010 cm^{-1} indicating the presence of SiC in the nanocoating network. Additional hump was found at approximately 3200 cm^{-1} is probably due to the hydrogen-bonded SiC nanoparticles.

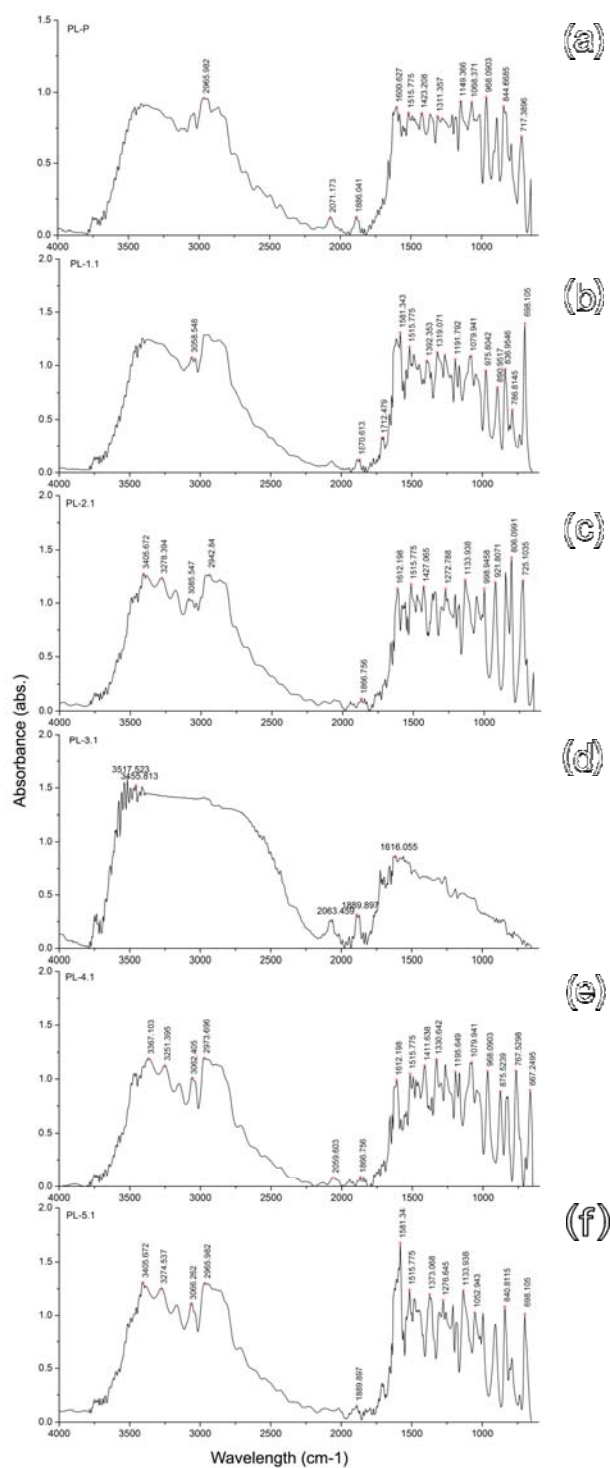


Fig. 4.2. FTIR spectral analysis of PL coating and nanocoatings. (a) Pristine polymeric coating. (b-f) Coatings containing nanoparticles.

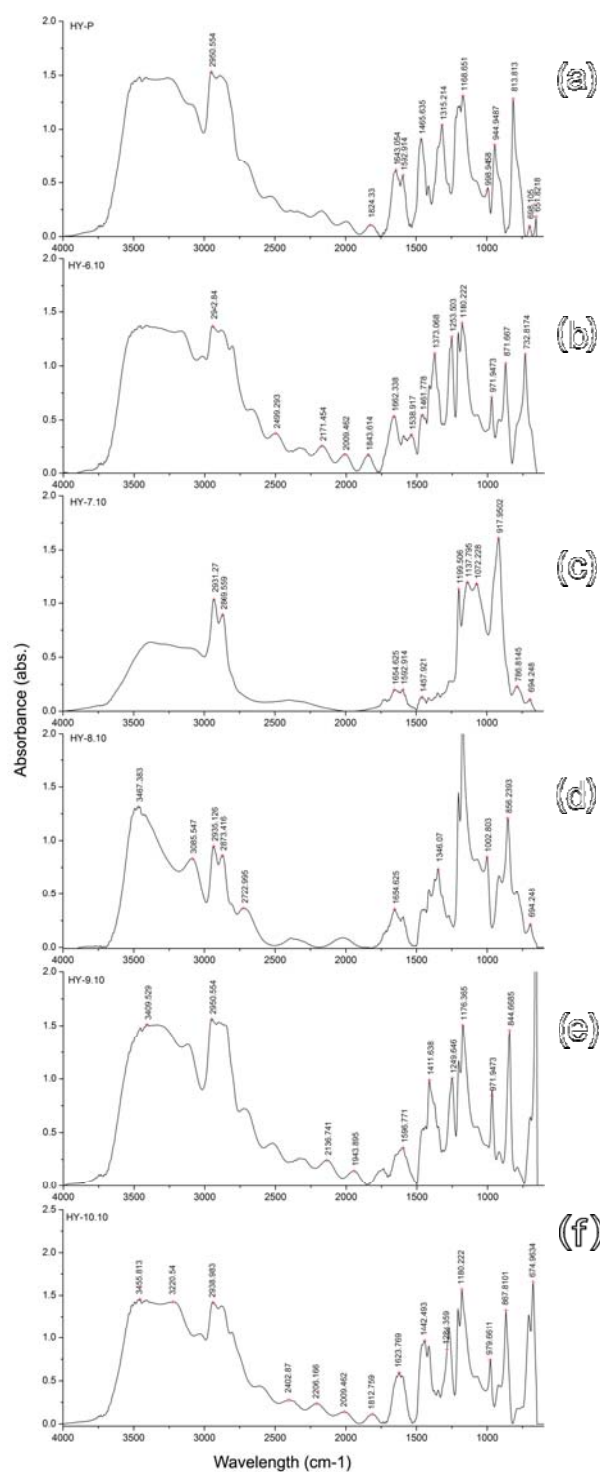


Fig. 4.3. FTIR spectral analysis of HY coating and nanocoatings. (a) Pristine polymeric coating. (b-f) Coatings containing nanoparticles.

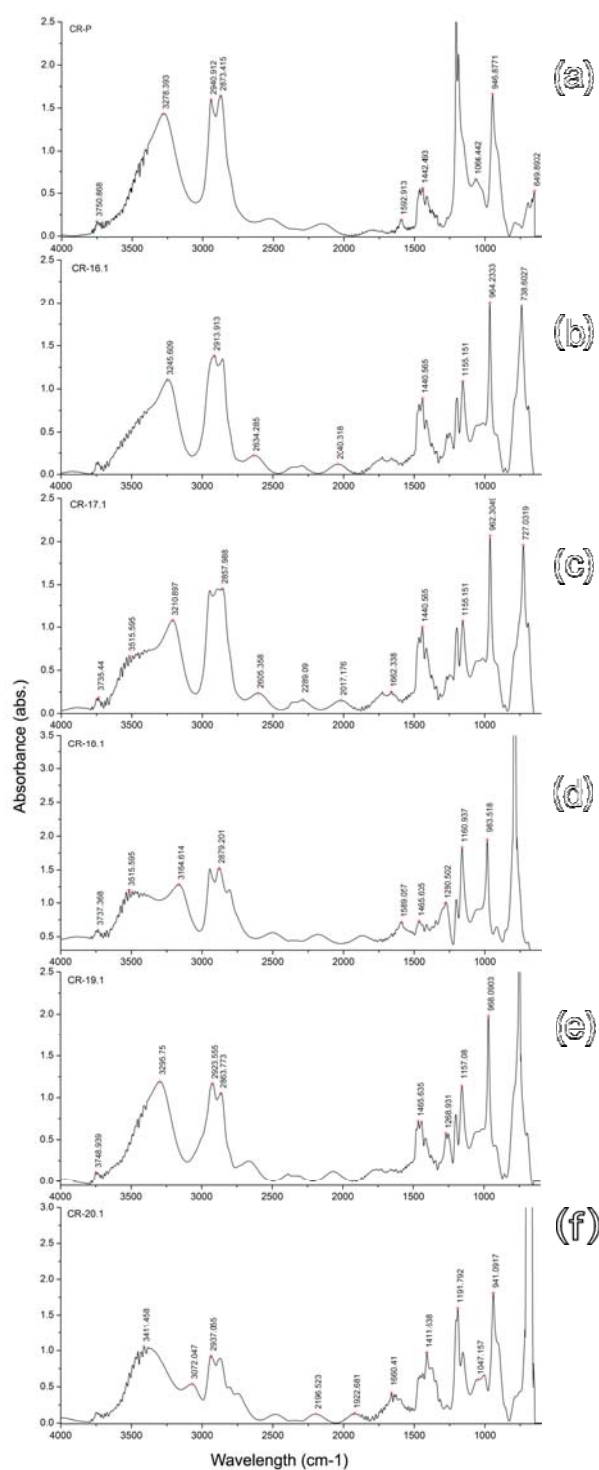


Fig. 4.4. FTIR spectral analysis of CR coating and nanocoatings. (a) Pristine polymeric coating. (b-f) Coatings containing nanoparticles.

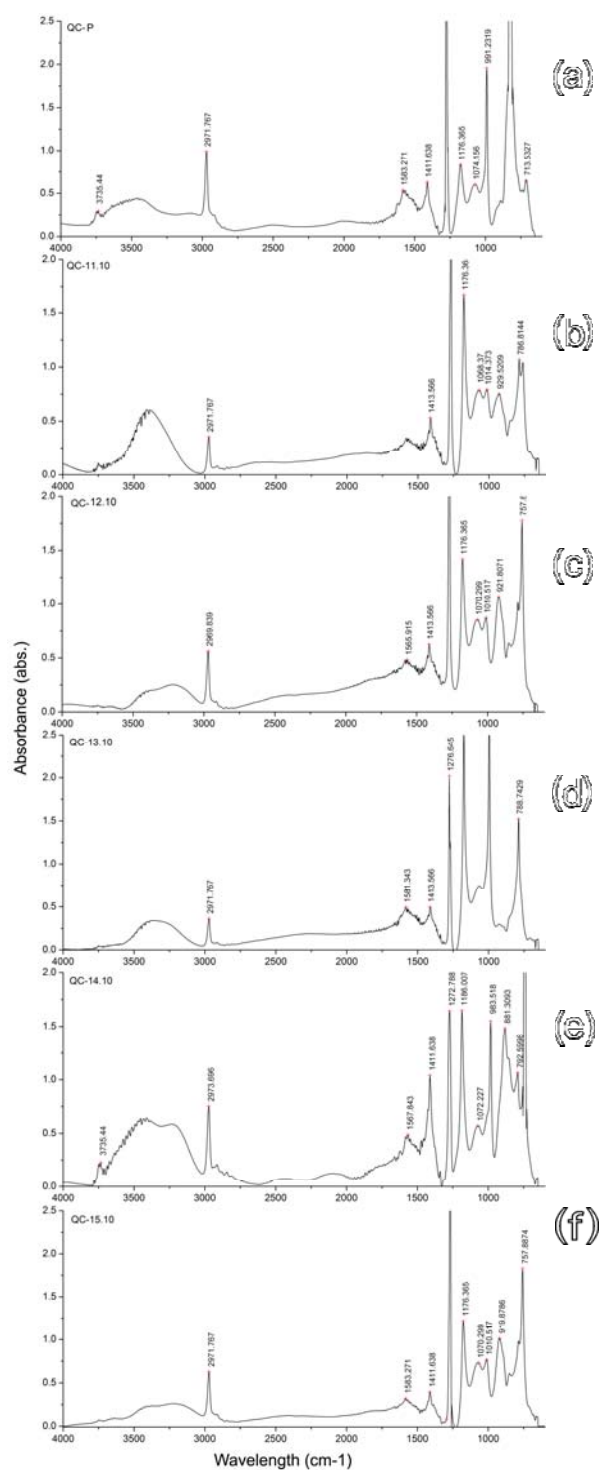


Fig. 4.5. FTIR spectral analysis of QC coating and nanocoatings. (a) Pristine polymeric coating. (b-f) Coatings containing nanoparticles.

4.1.3 Effect of Nanoparticle Concentrations

The purpose of conducting FTIR analysis on nanocoatings with variable concentrations of nanoparticles was to monitor the change in bonding mechanism in nanocoatings with increased concentrations of nanoparticles. Also, weak peaks that appear due to low nanoparticles content may increase when the content of nanoparticles is increased. Such an analysis may help in identifying the reaction pattern in the material.

The FTIR spectra of nanocoatings PL-,1,2,3,4,5 that have three variable concentrations of five different nanoparticles are shown in Appendix-A1. The hump at 3200 cm^{-1} has increased with the increase in TiO_2 concentration. Moreover, the peak position shifted to a higher wavelength with the increase in TiO_2 content in the nanocoatings. Similarly, when the quantity of $\text{Ti}(\text{OH})_4$ was increased, peak positions shifted to a higher wavelength. For SiO_2 -containing nanocoatings, the FTIR spectral appearance is unclear and is similar for each composition. The coating was probably not transparent enough or the exceeding quantity of nanoparticles did not allow the IR beam to reach the detector.

In the case of MMT nanoclay containing nanocoatings, the peak at 667 cm^{-1} representing nanoclay shows a shift toward the lower wavelength, while the peak at approximately 3200 cm^{-1} shifted to a higher wavelength, probably due to the increased interaction between the polymer and nanoclay. In the case of SiC nanowhiskers containing nanocoatings, there was no major peak shift except a peak at 1581 cm^{-1} shifted to 1612 cm^{-1} with the increase in SiC content, probably due to increased electronic interactions between the different forms of carbon moieties.

The FTIR spectra of nanocoatings HY-1,2,3,4,5, which have three variable concentrations of five different nanoparticles are shown in Appendix-A2. There were no major changes in the spectra except a sharp peak at 732 cm^{-1} shift to 794 cm^{-1} and a peak at 3031 cm^{-1} disappeared with the increase in TiO_2 concentration. The shifting could be attributed to the increased interaction with the nanoparticles and polymer chains, while the disappearance of peak at 3031 cm^{-1} could be due to the merging of the entire regime involved in creating hydrogen bonding. In the case of SiO_2 containing nanocoatings, a peak at 694 cm^{-1} that corresponded to silica, enhanced with increased silica content. In the case of MMT nanoclay containing nanocoatings, a peak at approximately 690 cm^{-1} and 844 cm^{-1} diminished in intensity with an increase in MMT concentration. In the case of HY nanocoating containing SiC nanoparticles, a peak appearing at 674 cm^{-1} shifted to a lower wavelength and finally disappeared with the increase in SiC concentration. This could be due to the increased inorganic content that shows spectral assignment at lower wavelengths. However, a sharp peak at 1511 cm^{-1} appears with the disappearance of peak at 674 cm^{-1} suggests that the contribution from inorganic counterpart increases with the enhanced concentration.

The FTIR spectra of nanocoatings CR-1,2,3,4,5 that have three variable concentrations of five different nanoparticles are shown in Appendix-A3. In this case peak positions shifted with an increase in nanoparticles, either because of the enhanced interactions between nanoparticles and silicone or because of the changed refractive index of the material. A clear change appeared in the regime between $3000\text{--}3500\text{ cm}^{-1}$ in each case, suggesting that there is a change in bonding pattern in the nanocoating structures.

The FTIR spectra of nanocoatings QC-1,2,3,4,5 that have three variable concentrations of five different nanoparticles are shown in Appendix-A4. The hydrocarbon portion was lower in this coating formulation, giving inorganic moieties fewer opportunities to form permanent bonds. However, with the increased nanoparticles concentration, there was a shift in peak positions in each case of nanocoating either because of the enhanced interactions between nanoparticles and silicone or because the changed refractive index of the material as discussed before. There were no major changes in the peak positions, suggesting that the coating was saturated with nanoparticles and the bonding pattern remained unaffected from the nanoparticles concentration.

4.2 Morphological Analysis of Nanocoatings

The durability of coatings or nanocoatings depends on the strength of chemical bonds inherited within the materials as well as the final surface morphology. A coated surface filled with defects such as pinholes, holidays and cavities may not be available for robust applications. The coating compositions containing a high volume of hydrocarbon often contain micropores, cavities or non-uniform surfaces. Inorganic materials are generally used to cover such defects; therefore, importance to check surface features associated with the synthesized coatings was realized.

The thin silicone coatings are transparent and difficult to analyze using conventional microscopic techniques. The atomic force microscopic (AFM) technique was therefore adopted to investigate the surface morphology of the coatings hardened over a polished aluminum surface. The PL coating consisting primarily of epoxy resin was analyzed using the AFM technique and compared with other hybrid silicone

coatings. Moreover, an area close to a scratched region was chosen for the scan so that undamaged morphology could be compared with the scratched region.

Fig. 4.6 shows an AFM image of pristine PL coating. The scratched region and another undamaged region were similar due to the plastic nature of the coating. The indenter head compressed rather than scratched or fractured the coating due to the plasticity in the coating. Very few to no coating defects were seen in the images obtained from AFM.

The HY coating (Fig. 4.7) that contained 10 wt. % epoxy resin and 90 wt. % silicone displayed brittle failure. However, the scratched region partially recovered likely due to the epoxy resin. The surface of this coating was a little rough compared to that of the PL coating, possibly due to the roughness associated with substrate metal. The estimated coating thickness of HY was approximately $8\mu\text{m}$, while the estimated thickness of PL coating was approximately $15\mu\text{m}$. A thicker coating normally masks the roughness of the substrate metal surface to a greater degree than thinner coating.

In the case of CR coating (Fig. 4.8), the hydrocarbon portion was low compared to that of the PL and HY coatings. The estimated thickness of the coating was approximately $6\mu\text{m}$, therefore AFM image of this coating surface displays the roughness associated with the metal surface. Moreover, the scratch region was clean and brittle with little to no plastic recovery. There were no surface defects such as pinholes or cavities in the region of the scan.

In the case of QC coating (Fig. 4.9), the hydrocarbon portion was smaller than that of the other coating compositions discussed above. The high silicone content leads to a quasi-ceramic type of network with high strength, but brittle nature. The estimated

thickness of the coating was approximately 5 μm , therefore, the AFM image of this coating surface displays the roughness associated with the metal surface as mentioned earlier. The scratched region clearly suggests that the coating was brittle and that there was no plastic recovery; however, the coating surface was smooth and defect free.

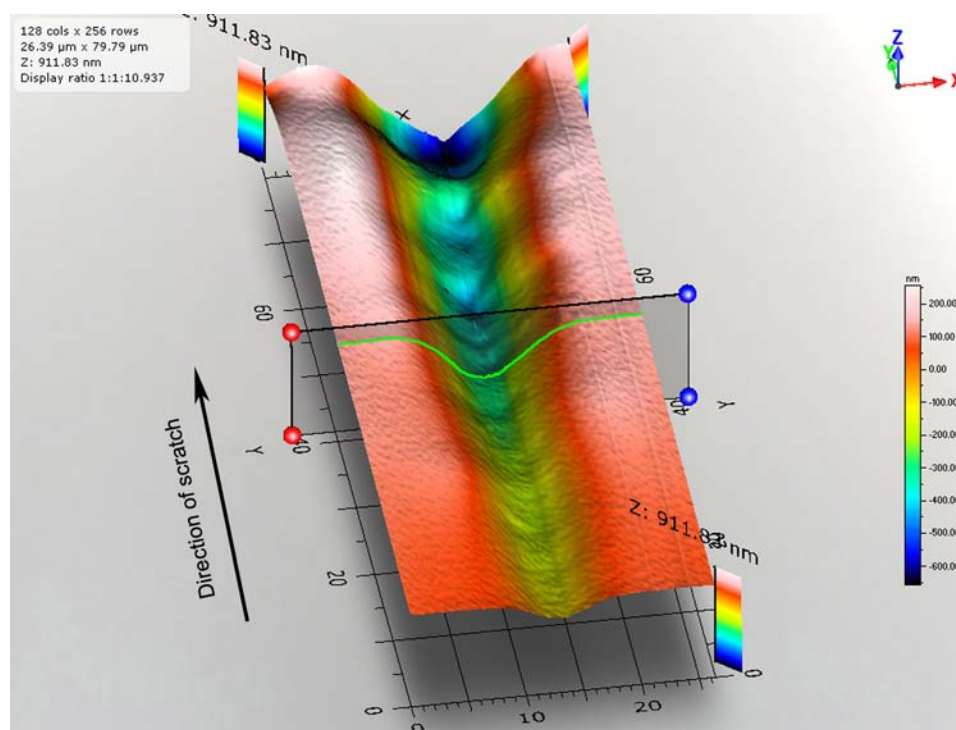


Fig. 4.6. Surface scan of PL coating showing compression in coating.

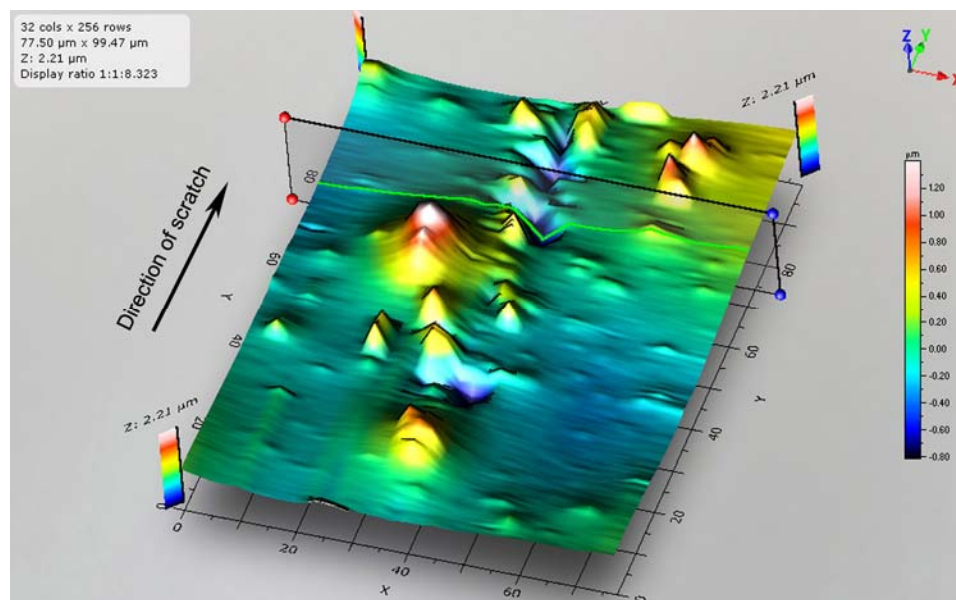


Fig. 4.7. Surface scan of HY coating showing elastic recovery after the scratch.

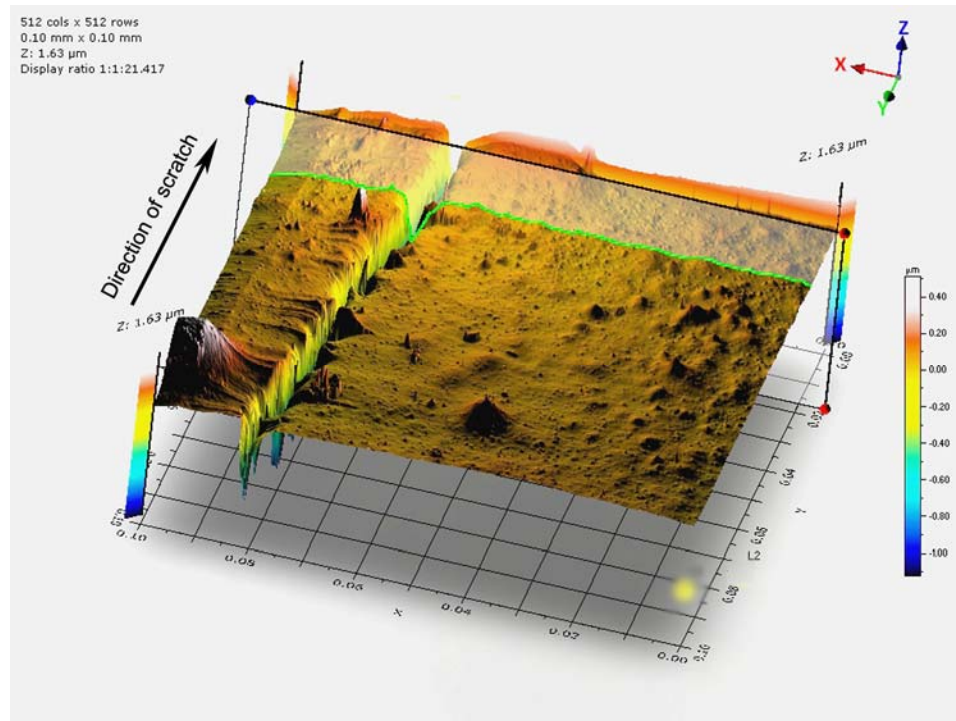


Fig. 4.8. Surface scan of CR coating showing clean brittle scratch.

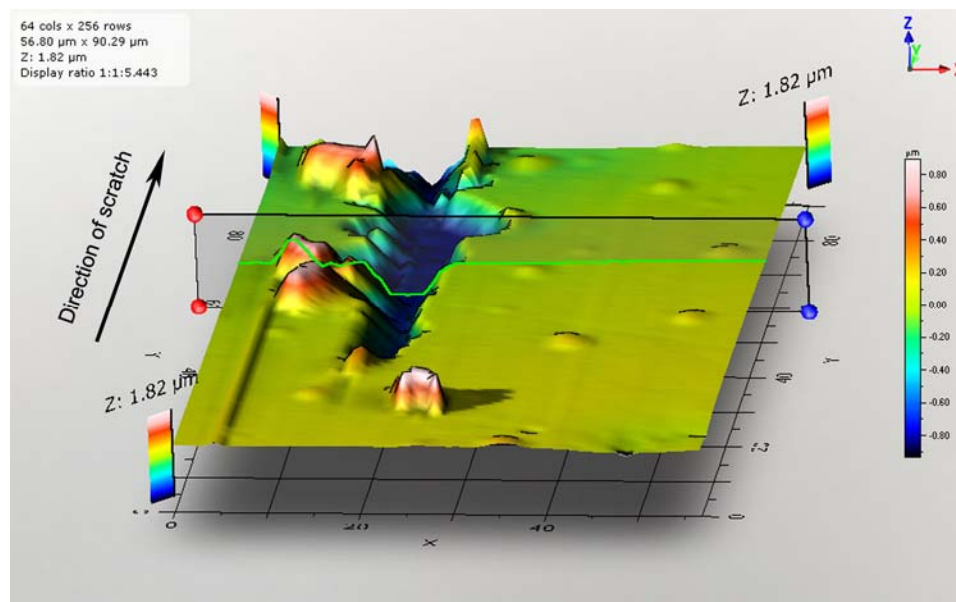


Fig. 4.9. Surface scan of QC coating showing brittle scratch.

Chapter 5

NANOMECHANICAL ANALYSIS

5.0 Introduction

The strength of a material is determined by its chemical bonds. The first appearance of material failure occurs after the final dissociation of such bonds. Mechanical properties of materials can be enhanced by increasing the number of chemical bonds which can be achieved by either using a higher number of functional groups or by incorporating nanoparticles. The effectiveness of incorporating nanoparticles in a material to enhance its overall mechanical properties is well documented. The high surface area of nanoparticles provides additional linkages, giving additional strength to the material network. The question is whether adding nanoparticles affects the localized properties of the material. The following section details the variation in nano-mechanical properties of coatings and corresponding nanocoatings.

5.1 Effect of Molecular Segment Length

Shorter bonds are stronger than the longer bonds; therefore, macromolecular segment length plays a vital role in strengthening a material. Flexible molecules are able to absorb higher impact energy than rigid molecules; however, rigid molecules may have better bond stability. It is therefore important to investigate the change in localized mechanical properties in a material upon altering the molecular chain length and chemical bonds [54, 55].

5.1.1 Hardness and Young's Modulus Investigations

The H & E values of pristine coatings are shown in Fig. 5.1 a, b, where it can be seen that the H values for PL, CR and QC coatings were not affected by the substrate but the influence of substrate was prominent for HY coating. However, the reported values were calculated from the thickness of coating before the substrate effect dominated.

In the case of PL coating, the H value was 0.226 GPa and the E value was 3.682 GPa. These values are comparable to those reported in the literature for epoxy based coatings [10, 56]. In the case of hybrid HY coating, the H value (0.309 GPa) was approximately 37% higher than that of epoxy (PL) coating, but the E value (3.781 GPa) was closer to that of PL coating. Similarly, the H value (0.273 GPa) for CR coating was approximately 21% higher, but the E value (3.492 GPa) decreased slightly compared to that of PL coating. Note that CR and HY coatings have similar compositions except that the HY coating contains 10 wt% epoxy resin. The H value was however 16% higher than that of the CR coating, although the E value was approximately the same. These differences suggest that hybrid materials have better nano-mechanical properties compared to those of neat polymer or neat ceramer coatings.

On the other hand, QC displayed an H value of 0.461 GPa and an E value of 3.841 GPa [41]. The H value in QC coating was approximately 104% higher and the E value was marginally (4%) higher compared to that of PL coating. Similarly, the H value for QC was approximately 67% higher than that of HY coating, but the E value was 33% less than that of HY coating and approximately 17% less than that of CR coating. These values were calculated considering PL coating values as a baseline.

These results suggest that QC coatings consist of a densely packed/crosslinked network compared to that of pristine polymeric coating.

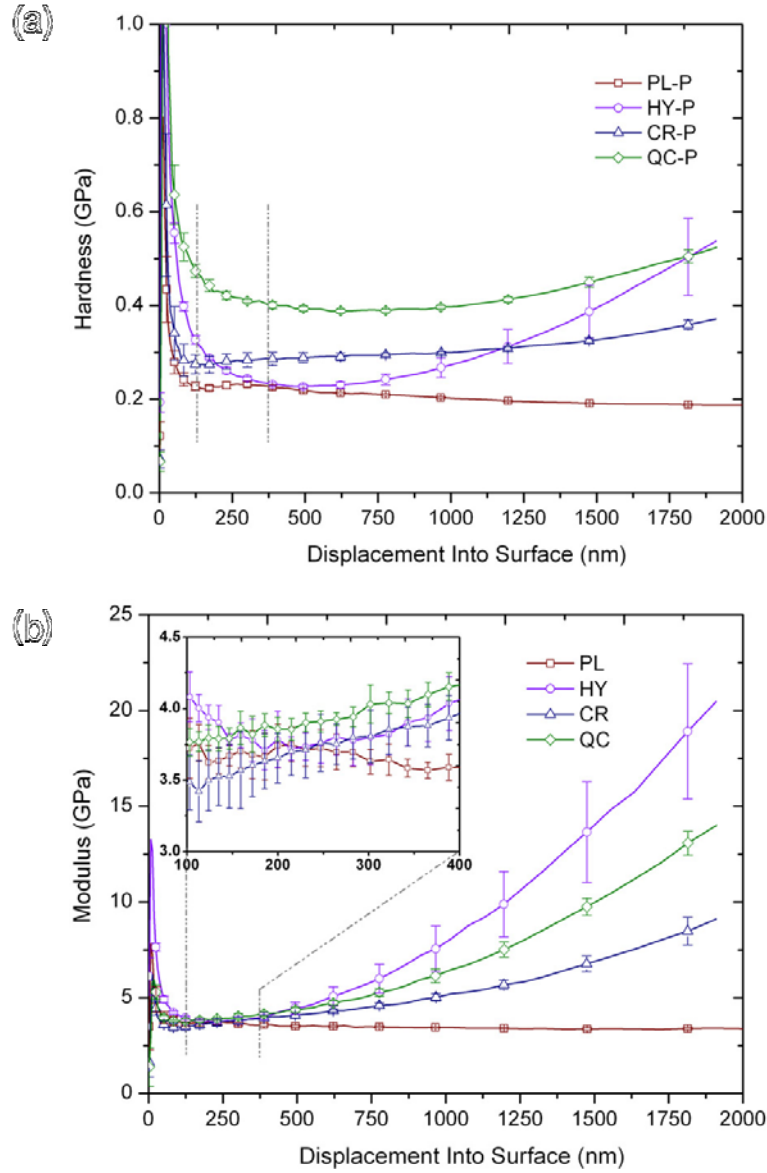


Fig. 5.1. Nanoindentation on pristine coatings. (a) H values as a function of displacement into the surface. (b) E values as a function of displacement into the surface.

5.1.2 Scratch Testing of Pristine Coatings

When a coating is subjected to a scratch test, the indenter can pass through three major regimes in the material: elastic, plastic and fracture. The fracture is immediately followed by the delamination or chipping of the coated surface. The estimation and application of the correct load required to study the above mentioned deformations is very important. The high load can fracture the coating upon contact, eliminating the appearance of the other two regimes. Several different loads were applied to study the deformation on the developed coatings and finally a fixed (500 mN) ramp load was applied to investigate and compare the scratch properties from different coatings.

Fig. 5.2 shows the penetration curve along with residual surface morphology as a function of scratch distance for PL coating [57]. The corresponding nanomechanical parameters derived from scratch tests are shown in Table 5.1. The curve of the original morphology of the coating was smooth. The penetration curves as well as the SEM images suggest that the coating was compressed with the increase in load and the propagation of the nanoindenter tip. At the critical load of approximately 61 mN, the tip penetrated the coating to a depth of approximately 4.3 μm , while the estimated thickness of the coating was 15 μm . The average scratch width was approximately 25 μm . No clear fracture was seen in this case, however, little cracking was observed that helped in estimating the critical load. The end of the scratch test shows the impression from the indenter tip, indicating that the coating was not fractured but that it plastically deformed as a result of the indentation load.

Fig. 5.3 shows the penetration curve along with the residual surface morphology as a function of the scratch distance for HY coating. The corresponding nanomechanical

parameters derived from scratch tests are shown in Table 5.2. The original morphology of the coating was rough in this case. It appears from the penetration curve that the indenter tip moved smoothly on the coated surface to approximately 550 μm before creating a fracture at a critical load of 170 mN. The average penetration depth at the critical load was approximately 4.0 μm . The estimated thickness of the coating was approximately 8 μm , suggesting that the indenter tip compressed the coating before creating a crack that was followed by a fracture. The SEM images indicate that the coating was brittle because a fracture occurred when the indenter head penetrated the coating. The coating was cracked on the surface with the progressive motion of the indenter, and a complete coating delamination was observed at the end of the scratch test. A significant amount of coating delamination was observed around the scratch, suggesting the presence of residual stresses in the coating.

Fig. 5.4 shows the penetration curve along with residual surface morphology as a function of the scratch distance for CR coating [58]. The corresponding nano-mechanical parameters derived from scratch tests are shown in Table 5.3. The original morphology of the coating was smooth with a curvature. The indenter head propagated and fractured the coating at a critical load of approximately 160 mN and after the scratch distance of 1.0 μm . The estimated thickness of the coating was approximately 6 μm , and the depth of penetration at critical load was approximately 3.0 μm , suggesting that the coating cracked before the fracture and was followed by delamination. The SEM images from the initiation, propagation and termination sites in the scratch suggest that the coating failed because of a brittle fracture mechanism.

Fig. 5.5 shows the penetration curve along with residual surface morphology as a function of the scratch distance for QC coating. The corresponding nano-mechanical parameters derived from scratch tests are shown in Table 5.4. The original morphology of the coating was smooth in this case, with a roughness in the nanometer regime. It appears from the penetration curve that the progressing load bearing the indenter tip pushed the coating and fractured at a critical load of approximately 84 mN after travelling a scratch distance of 350 μm . The estimated thickness of the coating was approximately 5 μm and the depth at critical load was approximately 4.3 μm , suggesting that it cracked and fractured simultaneously. The SEM images of the initiation, propagation and termination steps during the scratch suggest that the indenter scratched the surface after which the surface cracked. The coating and substrate chipped off at the termination point of the scratch test.

On comparing the results from scratch tests conducted on four pristine coatings, it appears that HY showed maximum fracture strength followed by CR coating. The presence of a hydrocarbon portion in these coating compositions may provide a better resilience capability in the coating that would enhance its fracture toughness. On the other hand, a low critical load in the case of PL coating could be an underestimation due to the absence of a clear fracture in the coating. The low critical load value in the case of QC coating could be due to the increased brittleness in the coating structure.

The coefficient of friction (COF) curves as a function of scratch distance are shown in Fig.5.6. The curves from at least three tests are shown for better clarity. In the case of PL coating, the COF value after a 600 μm scratch distance was between 0.35 and 0.40, while for HY coating, this value was between 0.15 and 0.19. The lower value in the

case of HY compared to polymer coating could be due to the presence of silicone. In the case of CR coating, the COF value was between 0.20 and 0.22. This value was lower than that of pristine polymer coating but closer to that of HY. The COF value for QC coating was between 0.30 and 0.35, a value closer to that of PL coating. The reason for the high COF value in this case is not known at this point and further analysis is needed to draw a meaningful conclusion.

The cross profile topography (CPT) of PL, HY, CR and QC coatings as a function of scratch distance is shown in Fig.5.7. The CPT was acquired at the end of the scratch test when the load was 10 mN for each coating. The positive values on the X-axis show the right side of the groove, while the negative values on the X-axis show the left side of the groove. Similarly, the positive values on the Y-axis show the pile-up after the scratch, while the negative values on the Y-axis show penetration in the coating. The CPT curve shown here is one of the five curves recorded on the same coating. The CPT curves were little different in each test. A representative curve is shown here for each coating.

In the case of PL coating, the penetration depth was approximately 80 nm, while the pile-up height was approximately 60 nm. For HY coating, the pile-up height was similar to that of PL coating but the depth of penetration was approximately 8 nm. In the case of CR coating, the penetration depth was approximately 80 nm, while the pile-up height was 30 nm. These figures suggest that HY has better scratch resistance than do pristine polymer and ceramer coating. Similarly, for QC coating, the pile-up height was approximately 20 nm, while the depth of penetration was approximately 25 nm. The lowest pile-up height and moderate depth of penetration achieved in the case of QC coating suggests that the material was hard and elastic in nature.

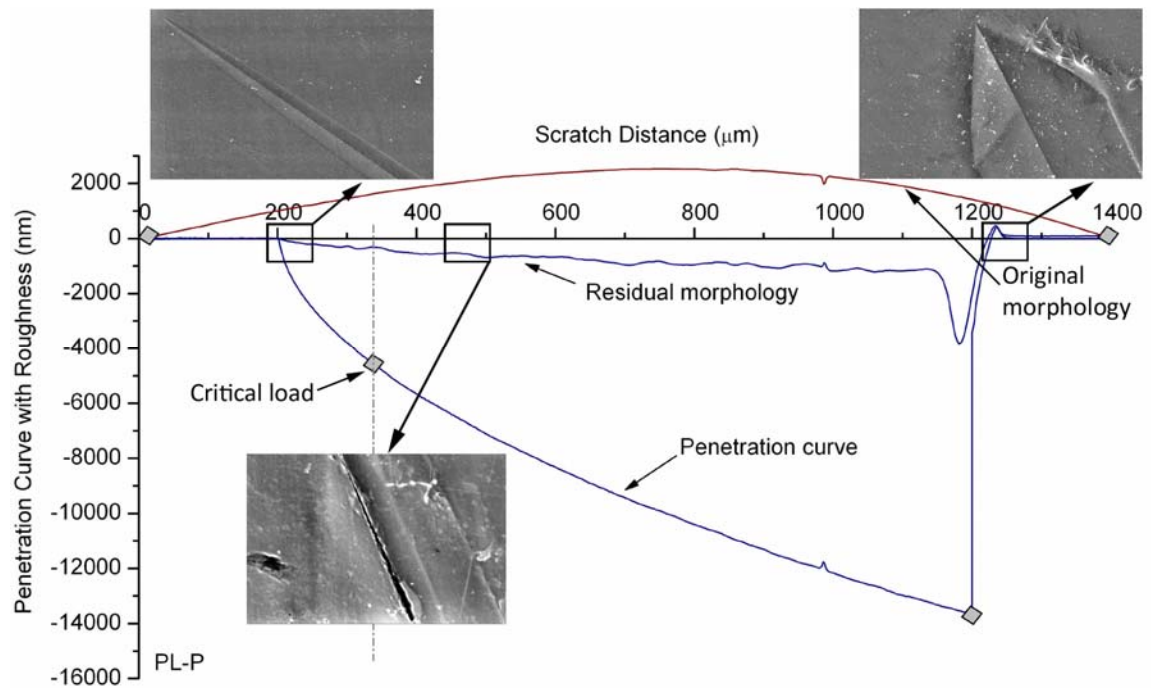


Fig. 5.2. Nanoscratch analysis of pristine coatings. (a) Initiation, propagation and termination steps in PL coating.

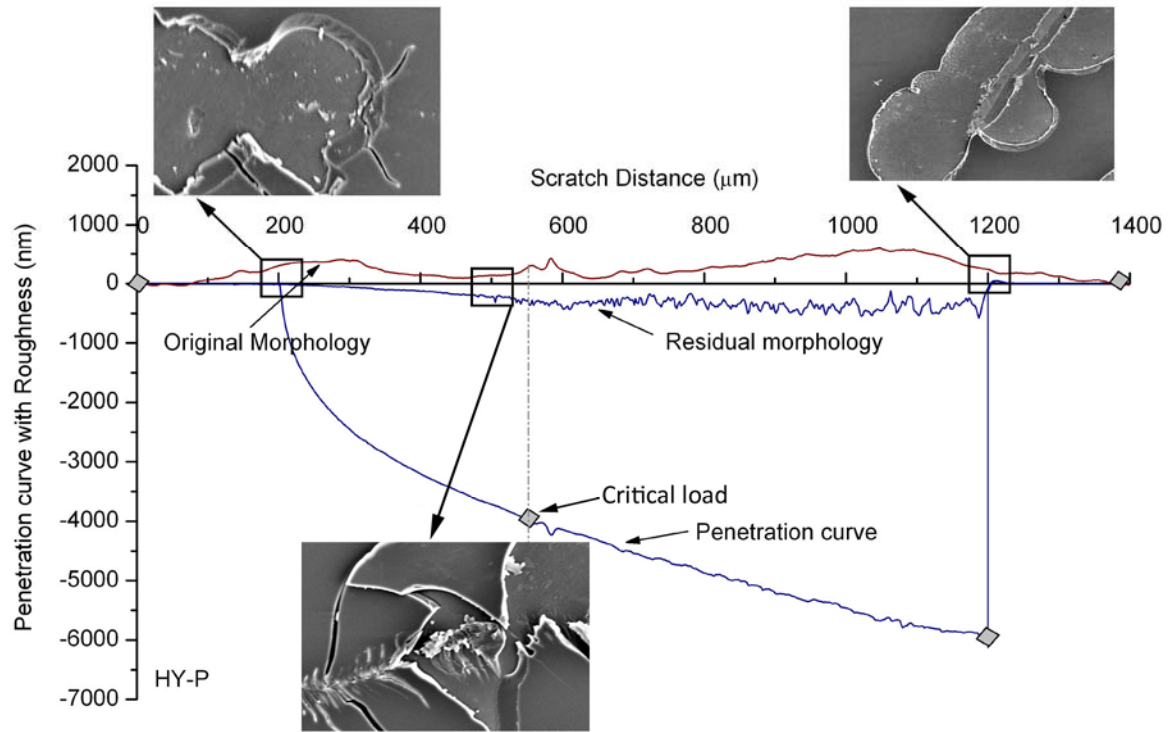


Fig. 5.3. Nanoscratch analysis of pristine coatings. (a) Initiation, propagation and termination steps in HY coating.

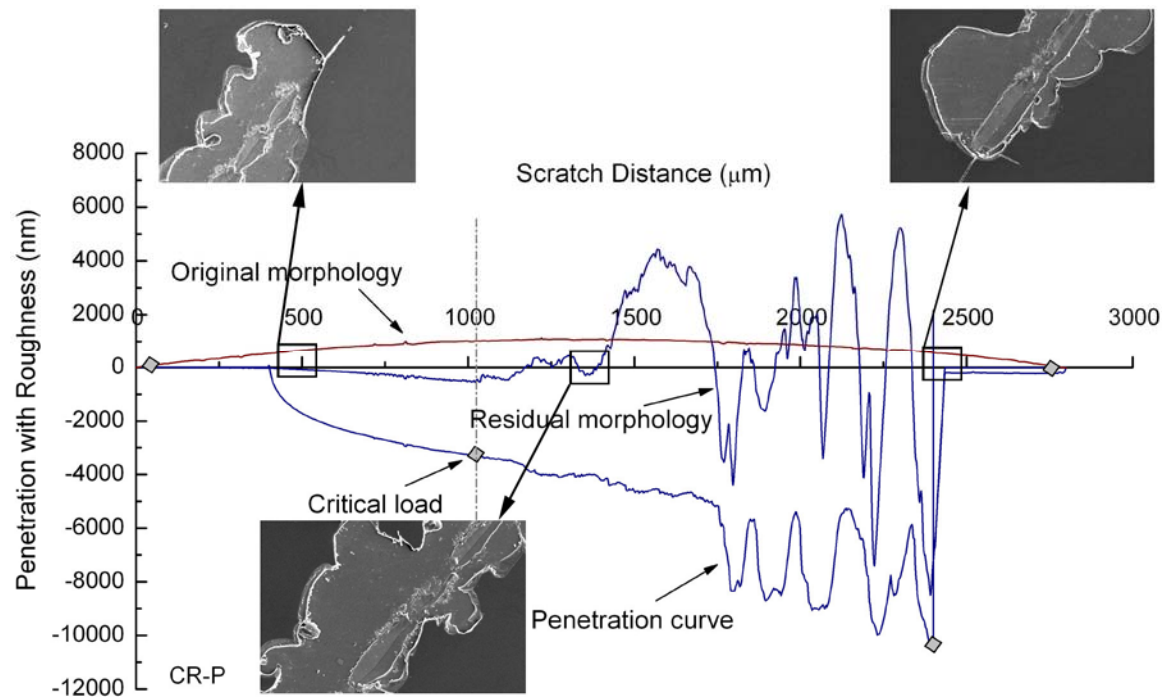


Fig. 5.4. Nanoscratch analysis of pristine coatings. (a) Initiation, propagation and termination steps in CR coating.

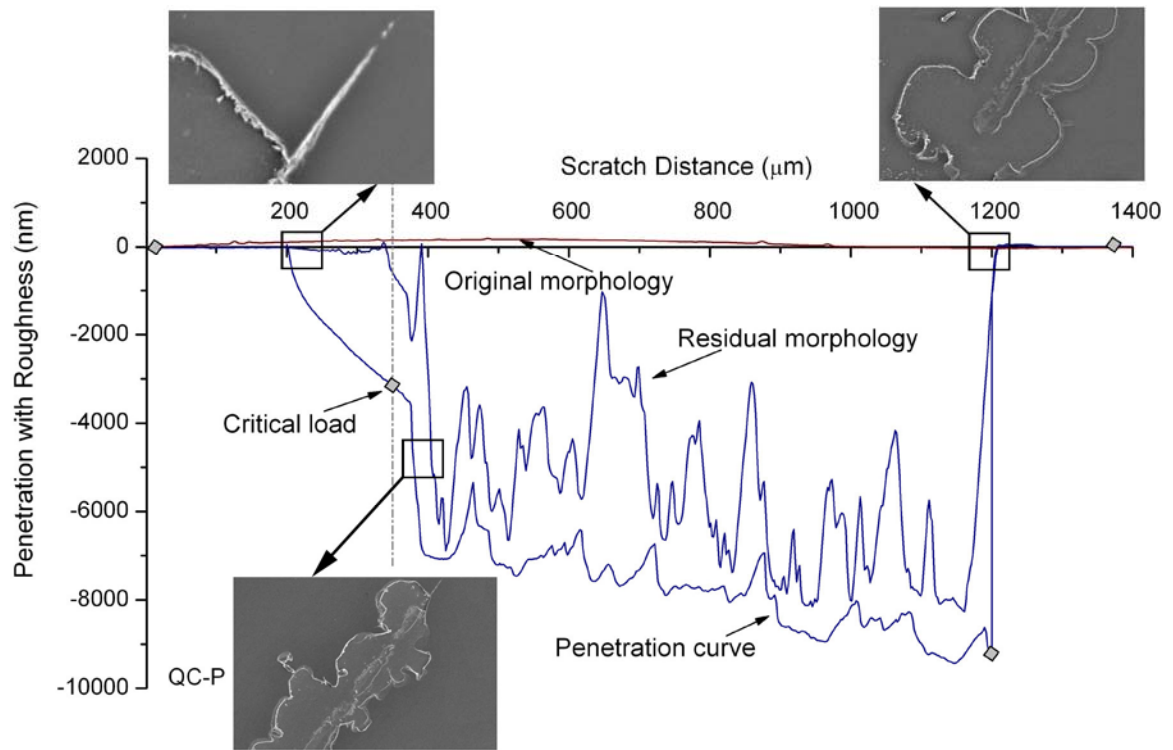


Fig. 5.5. Nanoscratch analysis of pristine coatings. (a) Initiation, propagation and termination steps in QC coating.

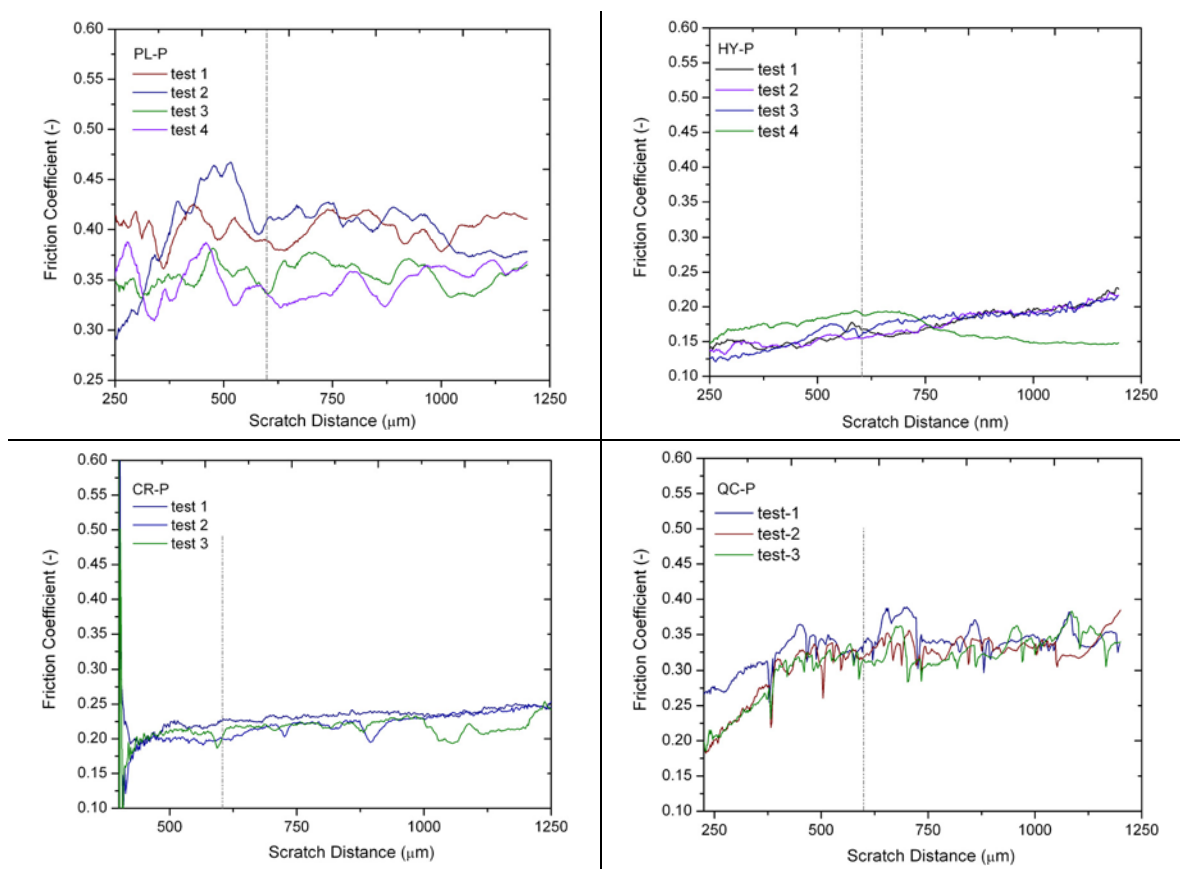


Fig. 5.6. Nanoscratch analysis of pristine coatings. The COF curve as a function of scratch distance.

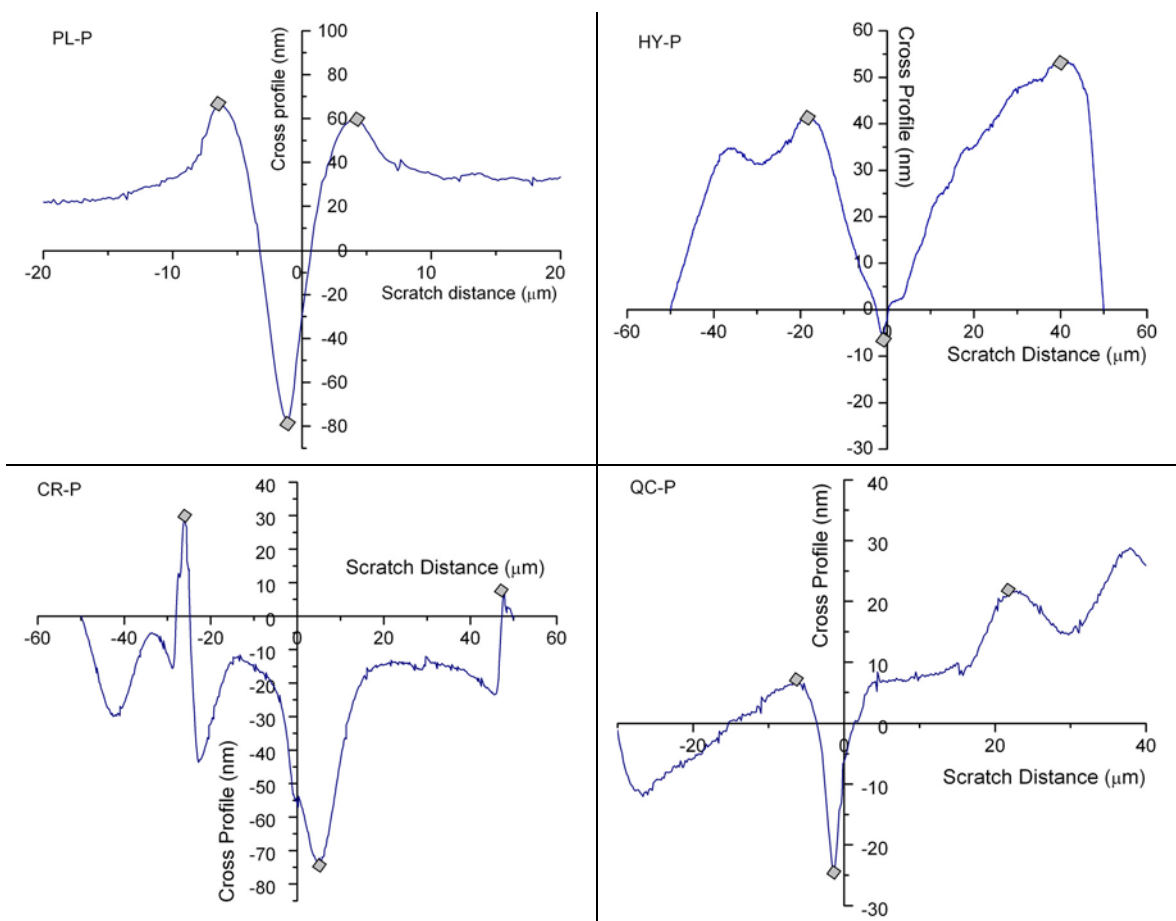


Fig. 5.7. Nanoscratch analysis of pristine coatings. The cross profile curve as a function of scratch distance.

Table 5.1 Nanomechanical parameters derived from nanoscratch testing of PL coating.

Test	Critical Load (mN)	Penetration Depth At Critical Load (nm)	Scratch Width (μm)	Total Height Of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
1	57.504	4138.441	42.189	171.848	105.08	66.768
2	65.48	4520.823	53.552	240.539	182.646	57.893
3	63.484	4430.201	10.395	140.25	77.158	63.092
4	62.532	4405.91	10.61	158.655	91.172	67.483
5	57.462	4087.989	10.001	146.79	39.959	106.83
Mean	61.292	4316.673	25.35	171.616	99.203	72.413
Std. Dev.	3.637	191.437	20.949	40.369	52.578	19.611

Table 5.2 Nanomechanical parameters derived from nanoscratch testing of HY coating.

Test	Critical Load (mN)	Penetration Depth At Critical Load (nm)	Scratch Width (μm)	Total Height Of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
1	171.551	4425.852	39.336	39.365	17.606	21.759
2	179.528	4154.22	78.113	43.068	35.581	7.487
3	171.752	3940.522	58.105	53.578	5.743	47.835
4	170.533	4237.607	98.717	127.102	124.054	3.048
Mean	173.341	4189.55	68.568	65.778	45.746	20.032
Std. Dev.	4.159	201.173	25.587	41.323	53.627	20.181

Table 5.3 Nanomechanical parameters derived from nanoscratch testing of CR coating.

Test	Critical Load (mN)	Penetration Depth At Critical Load (nm)	Scratch Width (μm)	Total Height Of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
1	168.697	3345.589	73.912	92.328	74.348	17.98
2	164.755	3355.818	91.476	37.484	31.829	5.655
3	153.766	3371.555	70.156	18.592	15.208	3.385
4	153.767	3415.923	41.042	16.823	0.055	16.768
5	165.768	2353.216	96.1	19.785	18.535	1.25
Mean	161.351	3168.42	74.537	37.002	27.995	9.008
Std. Dev.	7.073	456.505	21.757	32.03	28.271	7.807

Table 5.4 Nanomechanical parameters derived from nanoscratch testing of QC coating.

Test	Critical Load (mN)	Penetration Depth At Critical Load (nm)	Scratch Width (μm)	Total Height Of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
1	86.686	3511.214	73.518	61.433	24.386	37.047
2	85.485	3399.345	81.153	81.045	46.309	34.735
3	84.526	3517.302	98.108	1185.091	1168.203	16.888
4	79.664	5042.232	9.14	36.403	7.963	28.439
5	82.483	6266.557	97.498	1269.834	1203.941	65.893
Mean	83.769	4347.33	71.883	526.761	490.16	36.6
Std. Dev.	2.763	1270.141	36.637	640.547	635.549	18.145

5.1.3 Dynamic Mechanical Response of Pristine Coatings

The effect of molecular chain length on visco-elastic properties of the pristine coatings are investigated in this section. Our findings point toward a possible correlation between the polymer, ceramer, hybrid or quasi-ceramic materials [59].

Fig 5.8 shows storage modulus (E') and loss modulus (E'') of pristine coatings as a function of frequency. At least six tests were performed at each frequency; results are shown with the error bars. It can be seen that the test shows good repeatability. The E' values of pristine coatings were independent of frequency, while the E'' value increased slightly with the frequency. The CR coating showed the lowest E' (3.013 GPa) value, while the HY coating displayed the highest (3.952 GPa). Interestingly, the E' value for QC coating (3.847 GPa) was in between those of HY and PL coatings.

The E'' value (0.437 GPa) for HY coating was higher compared to that of other coatings, possibly due to the relaxation phenomenon associated with polymer, ceramer and hybrid domains in the material. The E'' values of PL, CR and QC coatings were close and independent of test frequency. These findings suggest that the macromolecular network in the coatings is similar in a 3-dimensional domain.

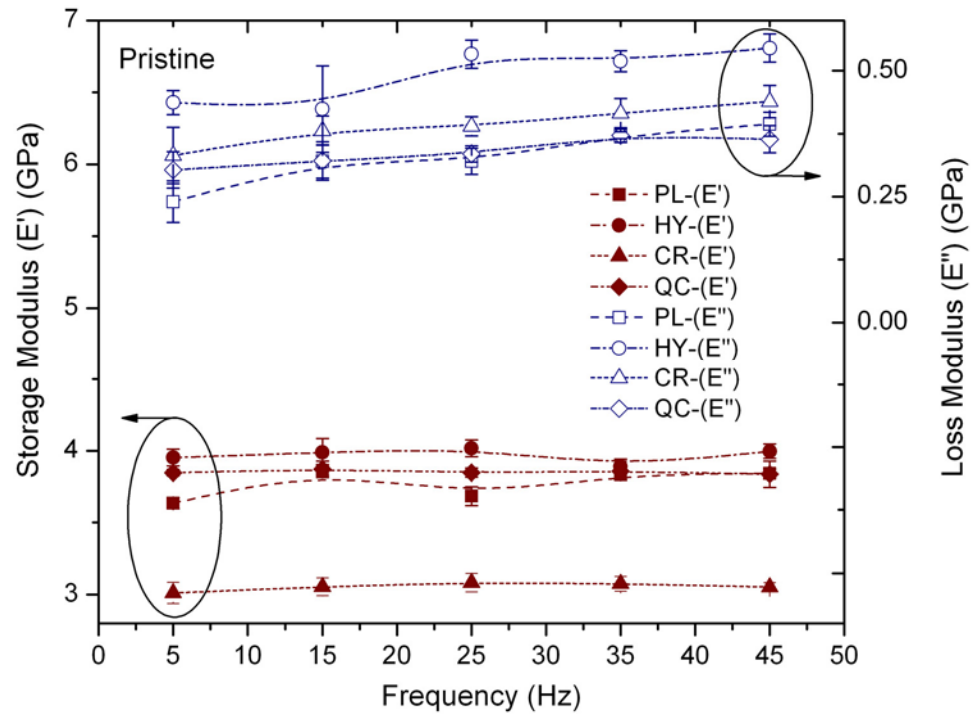


Fig. 5.8. Visco-elastic effect in pristine coatings. The E' and E'' curve as a function of test frequency.

5.2 Effect of Nanoparticles in Nanocoatings

The change in nano-mechanical properties of coatings and nanocoatings with the addition of nanoparticles is discussed in this section.

5.2.1 Hardness and Young's Modulus Investigations

Figs. 5.9 and 5.10 show the H and E values of coatings and nanocoatings as a function of displacement into a surface. Fig. 5.9 and 5.10 shows that H and E values were least affected in the case of PL and CR coatings and nanocoatings, probably due to the sufficient coating thickness on the substrate. The H values were affected beyond a 500 nm depth in the case of HY coatings and nanocoatings and beyond a 1000 nm depth in the case of QC coatings and nanocoatings.

Fig. 5.10 shows E values of coatings and nanocoatings as a function of displacement into the surface. E values remained unaffected up to a 500 nm depth of penetration in each case except with HY coatings and nanocoatings where this value remained unaffected up to a 300 nm penetration depth.

The effect of nanoparticles incorporation in coatings can also be seen in Figs. 5.9 and 5.10 where the pristine coatings are compared to nanocoating compositions containing 0.1 wt. % nanoparticles. There was an increase in H as well as E values with the addition of nanoparticles. In the case of PL nanocoatings, the maximum H value was achieved for nanocoating containing $\text{Ti}(\text{OH})_4$ mediated nanoparticles [60], while the E value was highest for nanosilica containing nanocoatings.

In the case of HY nanocoatings, high H and E values were seen for nanosilica and SiC nanowhisker containing nanocoatings. An increase in the H value between 15% and

18 % was observed when nanosilica and nanowhiskers were added to the coatings. The E values in these nanocoatings were as much as 21% higher compared to those of the pristine coating.

In the case of CR nanocoatings, the maximum H and E values were seen for the nanocoatings containing SiC nanowhiskers. The H value was 27% improved, while the E value improved approximately 14% compared to that of the pristine CR coating.

For QC coating, H and E values were highest for nanocoating containing Ti(OH)_4 mediated nanoparticles. The maximum H value in such a case was approximately 36% higher than that of QC, while the E value was approximately 19% higher compared to that of pristine QC coating.

The increment in the H value for PL nanocoating containing Ti(OH)_4 can be explained by the reactive ethoxy functional groups that form permanent covalent bonds with reactive epoxy functionalities, a reaction that enhances hardness. On the other hand, the H value increase in HY nanocoatings containing nanosilica and nanowhiskers may be due to the enhanced interaction between inorganic nanofillers and an inorganic silicone network. The organic portion in this composition may act as a binder that keeps inorganic fillers intact in the nanocoating structure.

In CR nanocoatings, the increment in the H value due to the presence of nanowhiskers could be attributed to the inorganic-filler interaction effect. The shape of SiC nanowhiskers is similar to a thin film or membrane that might interact with the electron cloud of silicone. Such an interaction provides additional strength to the coating network.

The composition of QC coating consists of little to no hydrocarbon. However, the reactive functionalities present in the coating form stable bonds with the additional functional groups originating from titanium ethoxide. These additional bonds provide added strength to the nanocoating structure.

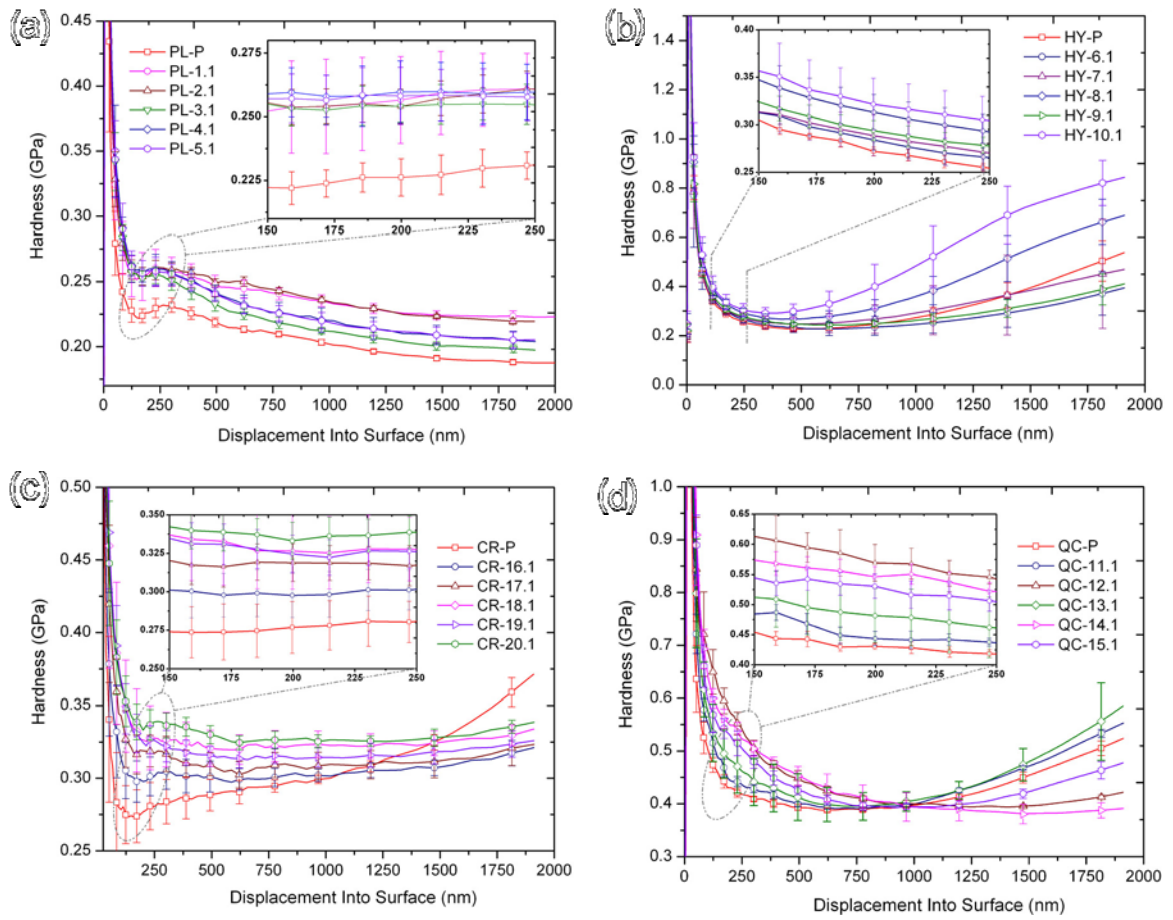


Fig. 5.9. Nanoindentation on coatings and nanocoatings. H values of coating as a function of displacement into the surface.

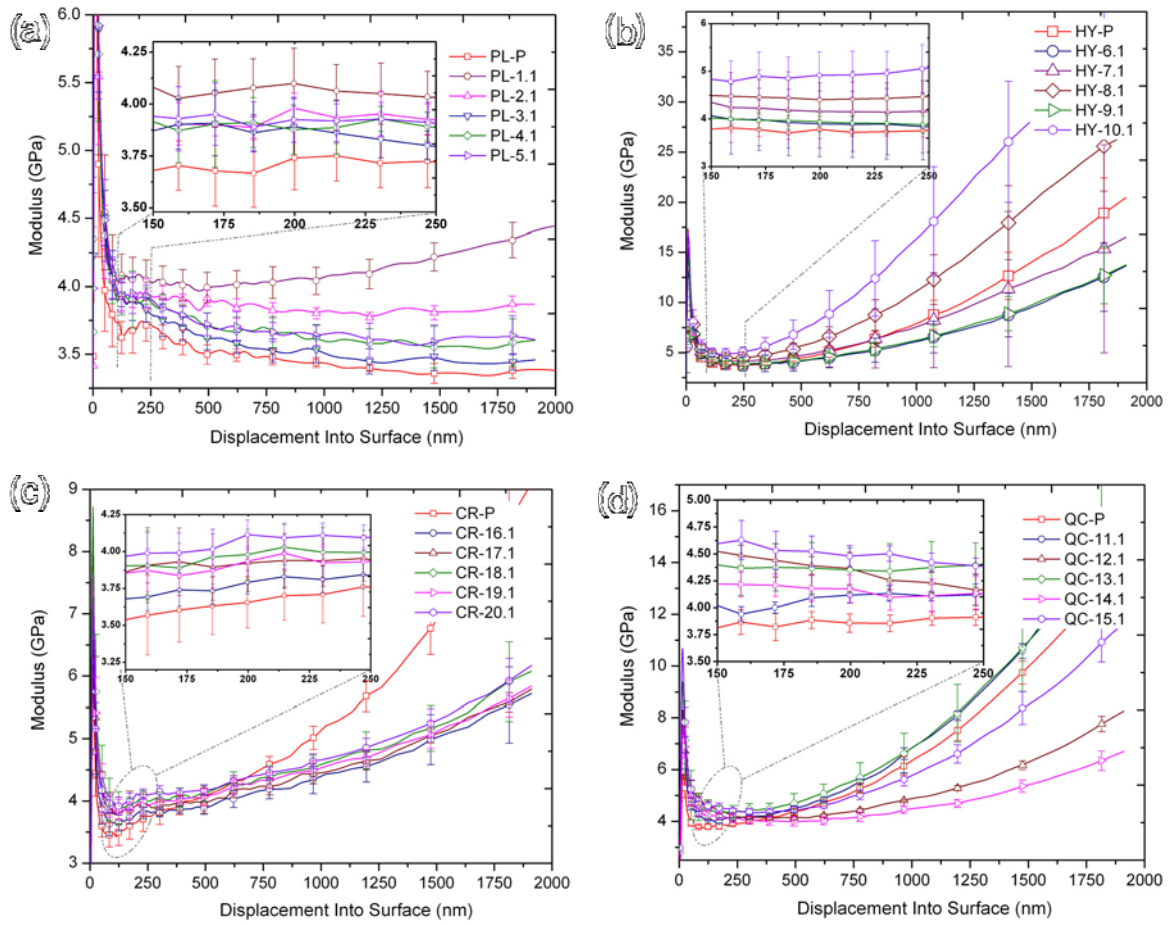


Fig. 5.10. Nanoindentation on coatings and nanocoatings. E values as a function of displacement into the surface.

5.2.2 Effect of Nanoparticles on Nanoscratch Testing of Nanocoatings

Different curves obtained from scratch tests conducted on nanocoatings can be found in Appendix –C1-C12. Corresponding nano-mechanical parameters are appended in Tables 5.5-5.8, which shows the enhancement in the critical load in nanocoatings compared to that of pristine coatings (Table 5.1-5.4). The comparison is made between pristine coating and nanocoatings containing 0.1 wt% nanoparticles.

In the case of PL nanocoating, the enhancement in the critical load was between 20 % and 182 % once nanoparticles were added. The maximum improvement was recorded for nanosilica containing nanocoating.

In the case of HY nanocoating, the critical load enhancement was between 24% and 80 % once nanoparticles were added. The maximum improvement was recorded for nanocoating containing SiC nanowhiskers.

In the case of CR nanocoating, the critical load increment up to 38% was achieved for nanocoating containing nanosilica. In the case of QC nanocoating, the critical load value enhancement was insignificant. In fact, it dropped by as much as 30% when nanoparticles were added with the exception of the TiO₂ nanoparticles. This result suggests that adding nanoparticles to the QC coating composition generally adversely affects the load bearing capacity of QC nanocoatings during scratch testing.

5.2.3 Dynamic Mechanical Response of Nanocoatings

In this section, the change in visco-elastic properties of four different coatings containing the same nanoparticles and their concentration are compared. This design reveals whether adding nanoparticles changes visco-elastic properties of a coating. The E'

and E'' values for pristine coating and nanocoating containing 0.1 wt% TiO_2 nanoparticles as a function of frequency are shown in Fig.5.11.

It appears from Fig. 5.11 that the E' value remained unaffected by test frequency. However, the E'' value changed with the frequency for each nanocoating. On comparing with pristine, E'' values were higher at lower frequencies for each nanocoating, indicating that the relaxation process associated with the regime containing nanoparticles. It is worth mentioning that molecular motions that are associated with polymer materials are more prominent at lower frequencies. On the other hand, such transitions are not visible at higher frequencies because molecules may not have enough time to undergo rapid molecular transformations. In other words, at lower frequencies, molecules have a longer time to react and the viscous term dominates, while at a higher frequency molecules may not have sufficient time to relax and the response is mainly due to elasticity with limited viscous nature. The quasi-linear increment in E'' could be due to the high frequency that results in a higher loading rate effect.

The E' values were similar for PL coatings and nanocoatings (0.1 wt. % TiO_2) but the E'' value was higher for nanocoatings compared to that of pristine coating at lowest frequency. However, the E' value for HY nanocoating (0.1 wt. % TiO_2) was higher compared to that of pristine coating, suggesting HY nanocoating has a tendency to store energy. On the other hand, the E'' values were similar for HY coating and (0.1 wt. % TiO_2) nanocoating. In the case of CR, E' value was slightly higher for (0.1 wt. % TiO_2) nanocoating than for that of pristine coating, but the E'' values were similar in both the cases.

A distinctly different behavior was observed in QC coating and nanocoating (0.1 wt. % TiO_2). The E' value decreased significantly when nanoparticles were added, indicating that this material may have a reduced ability to absorb energy. However, the E'' value increased with the addition of nanoparticles, indicating the likely presence of nanodomains in the material responsible for the localized molecular motions.

The complete investigation curves for visco-elastic properties of coatings and corresponding nanocoatings (0.1, 0.3 and 0.5 wt. %) as a function of frequency is shown in Appendix D1-D4. In the case of PL coatings and nanocoatings, E' values were not affected by the presence of nanoparticles. However, E'' values were higher at 5 Hz frequency in all of the nanocoatings, suggesting the presence of molecular motions in the nanocoating structure.

In the case of HY coating and nanocoating, both E' and E'' values varied with the addition of nanoparticles. Interestingly, both E' and E'' values varied with frequency. In all of the nanocoatings, the E' value increased when nanoparticles were added, suggesting the damping characteristic in the material. Similarly, E'' values changed as the frequency changed; however, the values were close to that in the pristine coating.

In the case of CR coating and nanocoatings, the E' value increased when nanoparticles were added and remained constant at different frequencies. These results suggest that nanocoatings may have a tendency to resist cyclic loading and unloading. Similar to above cases, the E'' value was higher at lower frequencies and similar to the E'' of pristine coating at higher frequencies.

In the case of QC coating and nanocoating, the E' and E'' values increased when nanoparticles were added, except when $\text{Ti}(\text{OH})_4$ was included. The E' value remained unaffected by frequency, while the E'' value changed with frequency. These results suggest that the incorporation of nanoparticles in the coating formulation creates free volume in the resultant nanocoating structure and that domains modified by nanoparticles were distributed in the coating network.

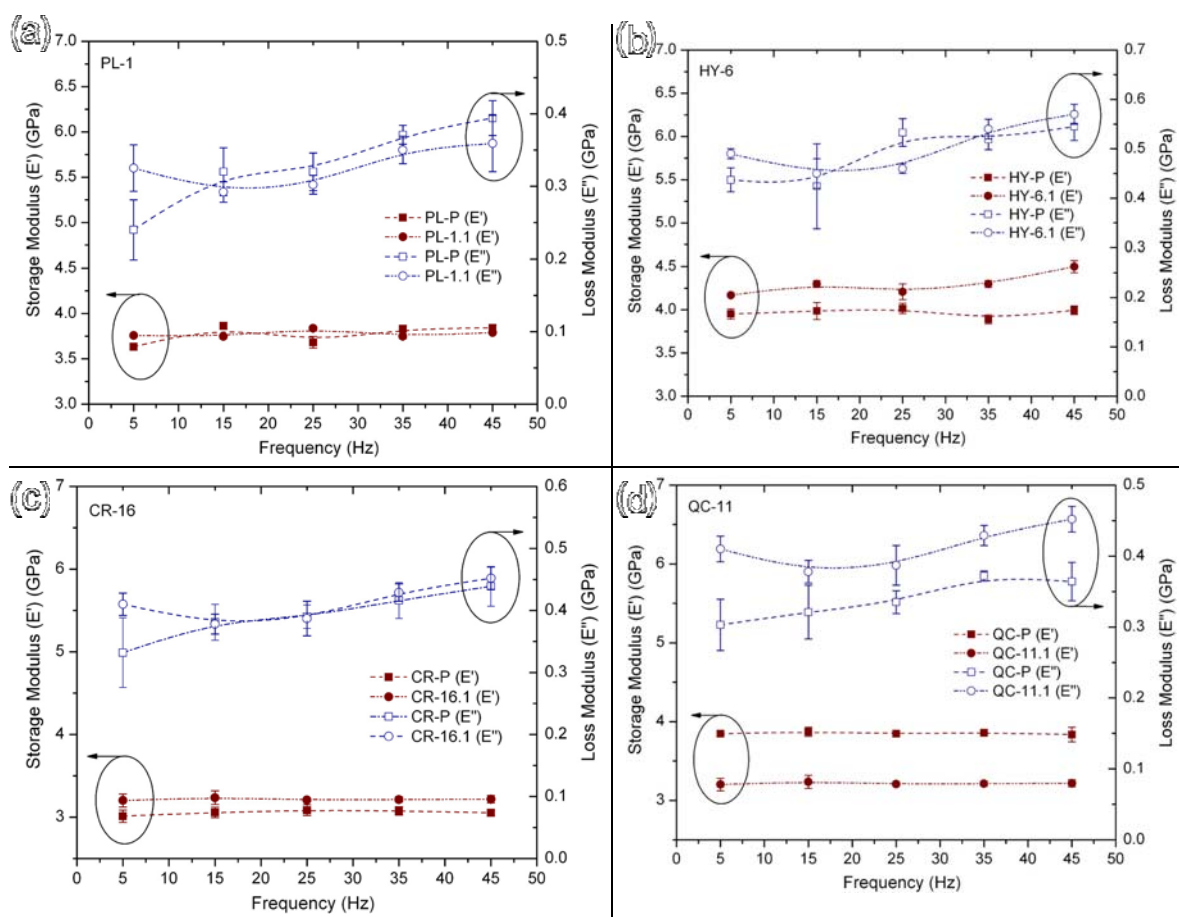


Fig. 5.11. Visco-elastic properties of pristine coatings and nanocoatings. The E' and E'' curve as a function of test frequency.

5.3 Effect of Nanoparticles Concentration in Nanocoatings

In this section we investigate how nano-mechanical properties are affected when the concentration of nanoparticles in the nanocoating structure are modified.

5.3.1 Hardness and Young's Modulus Investigations

Figs. 5.12 and 5.13 show changes in H and E values as a function of nanoparticles concentration in nanocoatings. Interestingly, in PL nanocoatings, the H value increased as the concentration of nanoparticles increased. The maximum improvement in H value was 42% for 0.5 wt% nanosilica containing nanocoating.

In the case of HY nanocoatings, the H value increased with the nanoparticles concentration except for the nanocoating containing SiC nanowhiskers where the H value decreased slightly with the increase in nanoparticles concentration, probably due to the agglomeration of SiC nanowhiskers. The largest H value increment was approximately 21% of pristine for nanosilica containing nanocoating.

In the case of CR nanocoating, the H value increased with the nanoparticles concentration except for the composition containing Ti(OH)_4 , in which case the H value increment was 25% for 0.3 wt% nanoparticles concentration. The largest H value increment was approximately 41% for 0.5 wt.% SiC nanowhiskers concentration. In the case of nanosilica containing nanocoating, the H value remained unaffected by changes in nanoparticles concentration.

In the case of QC nanocoating, the H value increment was random. Upon adding nanoparticles, the H value was higher than it was in pristine coating. However, the H value increment was not linear as in the cases mentioned above. The increment in the H

value decreased with the increase in $\text{Ti}(\text{OH})_4$ mediated nanoparticles. The H value increment remained unaffected by the concentration of nanoclay and nanowhiskers, while the value increased with the concentration of TiO_2 and nanosilica containing nanocoating. The maximum increment was approximately 41% for 0.5 wt. % TiO_2 nanoparticles containing nanocoating. This H value was approximately 188% higher compared to that of PL based coating.

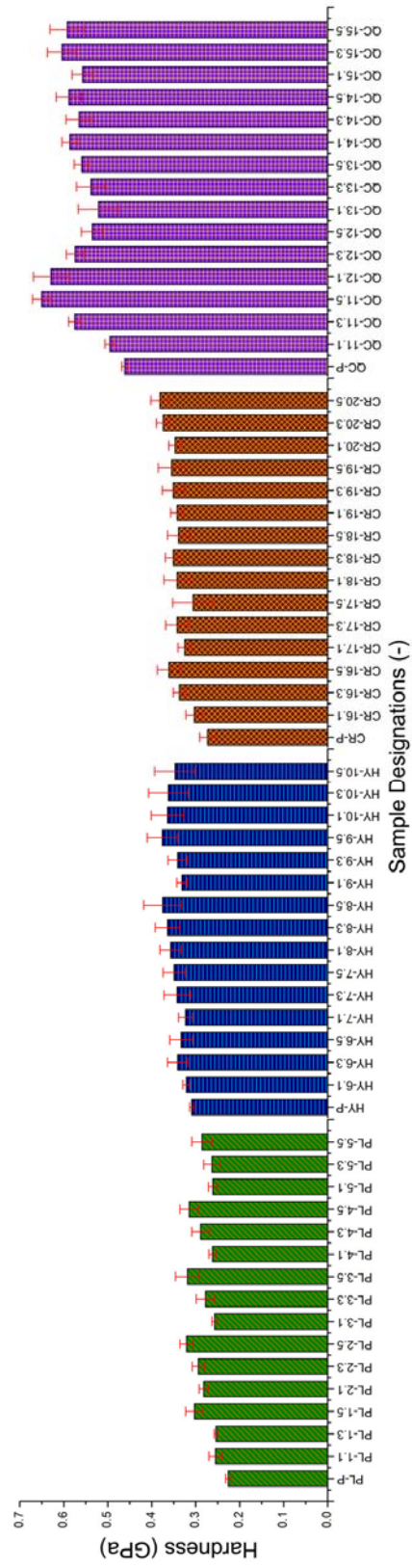


Fig. 5.12. The hardness (H) values obtained on 4 coatings and 60 nanocoatings.

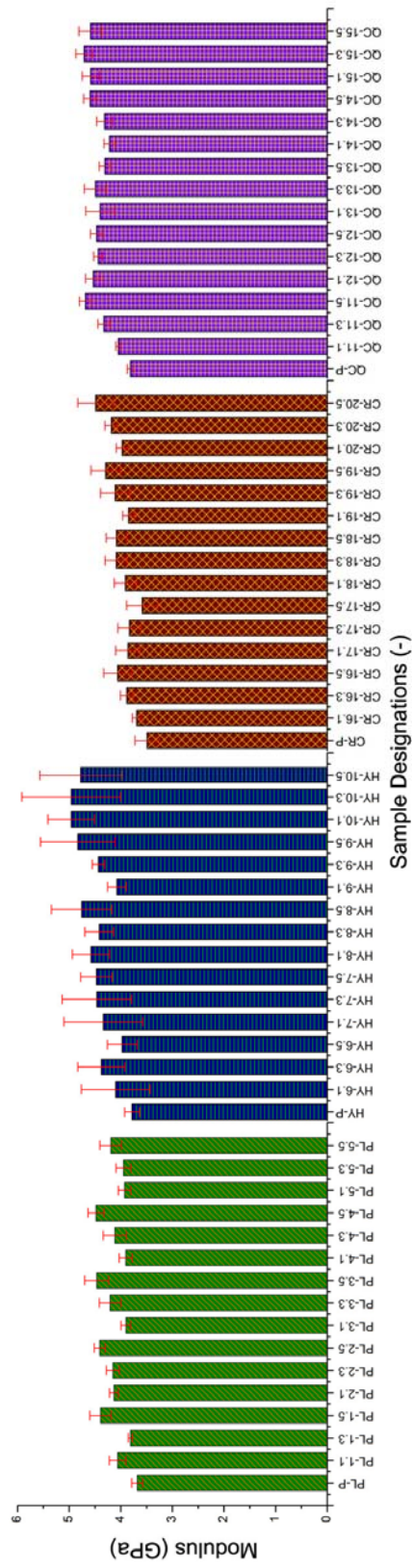


Fig. 5.13. The Young's modulus (E) values obtained on 4 coatings and 60 nanocoatings.

5.3.2 Effect of Nanoparticles Concentration on Scratch Testing of Nanocoatings

The nanomechanical parameters derived from nanoscratch testing of nanocoatings are shown in Tables 5.5–5.8.

It was expected that increasing the concentration of nanoparticles would increase the load bearing capacity of the nanocoatings. However, mixed results were obtained for PL nanocoatings. The critical load was highest for the 0.5 wt. % TiO₂ nanoparticles containing nanocoating. The first sign of a crack or fracture appeared at a depth of 8.5 μm, indicating that the coating was securely adhered to the metal surface and probably delamination followed fracture. The delamination was assessed on the basis of final surface morphology. A slight improvement was observed for nanowhiskers containing nano-coating that showed a high value for the total height of the groove, suggesting that the nanocoating was severely damaged during the scratch.

In the case of HY nanocoatings, the maximum value of the critical load was observed for the nanocoating containing 0.3 wt. % SiC nanowhiskers. The penetration depth at critical load was 6.9 μm, while the coating thickness was within 8 μm, suggesting that a crack or fracture may have occurred well before the nanocoating delamination. The total height of the groove and pile-up height of the nanocoating was moderate, suggesting that the nanocoating was toughened due to the presence of epoxy polymer in the coating formulation. The critical load value decreased when a higher amount of TiO₂ nanoparticles were added, probably due to agglomeration of nanoparticles in the final coated structure.

In the case of CR nanocoatings, the critical load value showed linear enhancement when more nanoparticles were added. The maximum critical load took place when 0.5

wt% TiO₂ nanoparticles were added. The estimated thickness of the coating was within 6 μm, while the depth of penetration at critical load was 4.8 μm, suggesting that fracturing and delamination occurred simultaneously. The minimum improvement in the critical load was observed 0.1 and 0.3 wt% Ti(OH)₄ nanoparticles containing nanocoatings. The scratch width and pile-up height were highest in the case of the SiC nanowhiskers containing nanocoating, suggesting its brittle nature.

In the case of QC nanocoating, the change in the critical load value was random when higher concentrations of nanoparticles were added in the nanocoatings. The maximum enhancement in the critical load value was achieved for 0.5 wt. % TiO₂ nanoparticle containing nanocoating. The estimated thickness of this nanocoating was approximately 5 μm, while the penetration depth at the critical load was approximately 5.3 μm, suggesting that fracture may have occurred with chipping-off the coating metal surface. It is important to mention that the critical load value decreased in the case of Ti(OH)₄ and SiC containing nanocoating. The decrease in the critical load value in the former case is not yet fully understood. The decrease in the critical load value in the later case could be due to the agglomeration of nanowhiskers in the area of the scratch. The residual scratch depth and pile-up height were low in all of the QC nanocoatings, clearly indicating that the coating was elastic and that the failure occurred through brittle failure followed by chipping off the coated surface.

Table 5.5 Nanomechanical parameters derived from nanoscratch testing of PL nanocoatings.

Test	Critical Load (mN)	Penetration Depth at Critical Load (nm)	Scratch Width (μm)	Total Height of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
PL-1.1	134.527	5996.786	9.786	152.892	138.152	14.74
PL-1.3	241.47	9412.913	8.818	112.655	67.709	44.946
PL-1.5	219.514	8543.318	9.606	152.51	69.445	83.064
PL-2.1	101.503	5343.954	11.65	207.922	169.806	38.116
PL-2.3	153.713	6323.38	11.972	270.519	211.483	59.036
PL-2.5	204.567	6918.257	11.399	238.202	193.984	44.218
PL-3.1	172.53	7444.257	10.789	225.435	105.508	119.927
PL-3.3	78.457	4480.693	11.757	261.354	137.631	123.723
PL-3.5	145.718	6724.217	11.936	251.275	194.796	56.48
PL-4.1	166.743	6142.846	10.789	231.213	74.991	156.222
PL-4.3	140.491	5353.909	11.972	265.272	185.209	80.063
PL-4.5	87.489	4993.817	12.187	251.904	180.039	71.865
PL-5.1	73.51	4237.892	11.865	242.474	222.717	19.757
PL-5.3	119.509	5312.556	12.761	360.11	270.575	89.535
PL-5.5	86.474	4541.261	11.793	283.787	258.592	25.195

Table 5.6 Nanomechanical parameters derived from nanoscratch testing of HY nanocoatings.

Test	Critical Load (mN)	Penetration Depth at Critical Load (nm)	Scratch Width (μm)	Total Height of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
HY-6.1	220.741	4873.448	47.344	14.828	10.455	4.373
HY-6.3	137.497	3952.548	47.423	39.079	20.505	18.574
HY-6.5	126.719	3763.53	73.446	36.275	15.246	21.03
HY-7.1	235.323	5277.836	66.887	19.713	12.16	7.553
HY-7.3	272.585	5962.099	56.826	17.222	14.023	3.199
HY-7.5	197.773	4548.139	57.173	20.024	15.005	5.019
HY-8.1	215.554	4402.404	77.604	27.679	11.947	15.732
HY-8.3	224.6	5182.784	34.375	27.422	2.888	24.534
HY-8.5	191.726	4451.291	73.116	34.919	33.986	0.932
HY-9.1	248.561	4614.452	73.59	25.881	22.622	3.258
HY-9.3	352.77	6885.242	55.058	41.276	20.967	20.309
HY-9.5	215.75	4133.273	86.35	29.155	16.237	12.918
HY-10.1	311.84	5658.775	56.742	51.148	31.98	19.168
HY-10.3	384.648	6938.772	45.666	23.377	15.19	8.187
HY-10.5	242.562	4709.329	39.143	64.731	19.049	45.681

Table 5.7 Nanomechanical parameters derived from nanoscratch testing of CR nanocoatings.

Test	Critical Load (mN)	Penetration Depth at Critical Load (nm)	Scratch Width (μm)	Total Height of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
CR-16.1	215.492	4248.608	33.873	52.72	44.131	8.589
CR-16.3	268.194	5061.331	77.282	88.204	63.547	24.658
CR-16.5	275.82	4810.916	67.926	75.812	37.156	38.656
CR-17.1	162.201	4026.557	73.518	28.334	10.239	18.095
CR-17.3	162.802	4403.569	65.847	39.183	29.044	10.139
CR-17.5	186.888	3888.585	62.621	48.558	19.251	29.307
CR-18.1	223.263	4464.355	40.326	36.587	23.579	13.008
CR-18.3	230.164	4567.749	77.21	92.85	80.666	12.183
CR-18.5	248.779	4501.918	56.097	86.767	50.898	35.869
CR-19.1	218.161	3612.262	59.933	50.287	7.177	43.11
CR-19.3	220.498	4148.714	98.573	295.511	285.467	10.044
CR-19.5	281.19	5535.928	21.077	273.982	57.042	216.94
CR-20.1	182.264	4368.316	71.905	932.96	133.349	799.611
CR-20.3	249.701	3313.606	80.293	5086.981	2899.408	2187.573
CR-20.5	261.714	2115.557	85.06	142.659	91.266	51.393

Table 5.8 Nanomechanical parameters derived from nanoscratch testing of QC nanocoatings.

Test	Critical Load (mN)	Penetration Depth at Critical Load (nm)	Scratch Width (μm)	Total Height of the Groove (nm)	Residual Scratch Depth (nm)	Pile Up Height (nm)
QC-11.1	96.523	4060.043	85.598	59.063	47.69	11.372
QC-11.3	136.738	4083.384	95.67	659.789	617.616	42.173
QC-11.5	165.499	5358.572	95.778	32.637	29.544	3.093
QC-12.1	76.197	3243.69	91.01	45.603	36.942	8.66
QC-12.3	59.719	2789.54	85.42	86.339	73.469	12.87
QC-12.5	95.478	3965.994	73.41	31.671	23.823	7.848
QC-13.1	57.458	3576.32	52.441	50.788	33.572	17.216
QC-13.3	96.495	3867.71	63.147	48.537	30.87	17.667
QC-13.5	91.717	3912.693	99.004	195.063	173.415	21.648
QC-14.1	82.459	3190.579	45.236	51.754	44.256	7.498
QC-14.3	93.678	3734.058	100.402	59.991	59.653	0.338
QC-14.5	59.689	2731.622	70.758	58.59	29.931	28.658
QC-15.1	63.524	2927.815	55.201	46.556	38.146	8.41
QC-15.3	76.689	3236.785	97.892	2255.369	2226.573	28.796
QC-15.5	77.687	3188.18	95.025	31.929	18.894	13.035

5.3.3 Effect of Nanoparticles Concentration on Dynamic Mechanical Properties of Nanocoatings

In this section we discuss how increasing the amounts of nanoparticles in nanocoatings change their visco-elastic properties [61, 62]. E' and E'' curves for different nanocoating concentrations as a function of test frequencies are shown in Fig 5.14–5.17.

In the case of PL nanocoatings, increasing the nanoparticles concentration had only a negligible effect on the E' value except in the case of $\text{Ti}(\text{OH})_4$ containing nanocoating. The E' value remained unaffected by test frequency in all the nanocoatings except $\text{Ti}(\text{OH})_4$ containing nanocoating and in this case the value fluctuated with the change in test frequency. Similarly, E'' values fluctuated with the increase in nanoparticles concentration and test frequency.

In the case of HY nanocoatings, the E' value showed variation with nanocoating compositions. The E' value in the case of TiO_2 nanocoating was highest at 5 Hz test frequency for 0.3 wt% nanoparticles. Similarly, E' value was highest at 5 Hz for 0.1 wt% MMT nanoclay nanocoating. The highest E' value was recorded for nanosilica containing nanocoating. On the other hand, there was no significant change observed in E'' values for most of the nanocoatings except in composition containing SiC nanowhiskers in which case the value fluctuated at 15 Hz test frequency. The reason for this anomalous behavior is not known.

In the case of CR nanocoatings, the E' values were constant and independent of nanoparticles concentrations and test frequencies for TiO_2 , $\text{Ti}(\text{OH})_4$ and MMT containing nanocoatings. The E' value increased slightly with increasing nanoparticles concentration

for nanosilica and nanowhisker containing nanocoatings. On the other hand, E'' values varied significantly according to the type of nanoparticles. The E'' values enhanced for nanosilica and nano-whiskers containing nanocoatings, while the lowest value was recorded for MMT containing nanocoating.

In the case of QC nanocoatings, the E' value remained unaffected by the concentration of nanoparticles and test frequency. A low E' value was recorded for TiO_2 and $\text{Ti}(\text{OH})_4$ containing nanocoatings. The E' values were similar for the other three nanocoatings. The E'' values, on the other hand, were random and varied with the test frequency. There was no significant variation observed in the E'' value with the change in the concentration of nanoparticles.

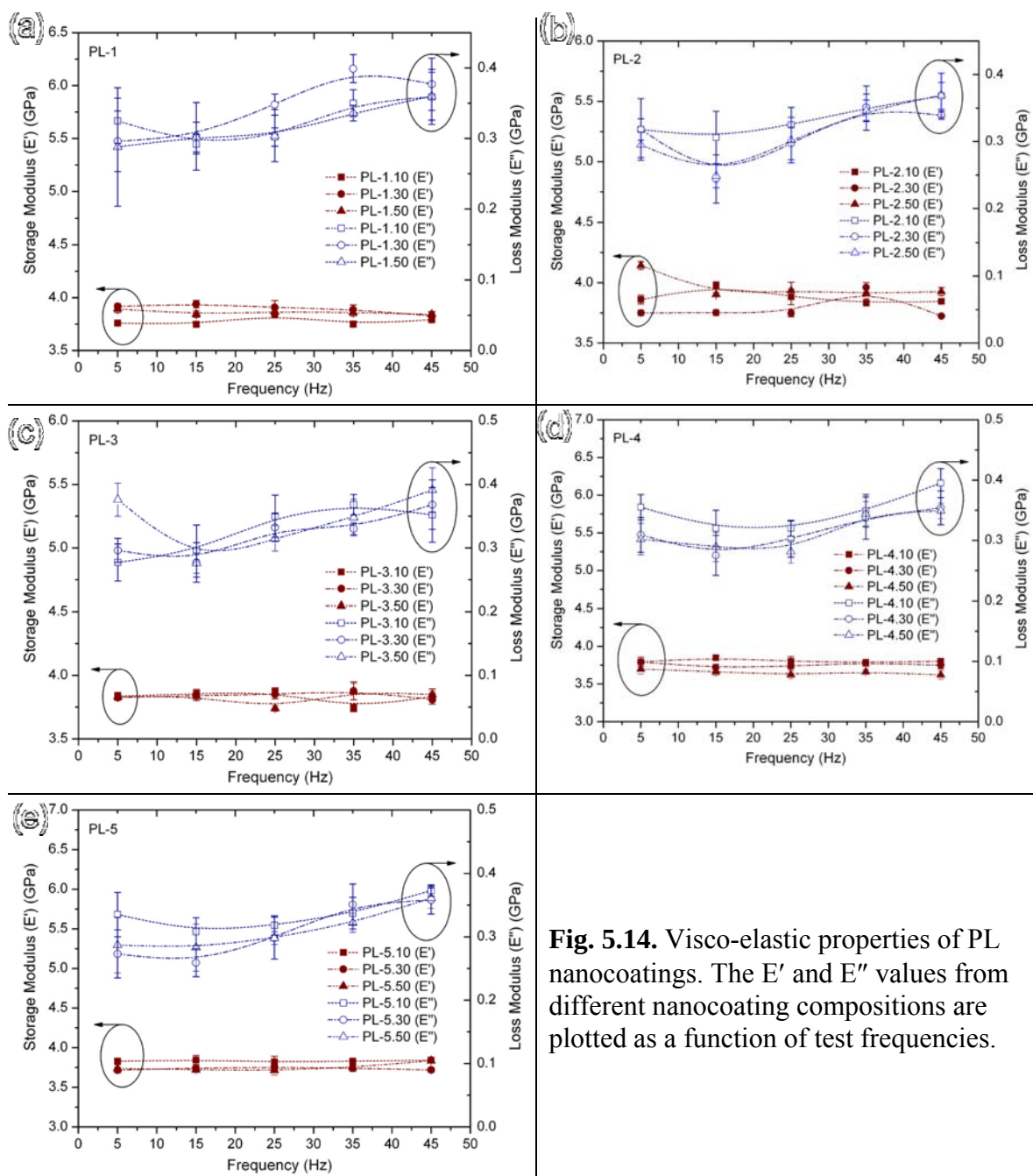


Fig. 5.14. Visco-elastic properties of PL nanocoatings. The E' and E'' values from different nanocoating compositions are plotted as a function of test frequencies.

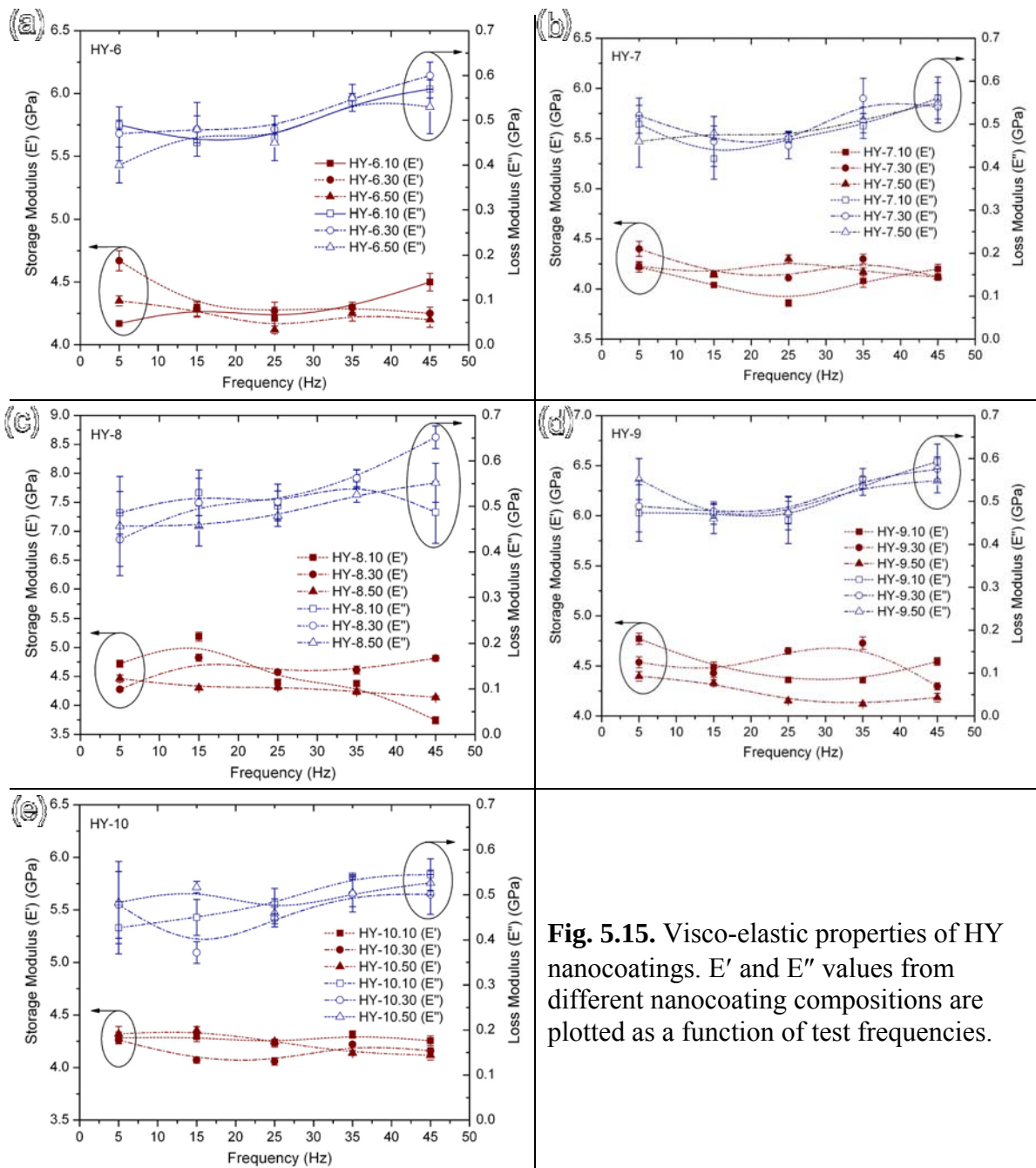


Fig. 5.15. Visco-elastic properties of HY nanocoatings. E' and E'' values from different nanocoating compositions are plotted as a function of test frequencies.

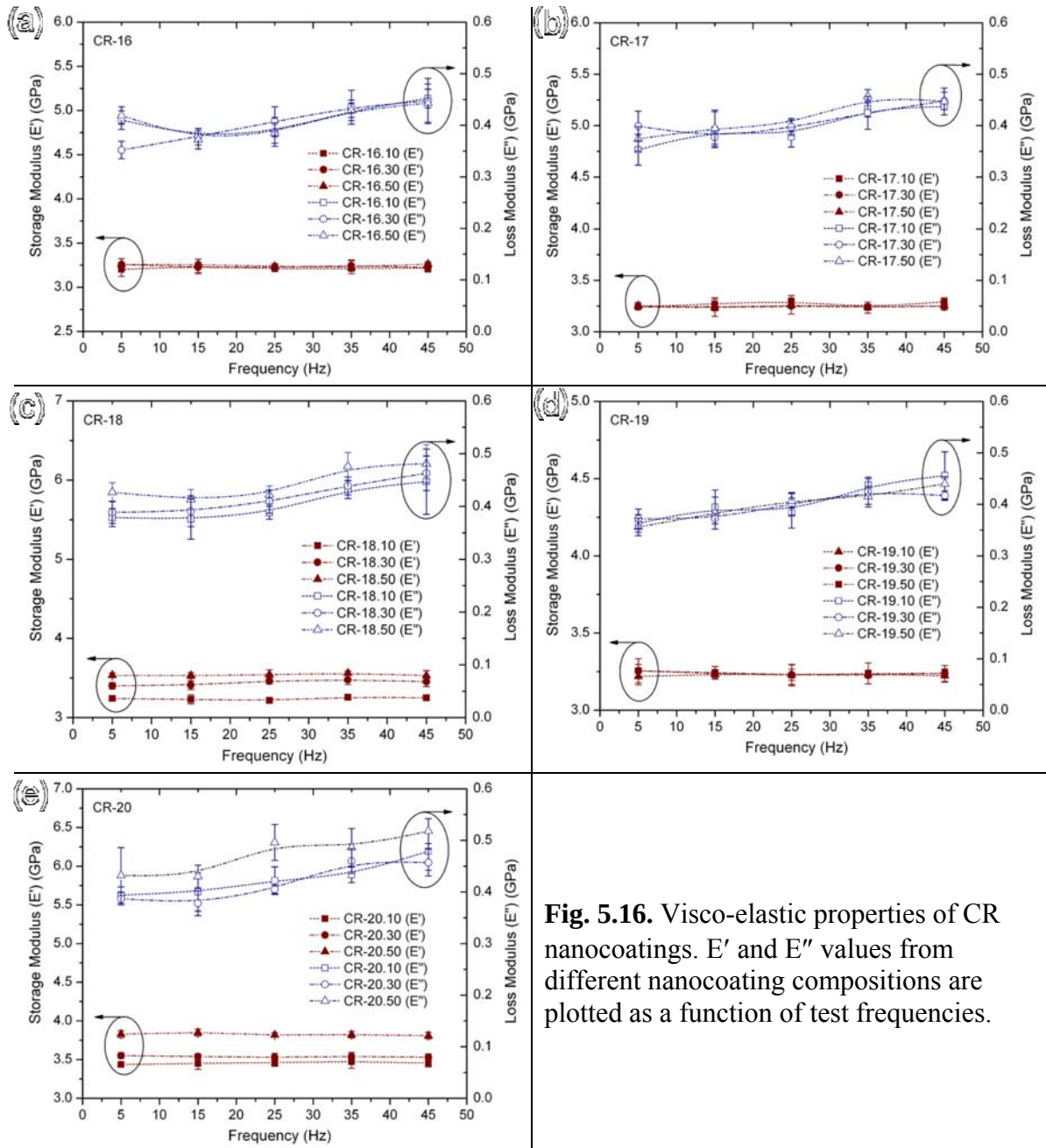


Fig. 5.16. Visco-elastic properties of CR nanocoatings. E' and E'' values from different nanocoating compositions are plotted as a function of test frequencies.

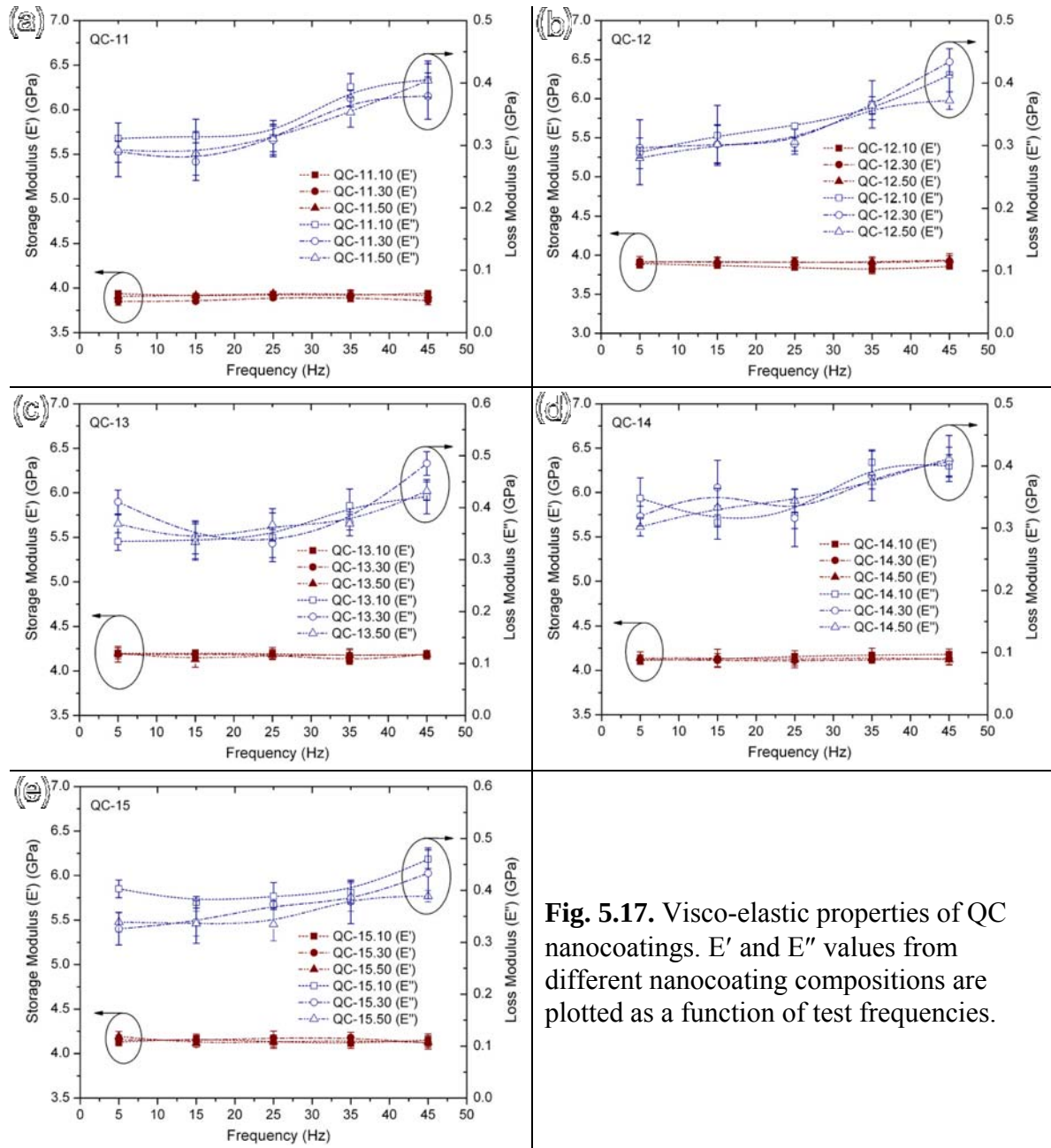


Fig. 5.17. Visco-elastic properties of QC nanocoatings. E' and E'' values from different nanocoating compositions are plotted as a function of test frequencies.

Chapter 6

CONCLUSIONS

In this research, four different coatings were developed based on varying amounts of hydrocarbon and silicone content. The resultant coatings were described as polymer, hybrid, ceramer and quasi-ceramic according to their chemical structures. The coatings were modified with five different nanoparticles that were chosen based on their shapes and properties. It was discovered that the incorporation of nanoparticles significantly modified the properties of the resulting nanocoatings. The dispersion of nanoparticles and their interfacial interactions with the surrounding matrix played a critical role in controlling the nano-mechanical properties of the resulting nanocoatings.

The five nanoparticles chosen for this study were TiO_2 , in-situ generated titanium nanoparticles using titanium ethoxide, functionalized SiO_2 , montmorillonite nanoclay and SiC nano-whiskers. The nanocoatings containing 0.1, 0.3 and 0.5 wt. % of each nanoparticle were used in different coating compositions. Each coating and nanocoating was characterized using FTIR spectroscopic technique, which confirmed the presence of nanoparticles in the nanocoatings. It was discovered that the nanoparticles were held in the coatings through hydrogen bonding except in the case of titanium ethoxide and functionalized nanosilica containing nanocoating in which chemical bonding was seen between the nanoparticles and backbone of the coatings.

Atomic force microscopy was used to scan the scratched coated surface. It was found that the PL epoxy based polymer coating consisted of a smooth surface that was

compressed when scratched using a nanoindenter. The HY hybrid coating showed a rough surface and a damaged recovery after the scratch test. The CR ceramer coating showed roughness in a nanometer dimension that originated from the roughness on the polished aluminum surface. The scratch on the CR coated surface was brittle but smooth with little to no elastic recovery. The QC quasi-ceramic coating showed fine surface morphology with roughness associated with the polished aluminum substrate. The scratch on the QC coated surface was brittle without elastic recovery.

The pristine coatings were tested for their nano-mechanical properties using the nanoindentation technique. The HY coating showed H hardness value that was 37% higher compared to PL coating. Similarly, the H value shown on the CR coating was 21 % higher compared to that of PL coating. The H value in the case of QC coating was 104 % higher compared to that of PL coating. The E modulus value was either a little lower or similar to that in the PL coating. These results suggest that HY coating was stronger than pristine PL and CR coating. Also, QC coatings consisted of densely packed crosslinked network compared to other coatings discussed here.

Scratch tests were performed on pristine coatings using a Berkowich indenter. No clear fracture was observed in the PL coating that was damaged at the critical load of 61 mN. This coating suffered major plastic deformation. HY coating was initially compressed during the scratch followed by a brittle fracture at 170 mN critical load. The SEM images of the damaged surface confirmed the brittle failure in the coating as a result of the penetration of the nanoindenter tip. A significant level of delamination was observed in the coating around the region of the scratch, suggesting the presence of residual stresses in the coating network. Similarly, the CR coating was damaged through

brittle fracture at a critical load of 160 mN and delamination followed the fracture. The failure in QC coating was brittle at a critical load of 84 mN. Moreover, the SEM micrographs suggest that the entire coated substrate chipped off at the end of the scratch test. The scratch test suggests that HY hybrid coating possesses an extreme tendency to resist the damage compared to the other three coatings. The presence of hydrocarbon in the hybrid coating compositions may impart better resilience capability to the coating, enhancing its fracture toughness.

The SEM micrographs were acquired for the initiation, propagation and termination steps in coating during the scratch test that helped elucidate the modes of failure. The COF values were recorded as a function of the scratch distance. High COF values were obtained for PL and QC coatings. The presence of hydrocarbon bearing silicone was attributed for the low COF value in the HY coating. The cross profile topography of the scratched surface suggests that the hybrid coating has better scratch resistance compared to that of pristine polymer and ceramer coatings. The moderate depth of penetration was seen in QC coating suggests high hardness and elastic nature.

Upon adding 0.1% nanoparticles, the nano-mechanical properties of the resultant nanocoatings increased significantly. For PL nanocoatings, the H value increased after adding $\text{Ti}(\text{OH})_4$, while E increased with the addition of SiO_2 . For HY and CR nanocoatings, the H value increased upon adding SiC. The critical load bearing capacity of nanocoatings increased upon adding nanoparticles when tested through nanoscratch. The addition of 0.1 wt% SiO_2 , the CL value increased in PL and CR nanocoatings, while SiC increased in HY nanocoating. Surprisingly, the critical load value decreased abruptly in QC nanocoating upon adding nanoparticles, probably due to the increased crosslinking

in the rigid network. The COF value increased in the PL nanocoatings upon adding SiO₂ or MMT. The addition of Ti(OH)₄ increased the COF value in the HY nanocoating but decreased it in the CR nanocoating. In the case of the QC nanocoatings, the COF value remained constant and unaffected by nanoparticles additions.

The addition of higher concentration of nanoparticles (up to 0.5 wt.%) increased the H value in the nanocoatings. A high H value improvement up to 42% for PL and 21% for HY (compared to pristine) was achieved in nanocoatings upon adding SiO₂ nanoparticles. The addition of a higher concentration of SiC in the CR coating increased the H value up to 39%. Similarly, the addition of TiO₂ increased the H value up to 41% in the QC nanocoatings. The highest H value in QC nanocoating was approximately 188% higher than that of the pristine PL coating. The scratch resistant increased in nanocoatings with the increase in nanoparticles concentrations. This increment, however, was random and depended on the type of nanoparticles. The critical load value increased in PL nanocoatings upon adding 0.5 wt% TiO₂, but the coating turned brittle and delaminated. Similarly, the critical load value increased in the HY nanocoatings upon adding 0.3 wt.% SiO₂ nanoparticles. The addition of 0.5 wt% TiO₂ increased the critical load value in both CR and QC nanocoatings.

The visco-elastic behavior of the coating and nanocoatings was tested at 5 different frequencies using nanoindentation technique. For pristine coatings, the storage modulus (E') remained independent of test frequency while loss modulus (E'') increased slightly with the increase in test frequencies. The CR coating showed highest and the HY coating showed lowest E' values. The E'' was high for the HY coating and nearly uniform for all other coatings.

Upon adding nanoparticles, the visco-elastic behavior of resultant nanocoatings changed slightly. The E' value increased marginally in each case with the addition of nanoparticles. On the other hand, E'' values fluctuated with the change in nanoparticles and test frequencies. On further increase in nanoparticles concentrations, the E' increase for TiO_2 containing PL and in each case of the HY nanocoatings, and the SiO_2 containing CR nanocoatings. No change in the E' value was seen for QC nanocoatings. The E'' values, however, changed for all the nanocoating compositions. These results clearly demonstrate that incorporating of nanoparticles in the coating compositions modifies the network structures of the final coatings.

UNIQUE OBSERVATIONS

The FTIR spectroscopic studies have shown that coatings containing epoxy groups had large peaks corresponding to the high fraction of hydrocarbons. The number of peaks and their intensity decreased with the reduction in the hydrocarbon fraction due to epoxide groups and increasing amounts of the silicone in the coating formulation. On complete elimination of the epoxide groups and hence further reduction in the hydrocarbon fraction, the peaks from silanol and SiOSi backbone predominated the FTIR spectrum. When nanoparticles were added to coatings, the FTIR peak positions were sifted. A sharp FTIR stretching band was observed in the case of $\text{Ti}(\text{OH})_4$ and functionalized SiO_2 containing nanocoatings. This was likely due to the reaction between the reactive functionalities in the coatings and the active functionalities in the titanium compound and the polymeric coating on the SiO_2 particles. This suggests that the functionalized nanoparticles chemically modified the coating backbone structure while being physically bound within the macromolecular network of the coating.

The HY coating displayed higher hardness value compared to PL and CR coating due to an appropriate balance between epoxide and silanol functionality in the formulation. The QC coating displayed 104% higher hardness compared to PL coating due to highly crosslinked ceramic-type structure. However, modulus value in QC coating was similar to PL coating but lower than HY and CR coatings. When these coatings were scratched, the HY coating showed highest critical load value compared to other coatings due to the use of appropriate concentration of hydrocarbon and silicone in the formulation as discussed above. Additionally, the HY coating displayed better scratch resistant while QC coating showed brittle failure. The storage moduli of these coatings were independent of test frequencies while the loss modulus increased slightly with frequency. The highest modulus value was recorded for HY coating due to the relaxation processes associated with the polymer, ceramer and hybrid material domains.

When nanoparticles were added, the $\text{Ti}(\text{OH})_4$ and SiC containing nanocoatings showed increase in hardness and modulus values. The formation of new bonds between the titanium compound and coating functionalities could be attributed to the enhancement in nanomechanical properties. Similarly, high strength SiC nano whiskers bound within the macromolecular chains provided additional strength to the nanocoating network. When nanocoatings were scratched, the highest critical load was observed for SiO_2 modified nanocoatings except in case of QC nanocoating where TiO_2 enhanced the critical load. The loss and storage modulus values of nanocoating enhanced slightly with the addition of nanoparticles and maximum enhancement was observed on TiO_2 and nanoclay modification. The increase in free volume as a result of nano-modification could be attributed to such an effect. The hardness and modulus values changed on

increasing the concentration of nanoparticles. The maximum hardness improvement of 41% was observed for 0.5 wt.% TiO₂ containing QC nanocoating. The maximum modulus improvement was 32% for 0.5 wt.% SiC containing nanocoating. The incorporation of inorganic nanoparticles in higher concentration could be attributed to such an effect. When TiO₂ nanoparticle concentration was increased, the critical load value increased with increased tendency of delamination in the nanocoating. The agglomeration of nanoparticles and enhanced crosslinking density could be attributed to this effect.

VARIOUS PARAMETERS AFFECTING THE NANOMECHANICAL PROPERTIES

1) EFFECT OF BACKBONE STRUCTURE

Epoxy Polymer vs Hybrid: The hardness value increased in hybrid coating compared to pristine epoxy coating. However, the modulus value was similar in both the coatings. The enhanced cross-linking in hybrid coating and less defect sites in the hybrid network could be attributed to this effect. On comparing with pristine epoxy coating, the hybrid coating showed higher critical load required for the fracture confirming the strongly cross-linked network.

Hybrid vs Quasi Ceramic: The hardness as well as modulus value was higher in quasi-ceramic coating compared to hybrid coating. The higher amount of cross-linking and densely packed stronger ceramic bonds could be attributed to such an effect. On comparing with hybrid coating, the quasi-ceramic coating showed low critical load to fracture. The brittle nature of the quasi-ceramic network could be attributed to the low critical load value.

2) EFFECT OF NANOPARTICLES

Functionalized vs Inert: The functionalized nanoparticles (i.e. $\text{Ti}(\text{OH})_4$ or SiO_2) consist of high active surface area that helps in formation of stronger bonds with the continuous matrix. The inert inorganic nanoparticles (i.e. TiO_2 , MMT or SiC) on the other hand could be physically bound within the coating network that increases the inorganic contribution to the structure. The strong electronic interactions between the nanoparticles and continuous matrix could be attributed to the enhancement in the nanomechanical properties of the coatings.

Size effect: The size of the nanoparticles affects the condensation and hardening mechanism of the coating material. The larger size particle may interfere during the cross-linking process and may lead to defective network. The smaller nanoparticles however, could hide within the free volume of the material thereby reducing the defect sites and hence increasing the overall strength of the material. The in-situ generated TiO_2 nanoparticles through $\text{Ti}(\text{OH})_4$ may result into a self assembly within the network without affecting the condensation process between silanols. Such nanoparticles forms a better bonding network compared to the inorganic nanoparticles (i.e. TiO_2 , MMT or SiC) and therefore enhances the strength more than its counterparts.

Distribution: The agglomeration of nanoparticles in the coating formulation due to attractive van der Waals forces in is a challenging problem. The agglomeration results into microstructural in-homogeneities leading to stress concentration regimes. The functionalized nanoparticles (i.e. SiO_2) and in-situ generated nanoparticles (i.e. $\text{Ti}(\text{OH})_4$) are attracted towards the reactive sides (i.e. $-\text{OH}$ groups) in the matrix and therefore have less chances of agglomeration. Such uniformity in distribution of nanoparticles

results into high nanomechanical properties in nanocoatings compared to inert inorganic nanoparticles (i.e. TiO_2 , MMT or SiC).

UNIQUE CONTRIBUTION

- a) The development and characterization of four coating compositions containing three different concentrations of five different nanoparticles has been accomplished.
- b) A total of 64 coating and nanocoatings were tested for the variation in nanomechanical properties. The nanoindentation, nanoscratch and visco-elastic properties of the coatings and nanocoatings were investigated as a function of change in chemical structures of the material.

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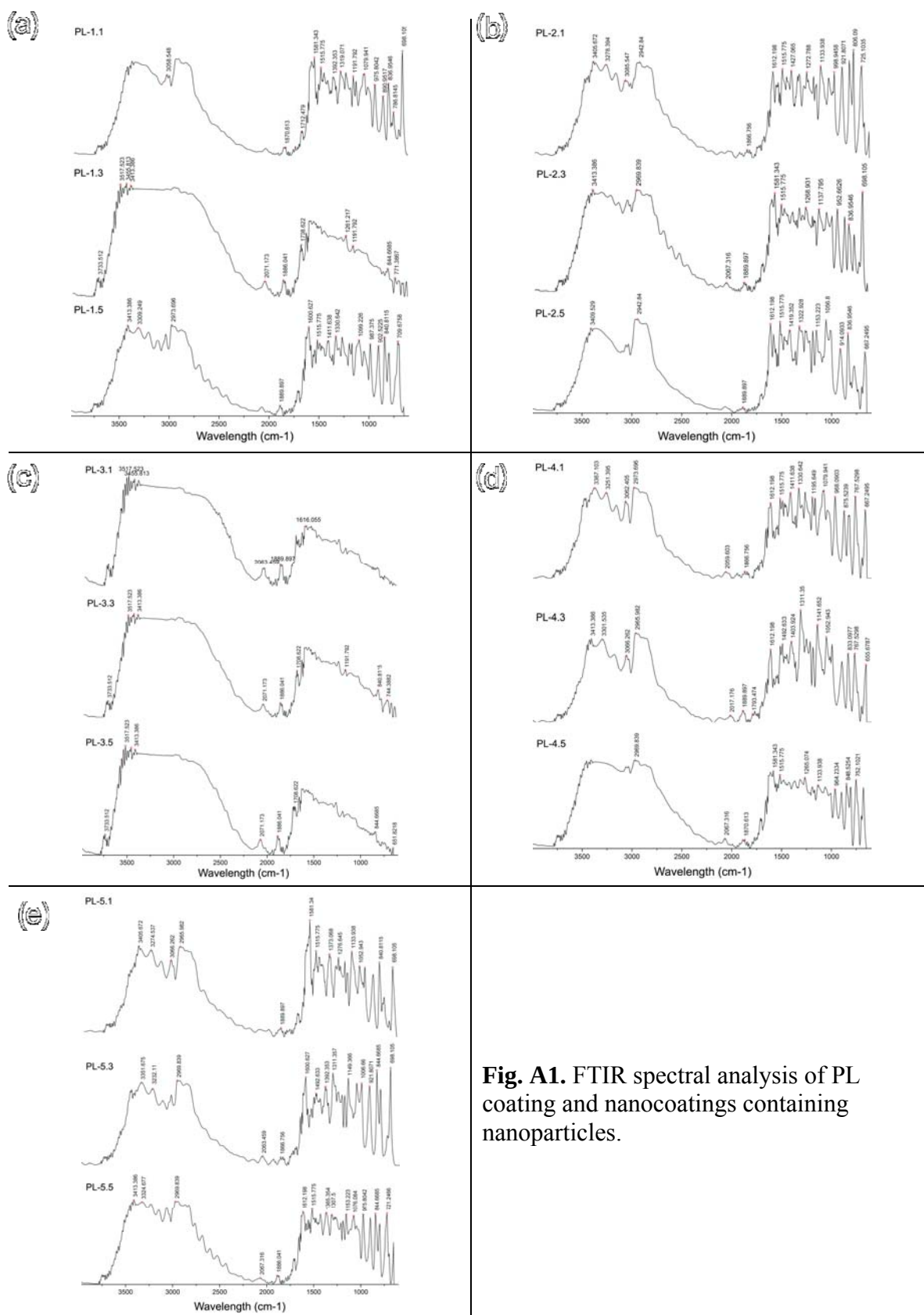
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APPENDIX A

This section appends the FTIR spectra recorded on nanocoatings. The spectrum from the nanocoatings consisting of 0.1, 0.3 and 0.5 wt.% nanoparticles were captured with the help of FTIR spectrophotometer operating in reflectance mode.



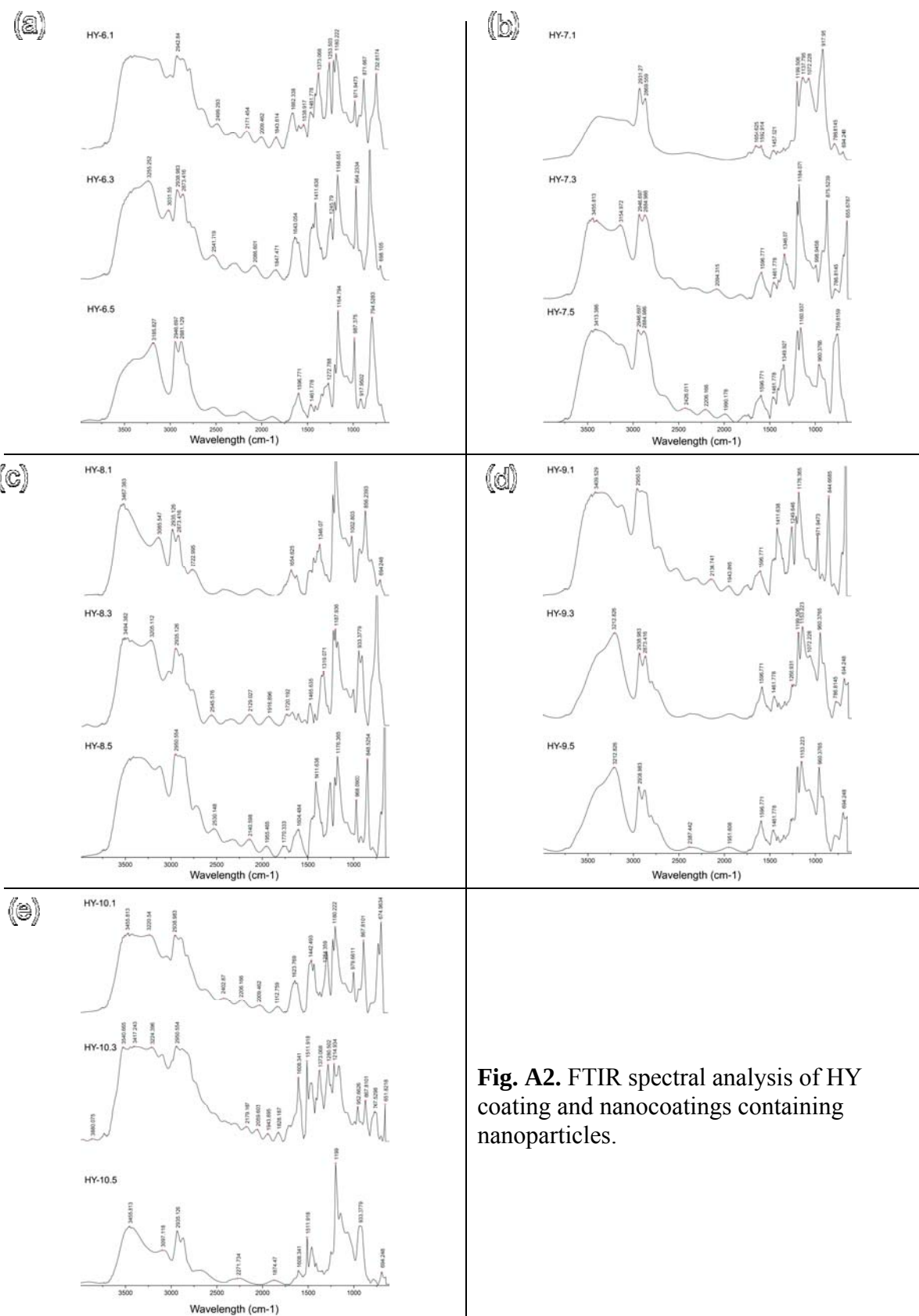
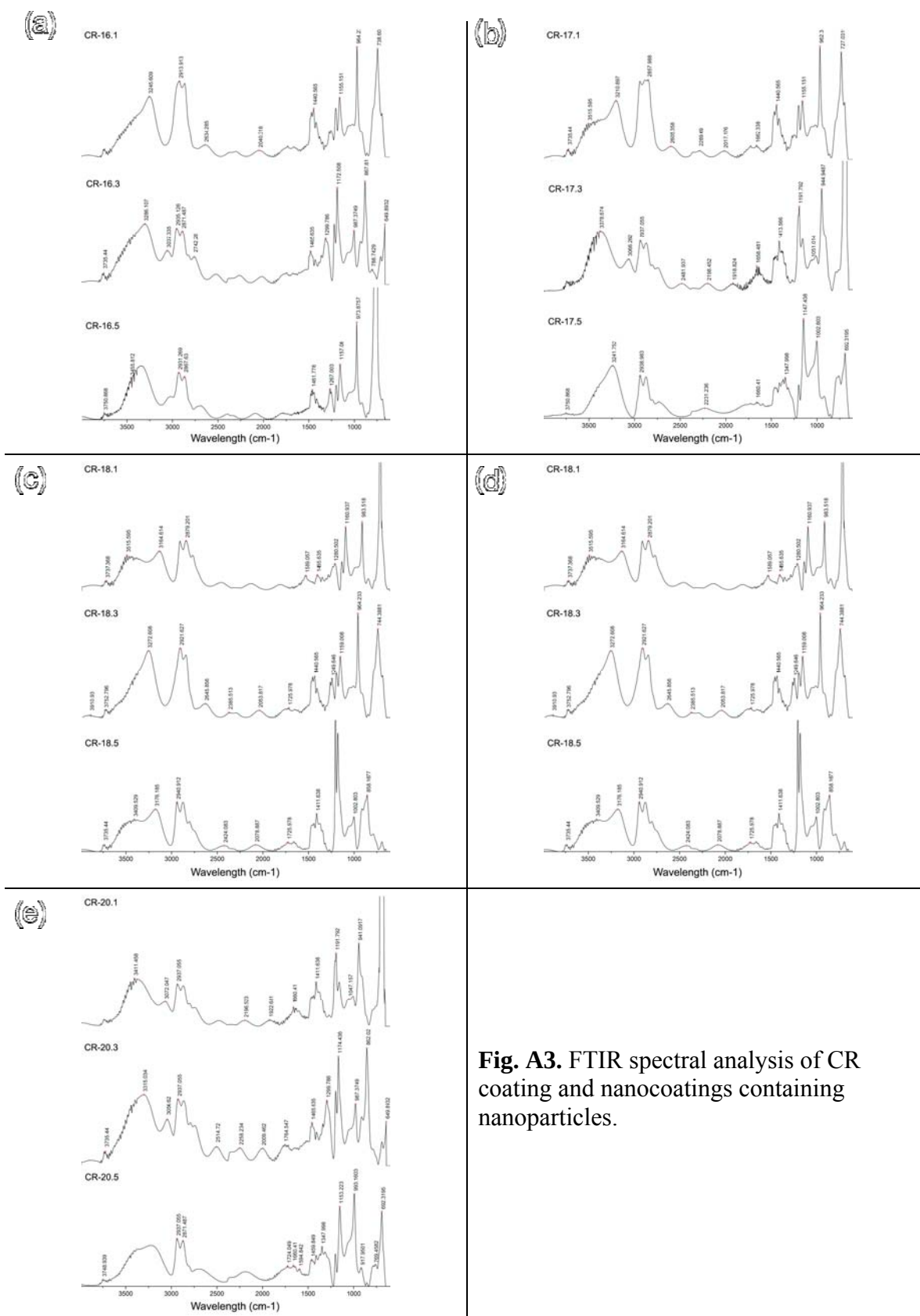
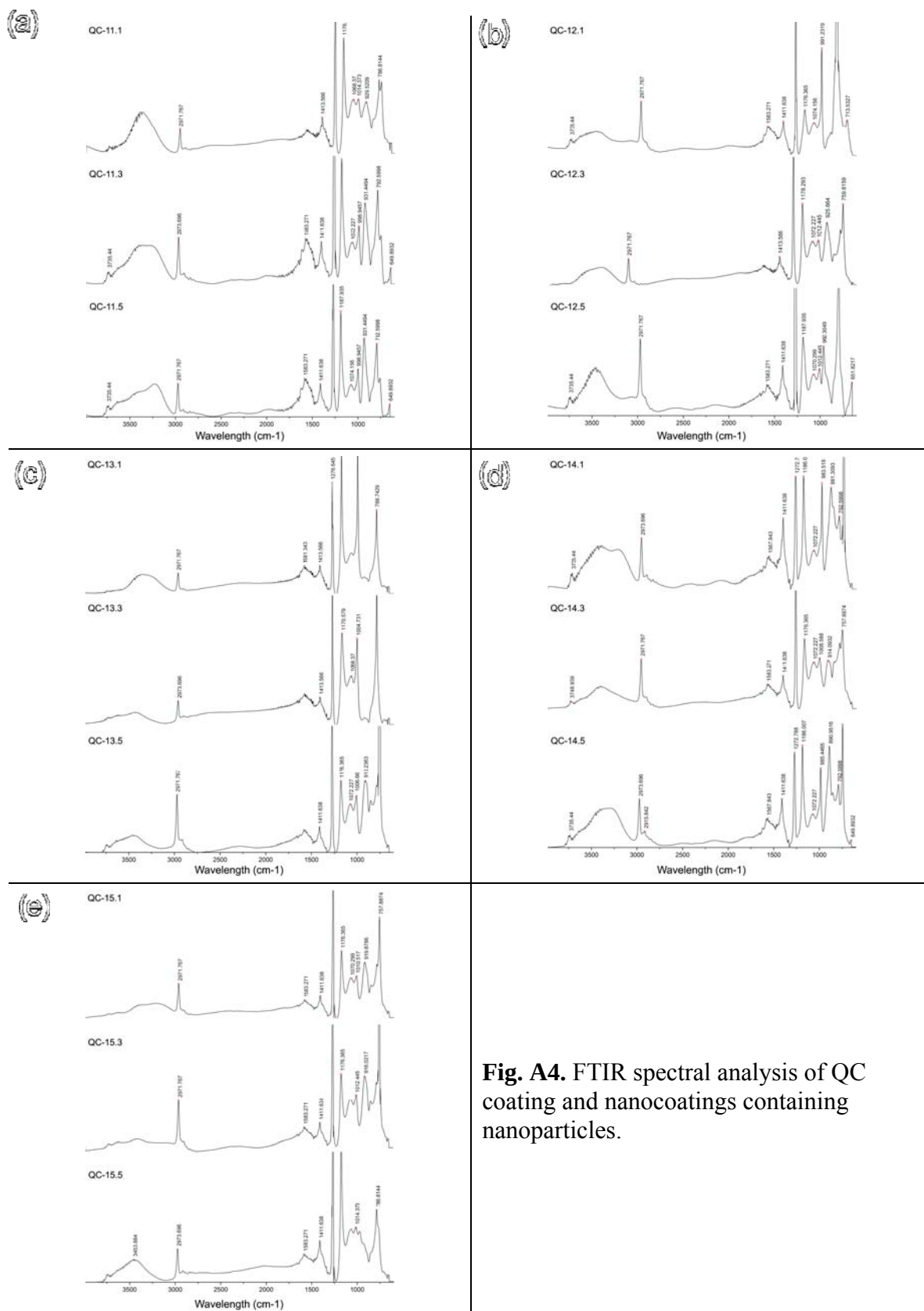


Fig. A2. FTIR spectral analysis of HY coating and nanocoatings containing nanoparticles.





APPENDIX B

This section appends the nanoindentation curves recorded on different pristine coatings. The load on sample is displayed as a function of displacement into the surface. The loading and unloading curves are used to calculate the hardness (H) and Young's modulus (E) values of the coating materials.

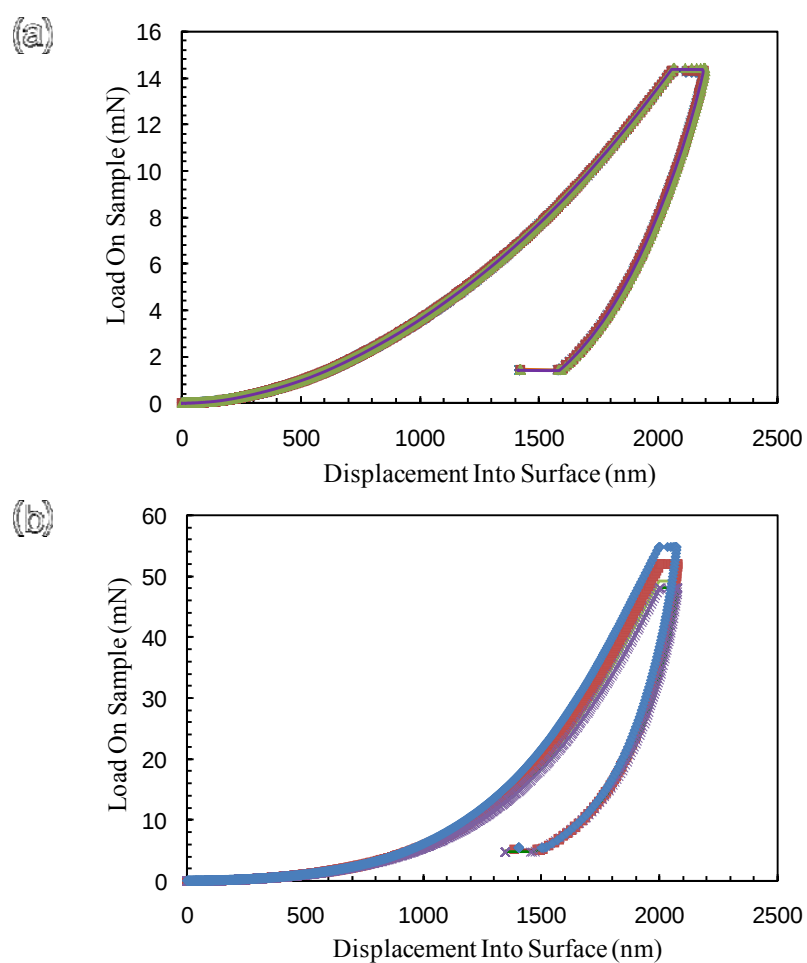


Fig. B1. Load on sample Vs displacement curves. (a) Pristine PL coating. (b) Pristine HY coating.

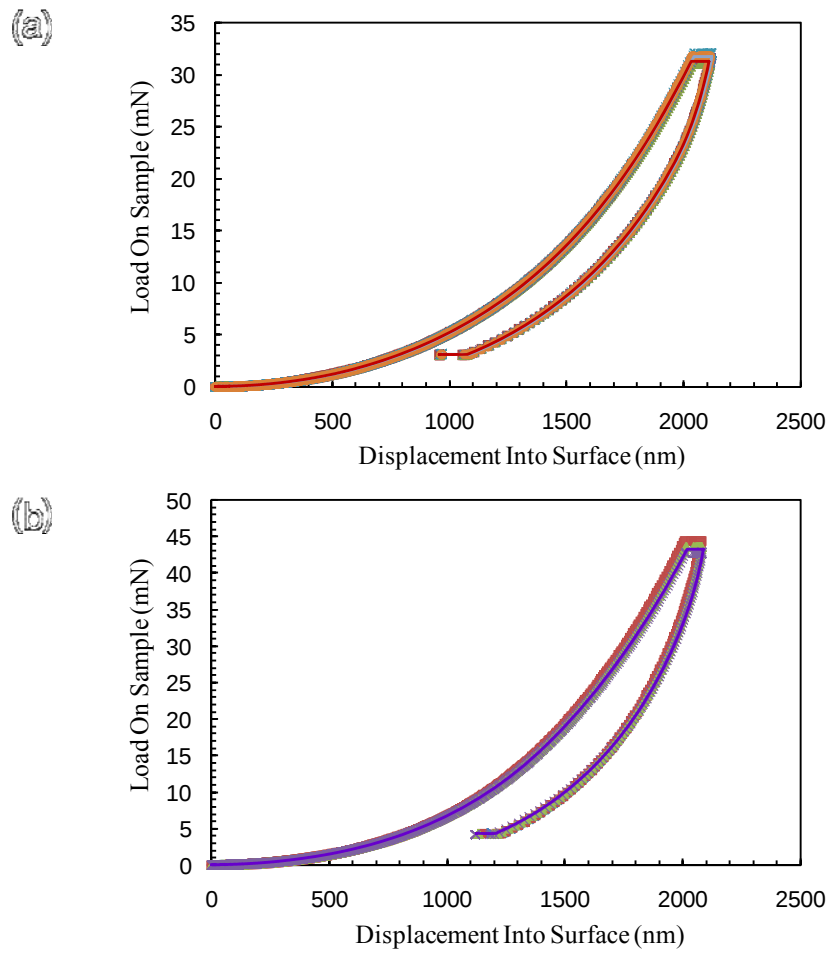


Fig. B2. Load on sample Vs displacement curves. (a) Pristine CR coating. (b) Pristine QC coating.

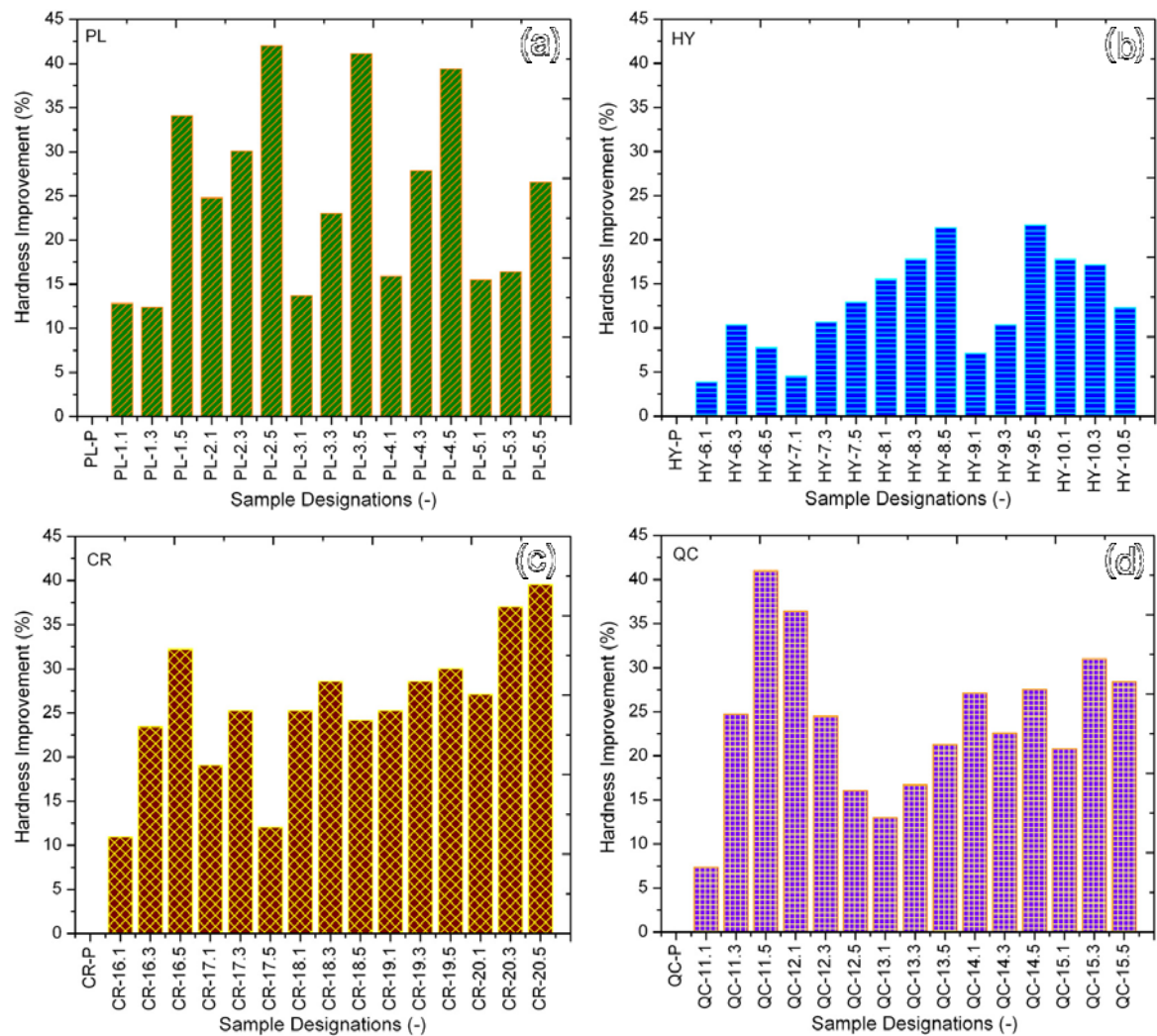


Fig. B3. Percentage improvement in H value in nanocoatings compared to pristine coatings.

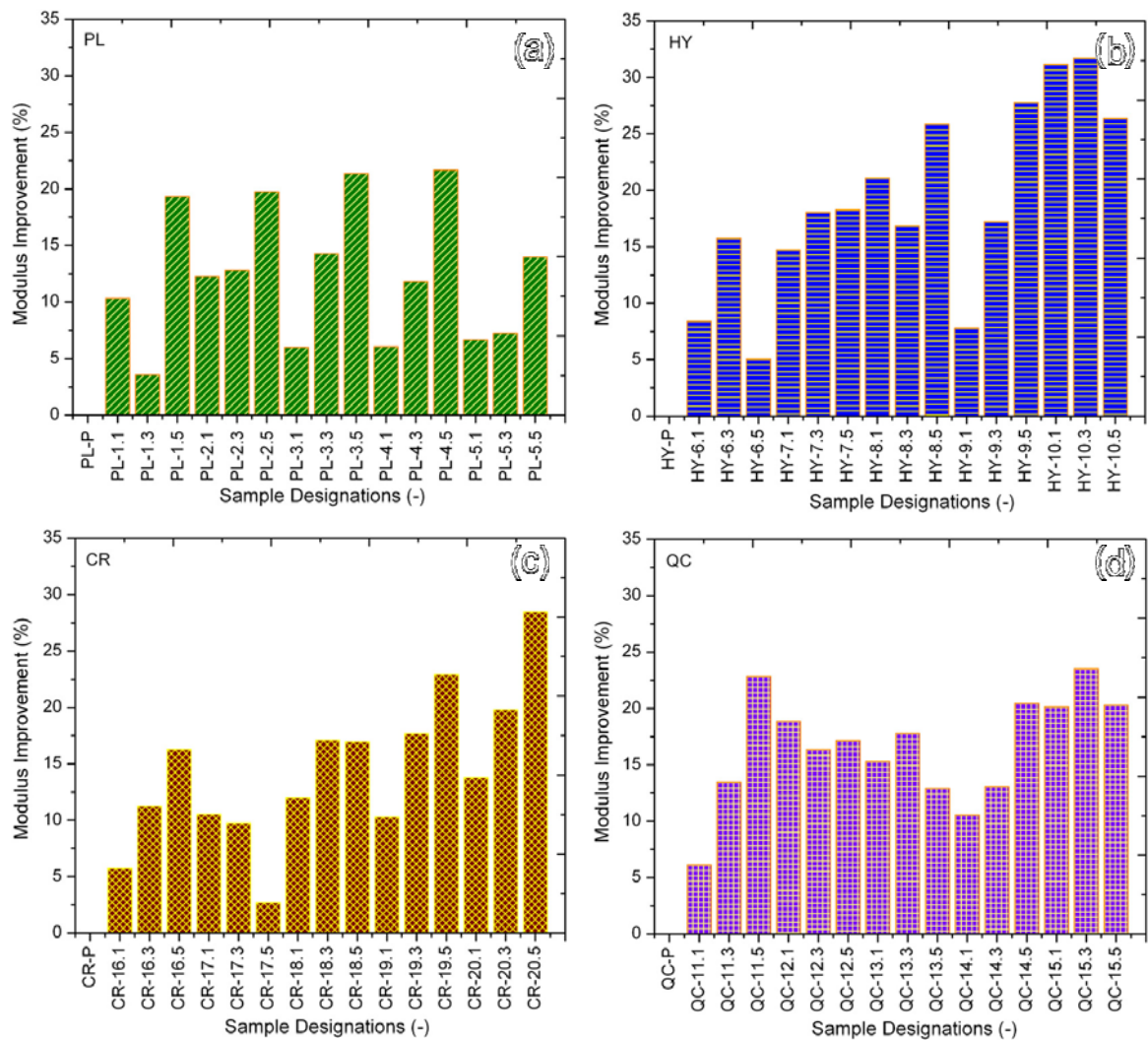


Fig. B4. Percentage improvement in E value in nanocoatings compared to pristine coatings.

APPENDIX C

This section appends the curves obtained from nanoscratch tests on coatings and 0.1 wt.% nanoparticles containing nanocoating. Curves are shown for additional information on the fracture and delamination occurring in the coating and corresponding nanocoatings. Such a comparison helps in compare the scratch properties of coatings and nanocoatings.

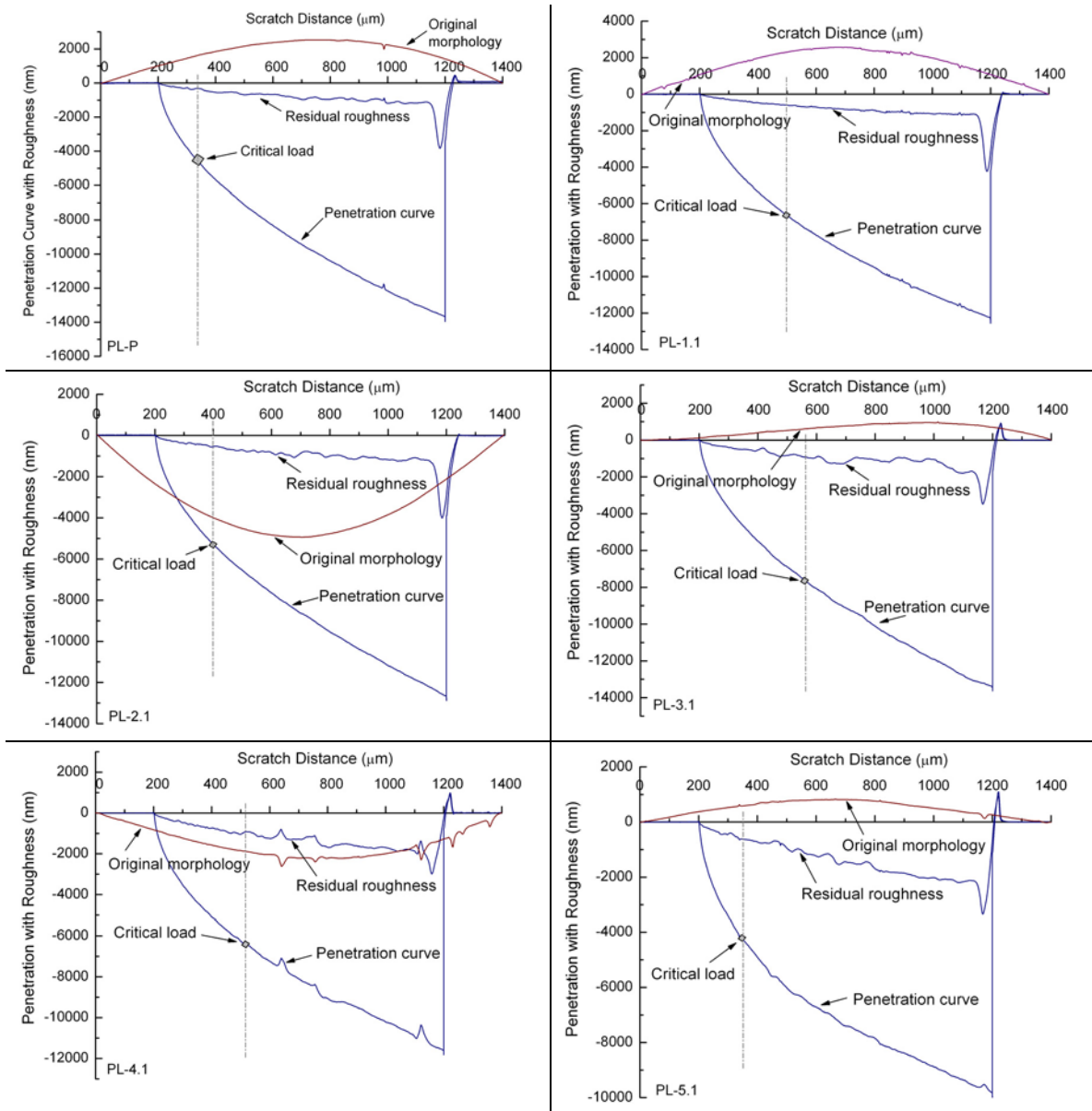


Fig. C1. Nanoscratch analysis of PL coating and nanocoatings. Penetration and roughness curves as a function of scratch distance.

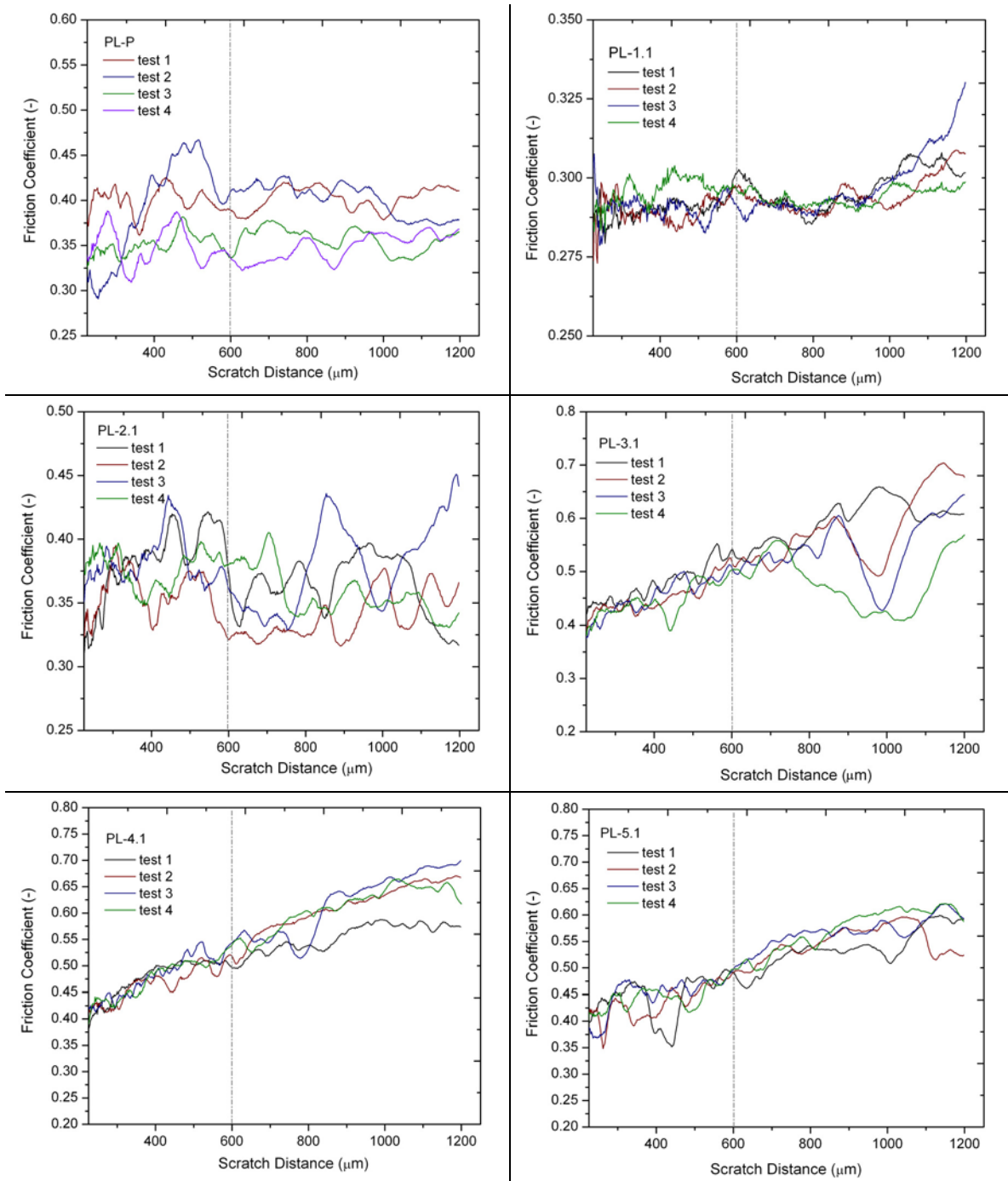


Fig. C2. Nanoscratch analysis of PL coating and nanocoatings. COF curves as a function of scratch distance.

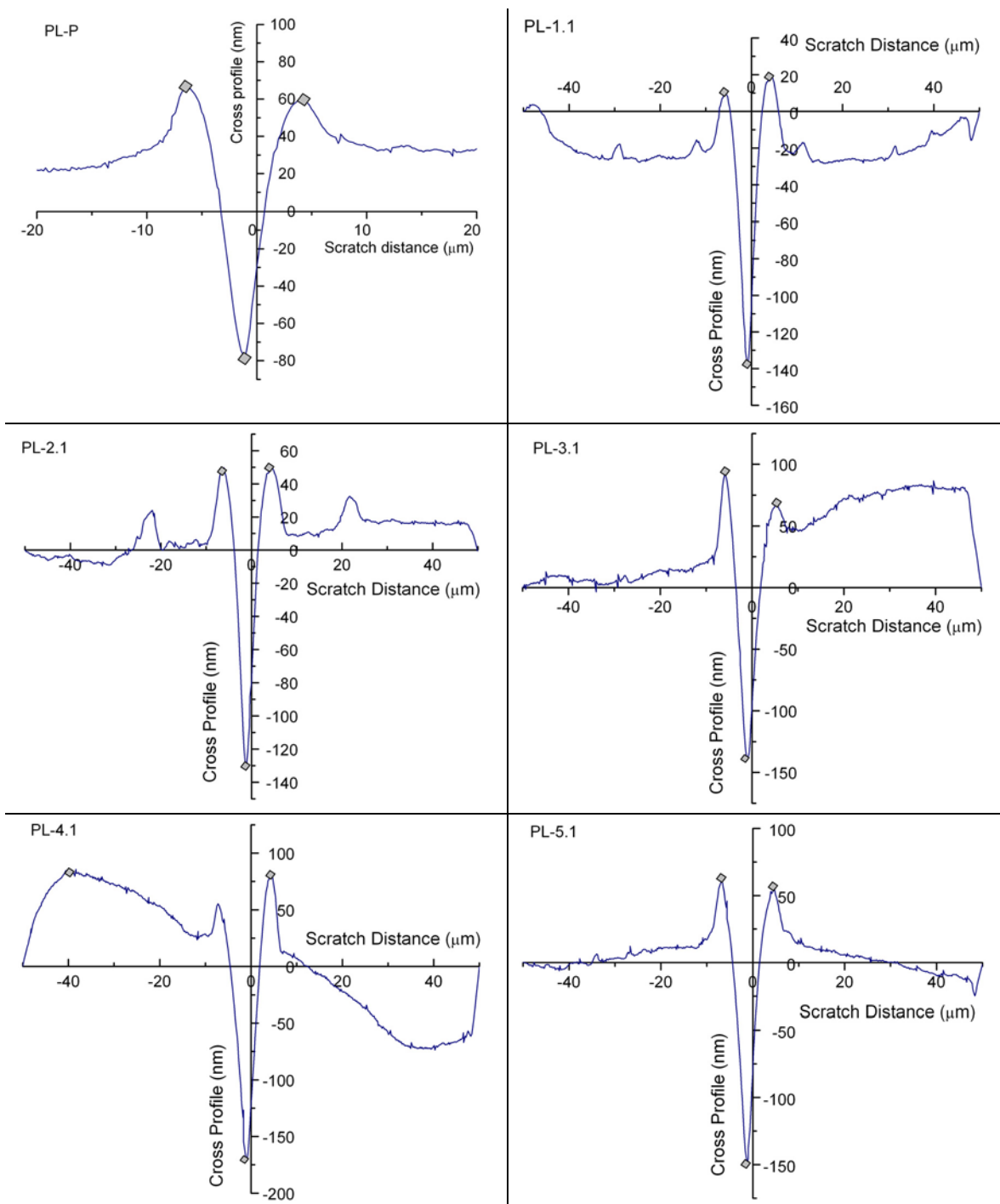


Fig. C3. Nanoscratch analysis of PL coating and nanocoatings. Cross profile curve as a function of scratch distance.

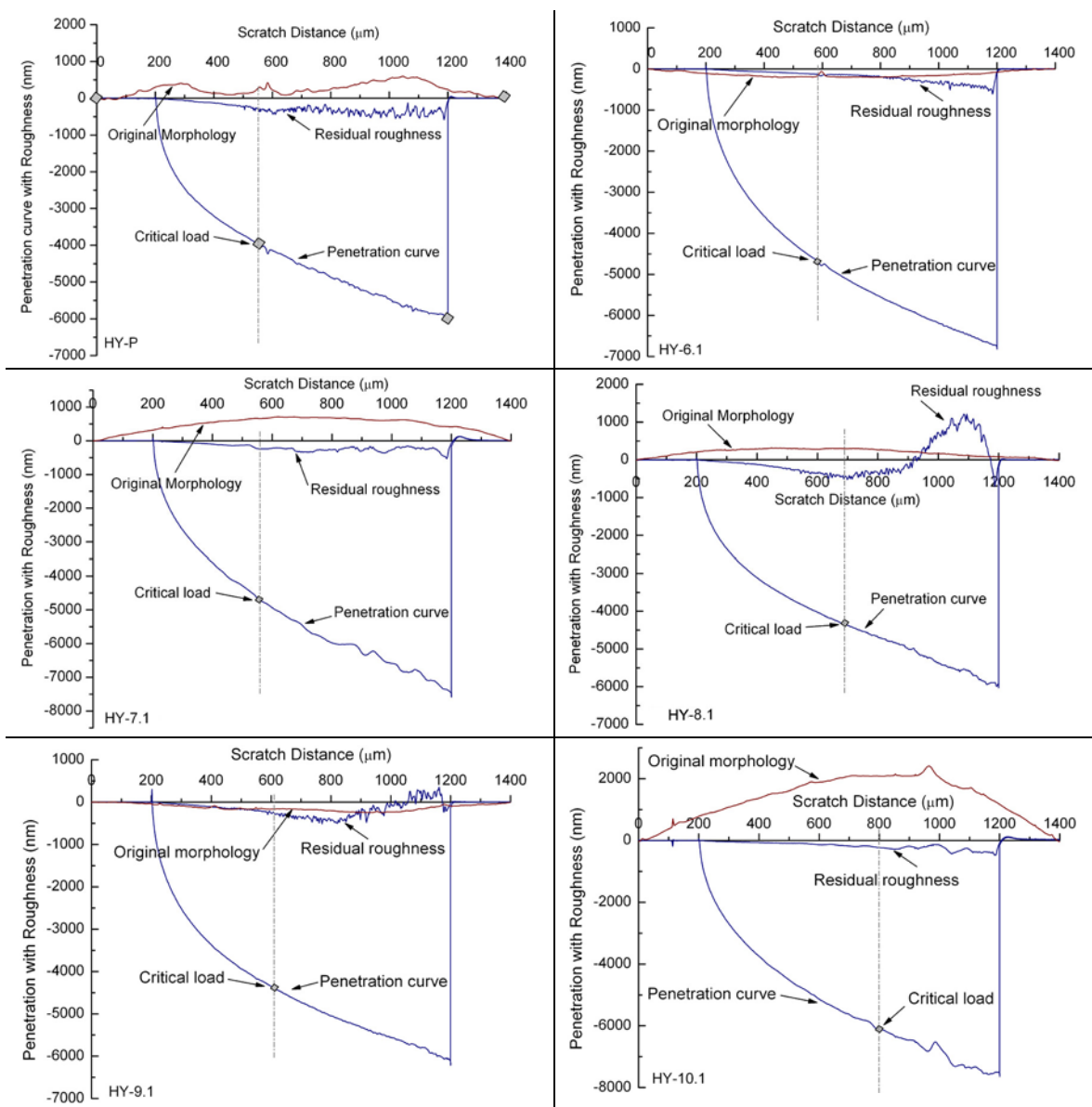


Fig. C4. Nanoscratch analysis of HY coating and nanocoatings. Penetration and roughness curves as a function of scratch distance.

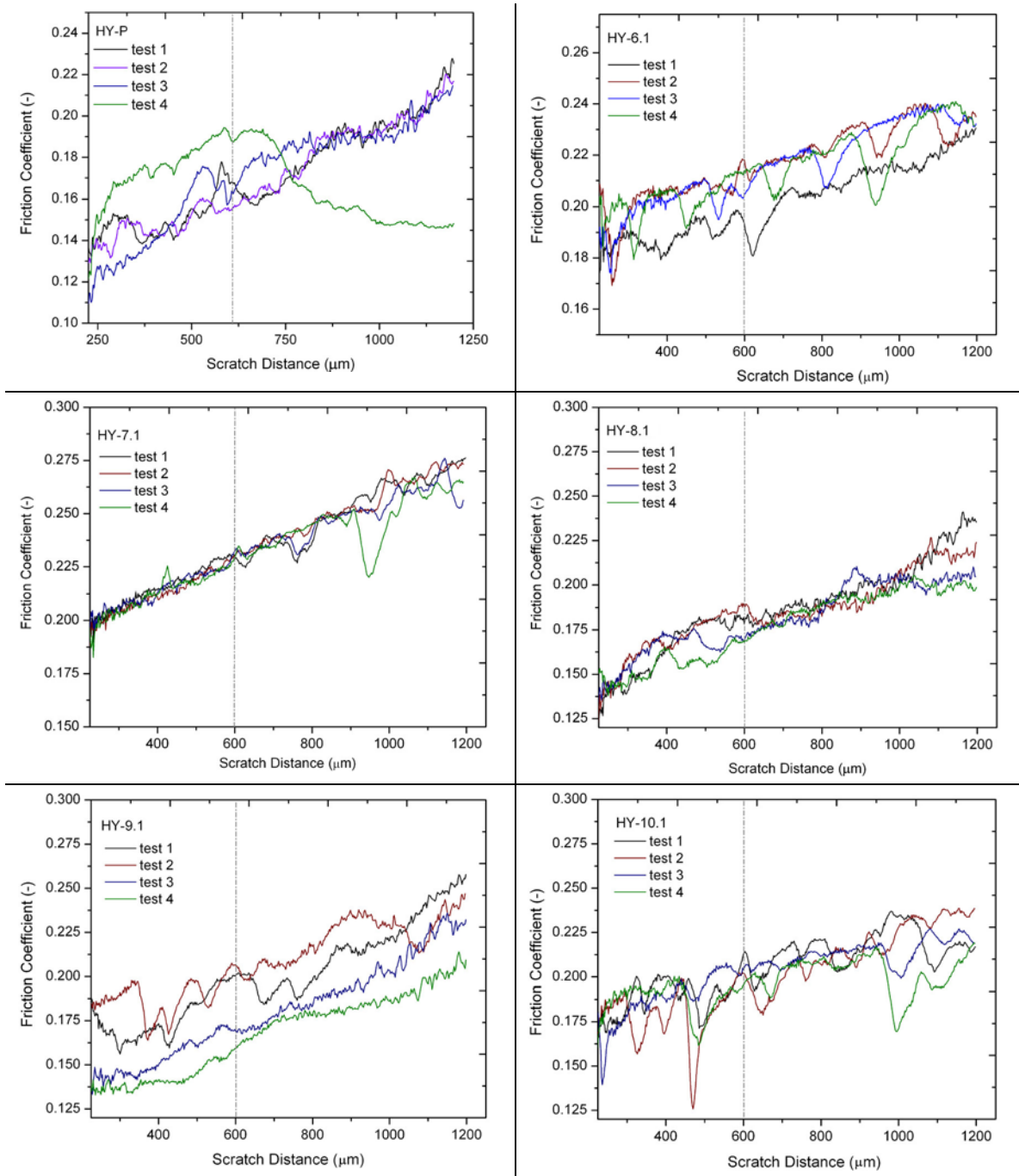


Fig. C5. Nanoscratch analysis of HY coating and nanocoatings. COF curves as a function of scratch distance.

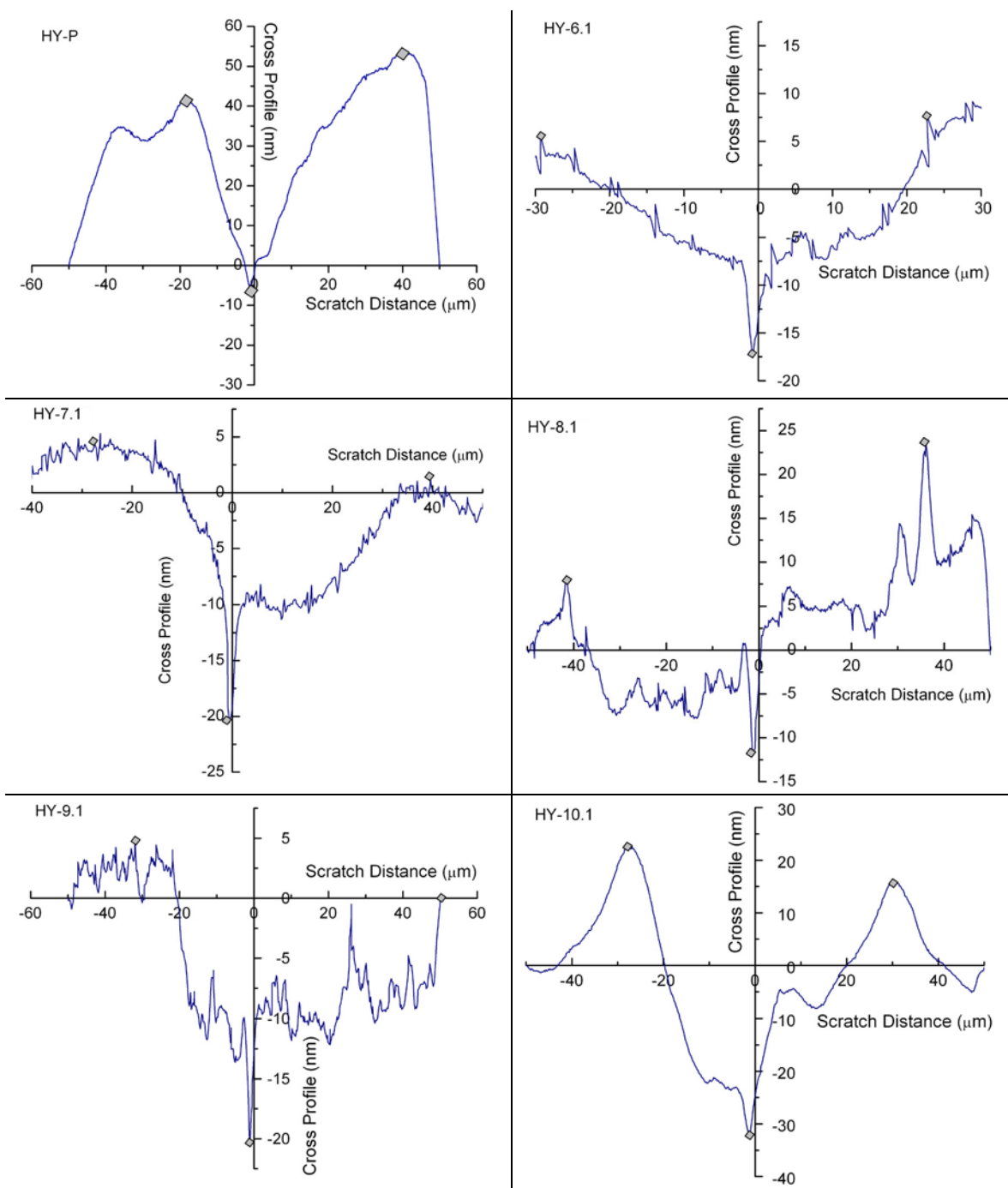


Fig. C6. Nanoscratch analysis of HY coating and nanocoatings. Cross profile curve as a function of scratch distance.

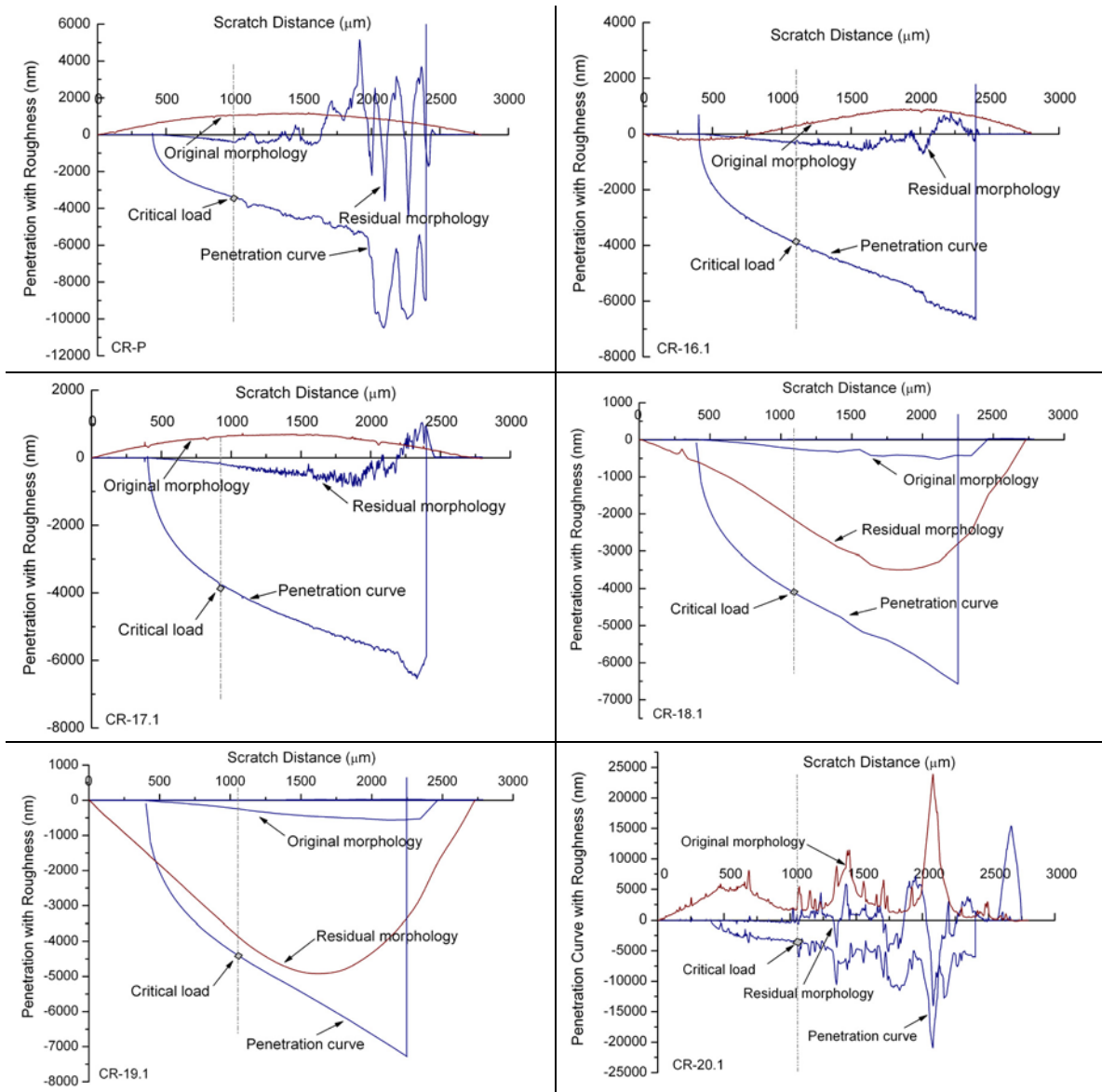


Fig. C7. Nanoscratch analysis of CR coating and nanocoatings. Penetration and roughness curves as a function of scratch distance.

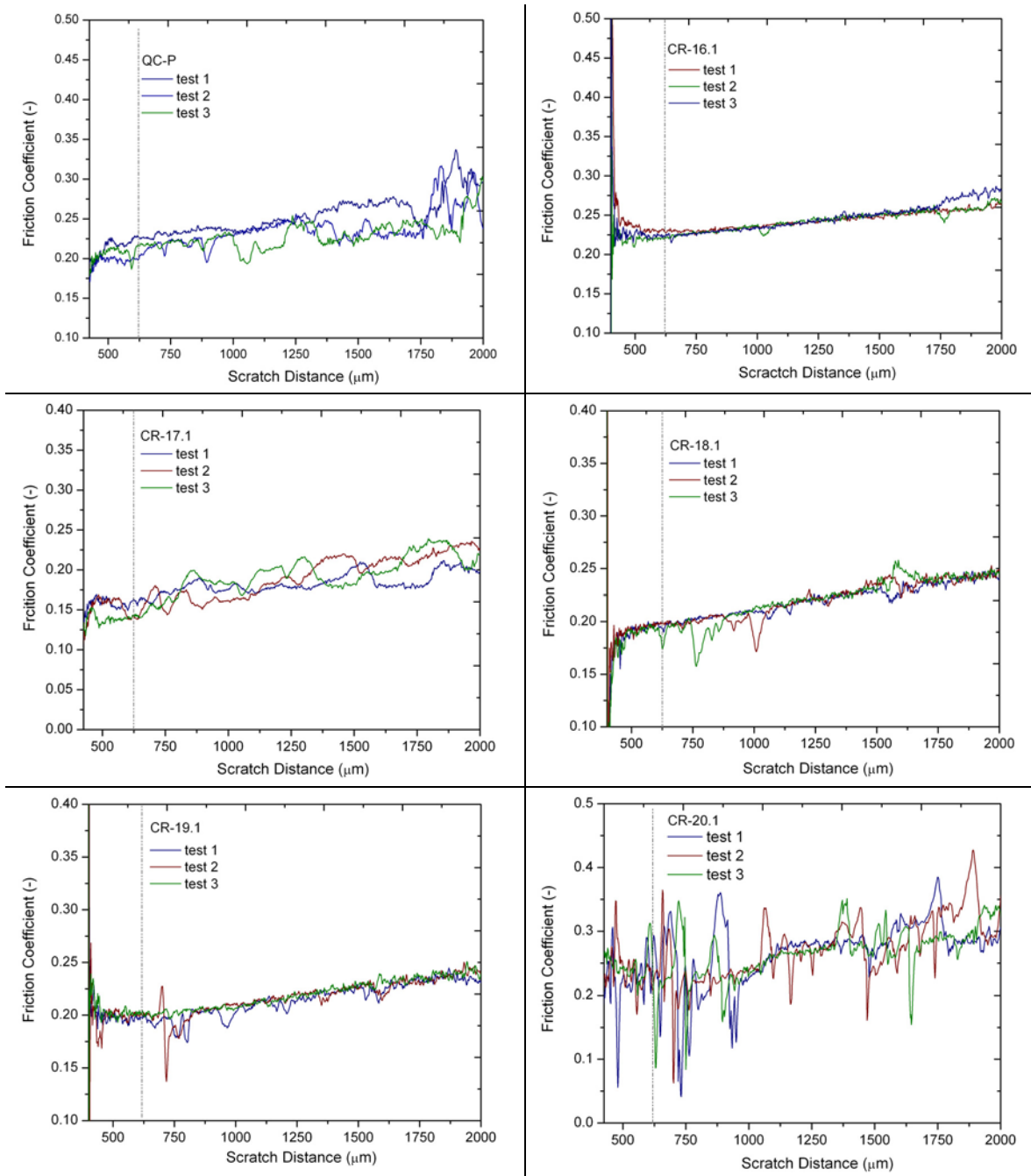


Fig. C8. Nanoscratch analysis of CR coating and nanocoatings. COF curves as a function of scratch distance.

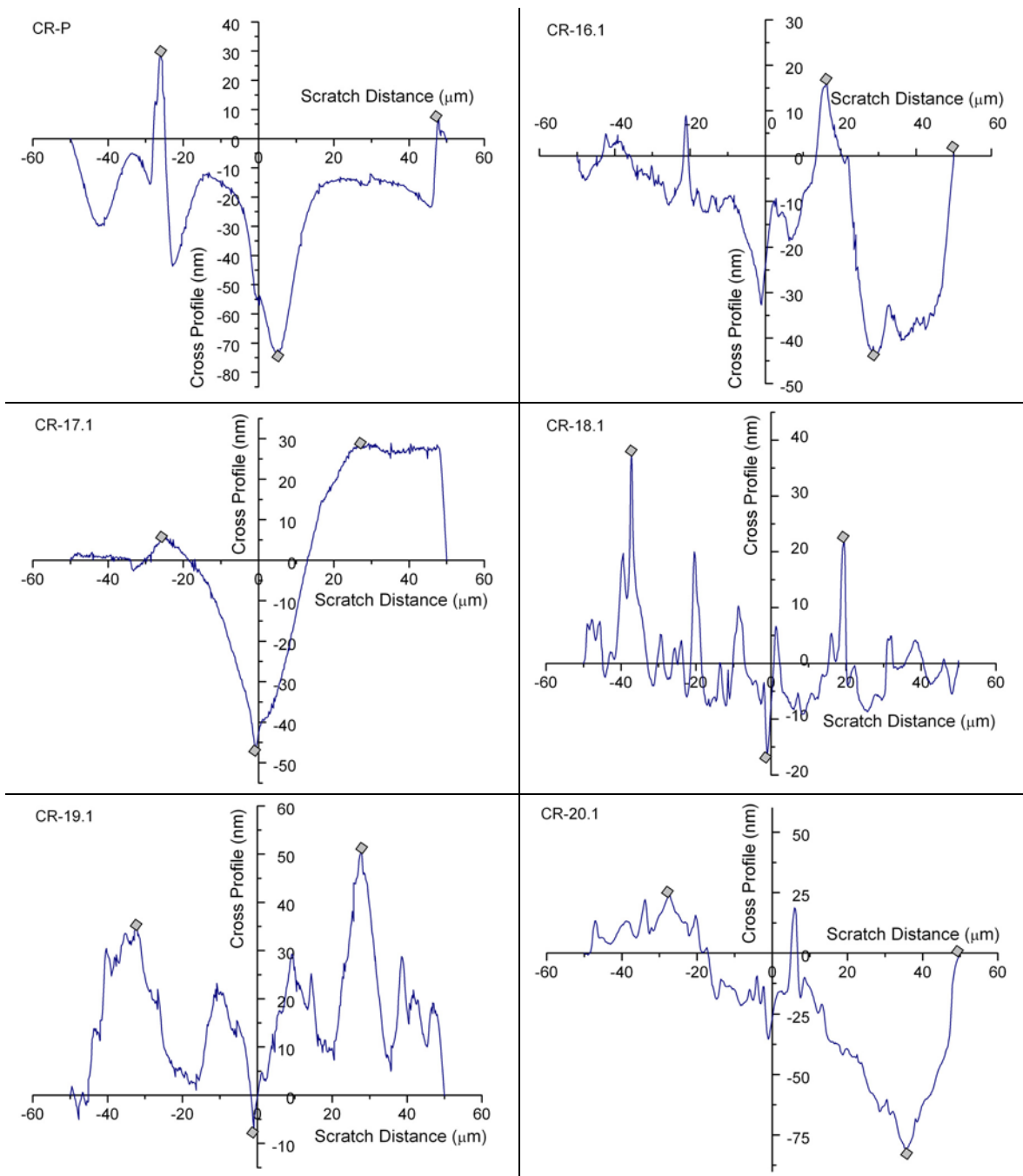


Fig. C9. Nanoscratch analysis of CR coating and nanocoatings. Cross profile curve as a function of scratch distance.

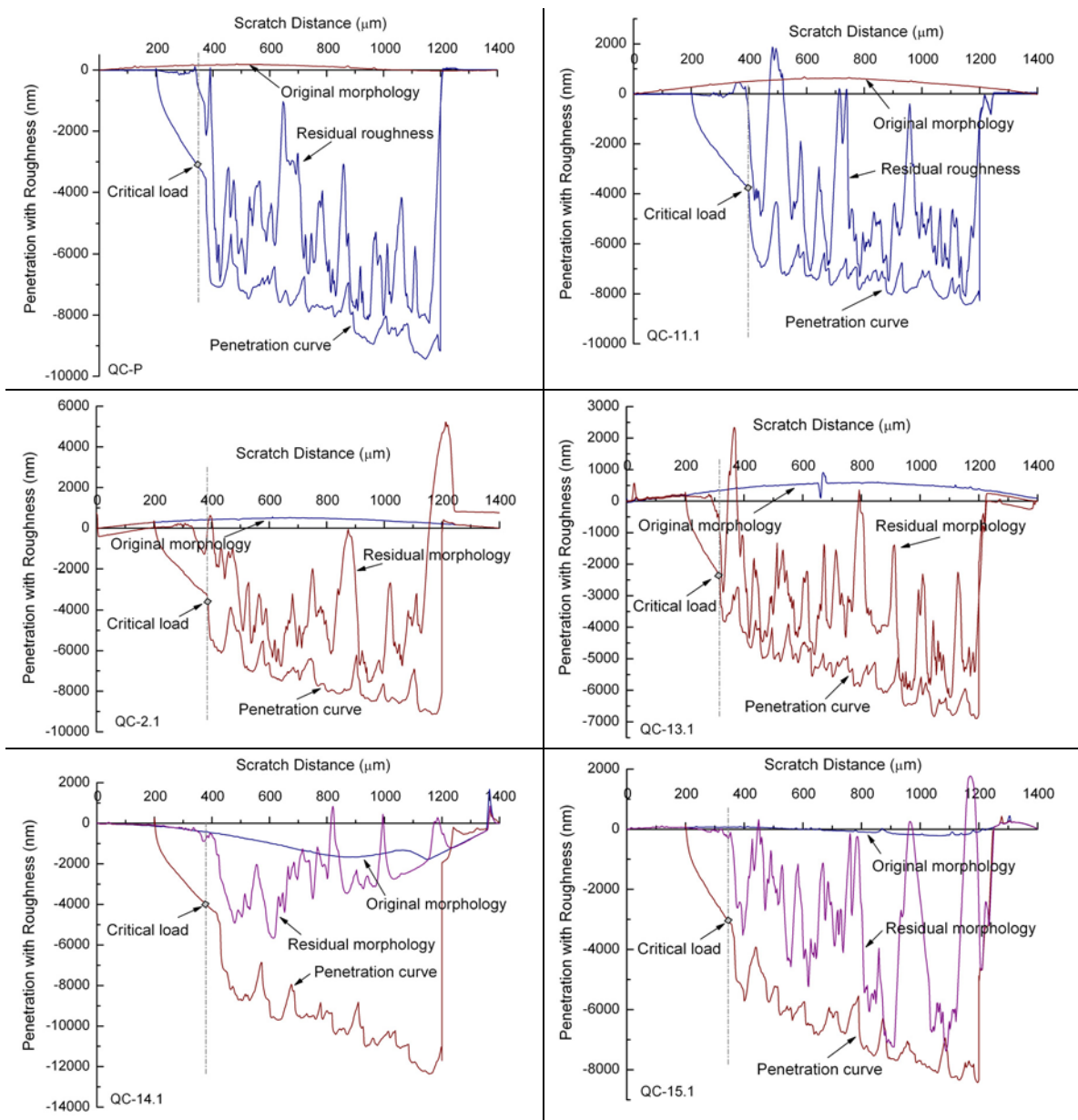


Fig. C10. Nanoscratch analysis of QC coating and nanocoatings. Penetration and roughness curves as a function of scratch distance.

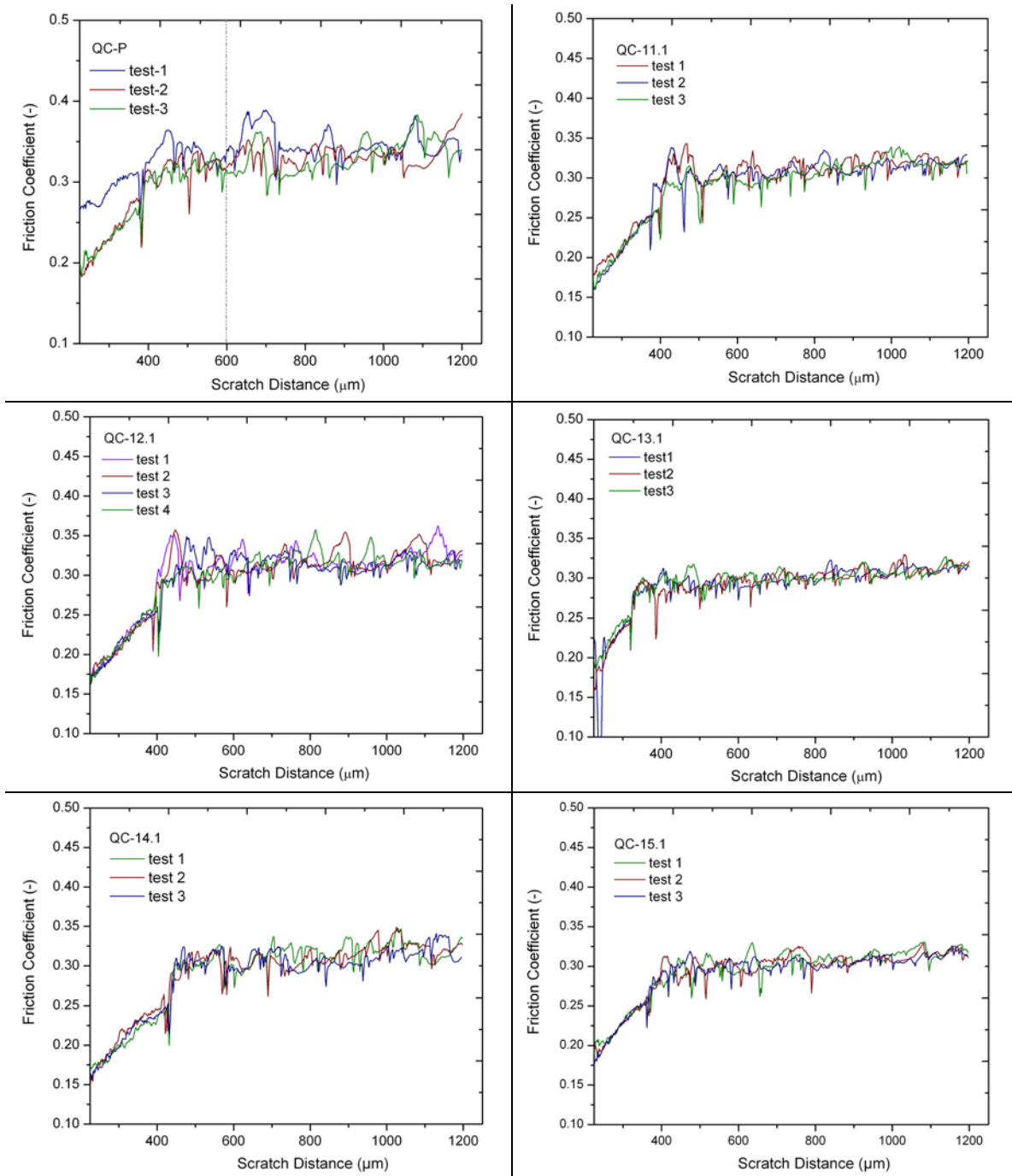


Fig. C11. Nanoscratch analysis of QC coating and nanocoatings. COF curves as a function of scratch distance.

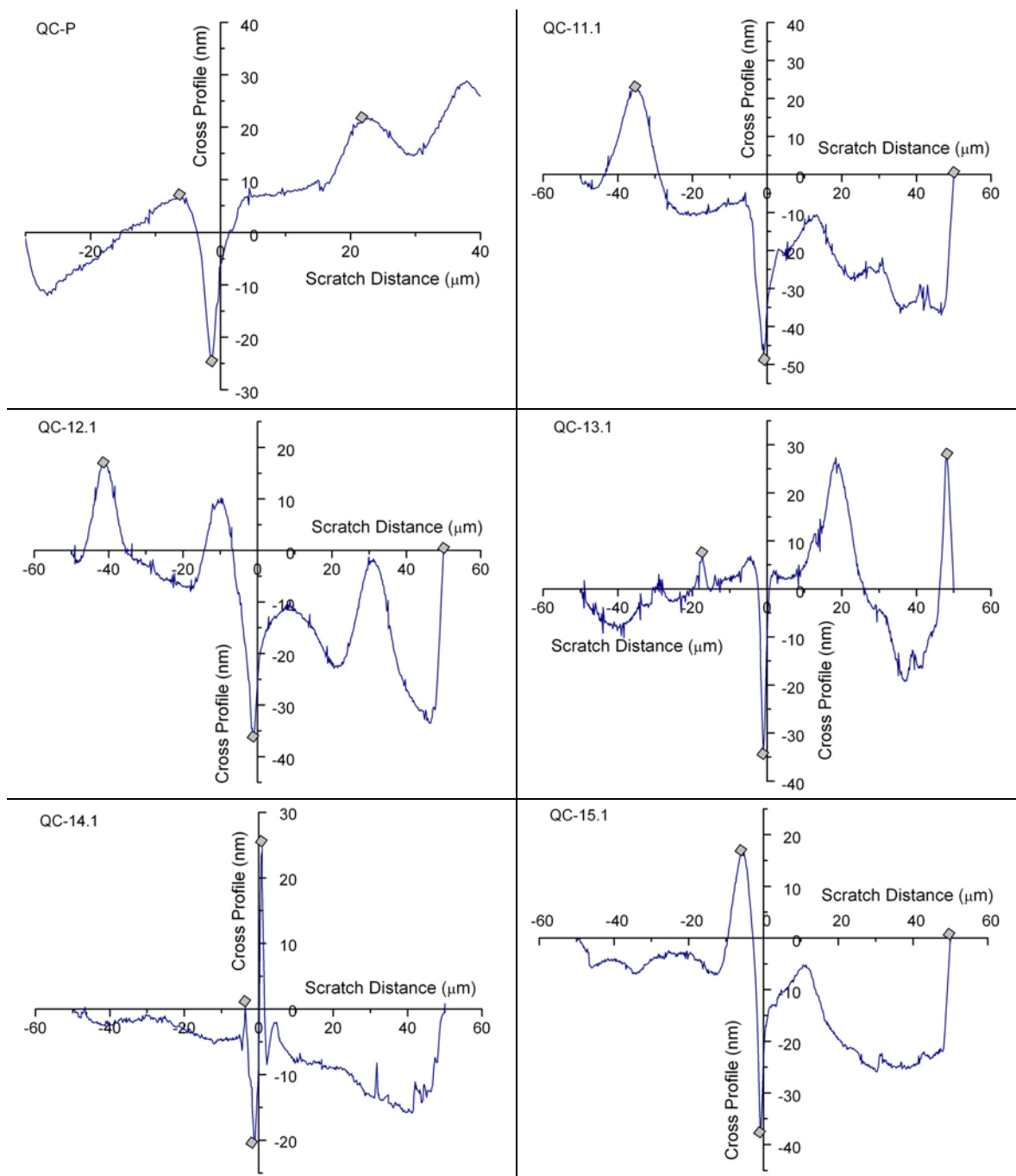


Fig. C12. Nanoscratch analysis of QC coating and nanocoatings. Cross profile curve as a function of scratch distance.

APPENDIX D

This section appends the visco-elastic properties of coatings and nanocoatings. E' and E'' values are plotted for coatings and 0.1 wt.% nanoparticles containing nanocoatings as a function of test frequencies. These data help in the investigation of the changes visco-elastic behavior of coatings on incorporation of nanoparticles. Moreover, helps explaining the fatigue behavior of nanocoatings.

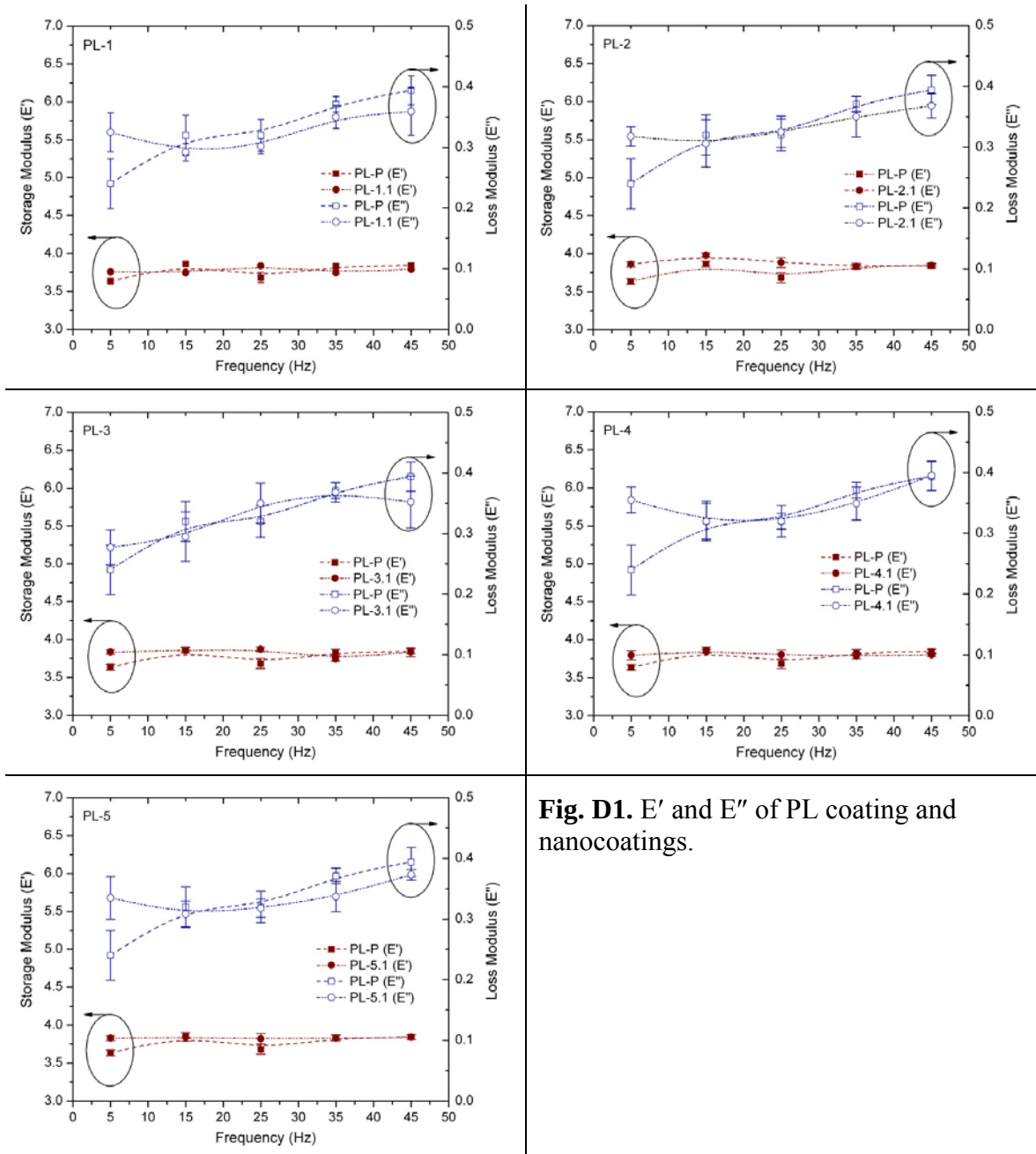


Fig. D1. E' and E'' of PL coating and nanocoatings.

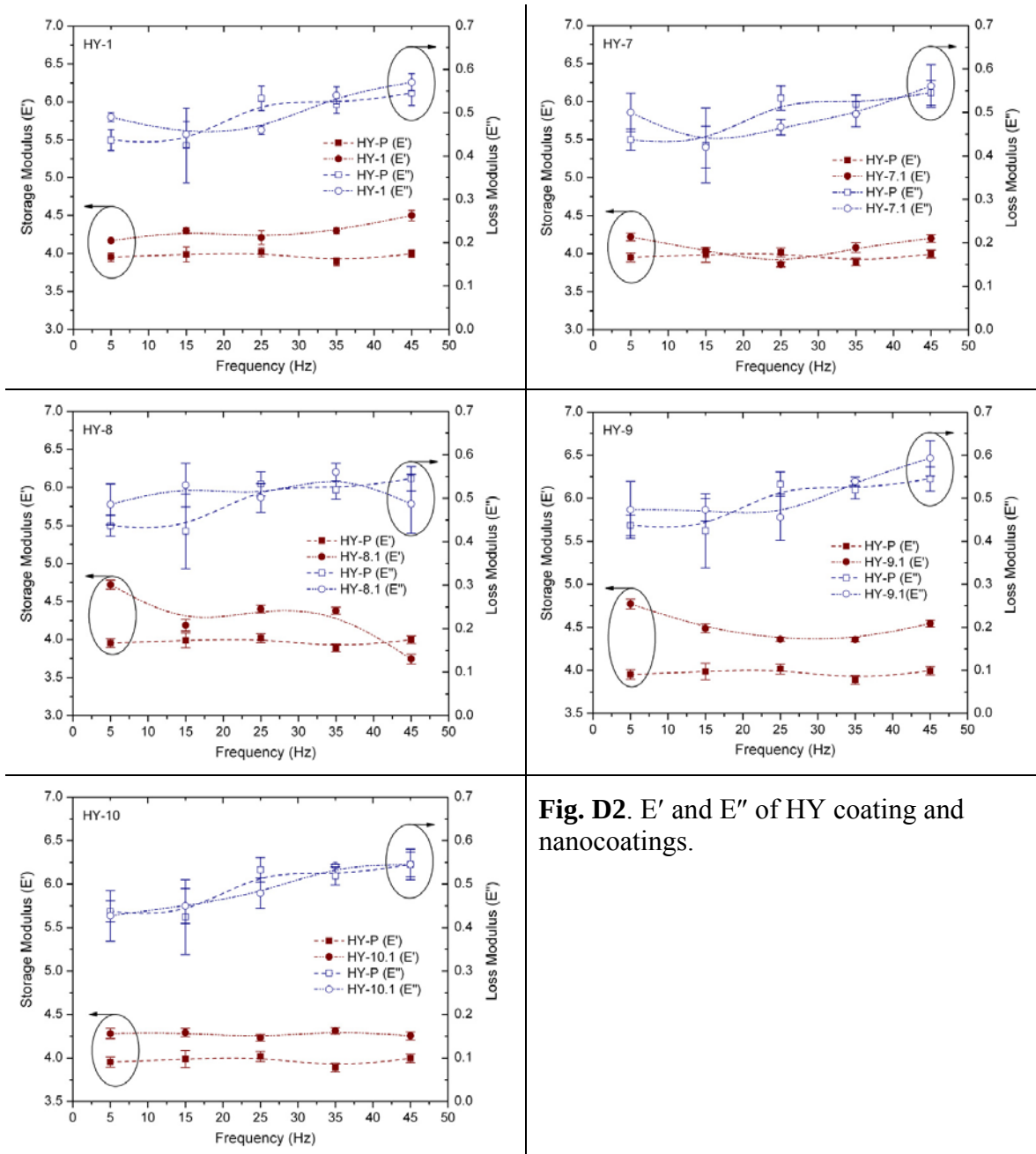


Fig. D2. E' and E'' of HY coating and nanocoatings.

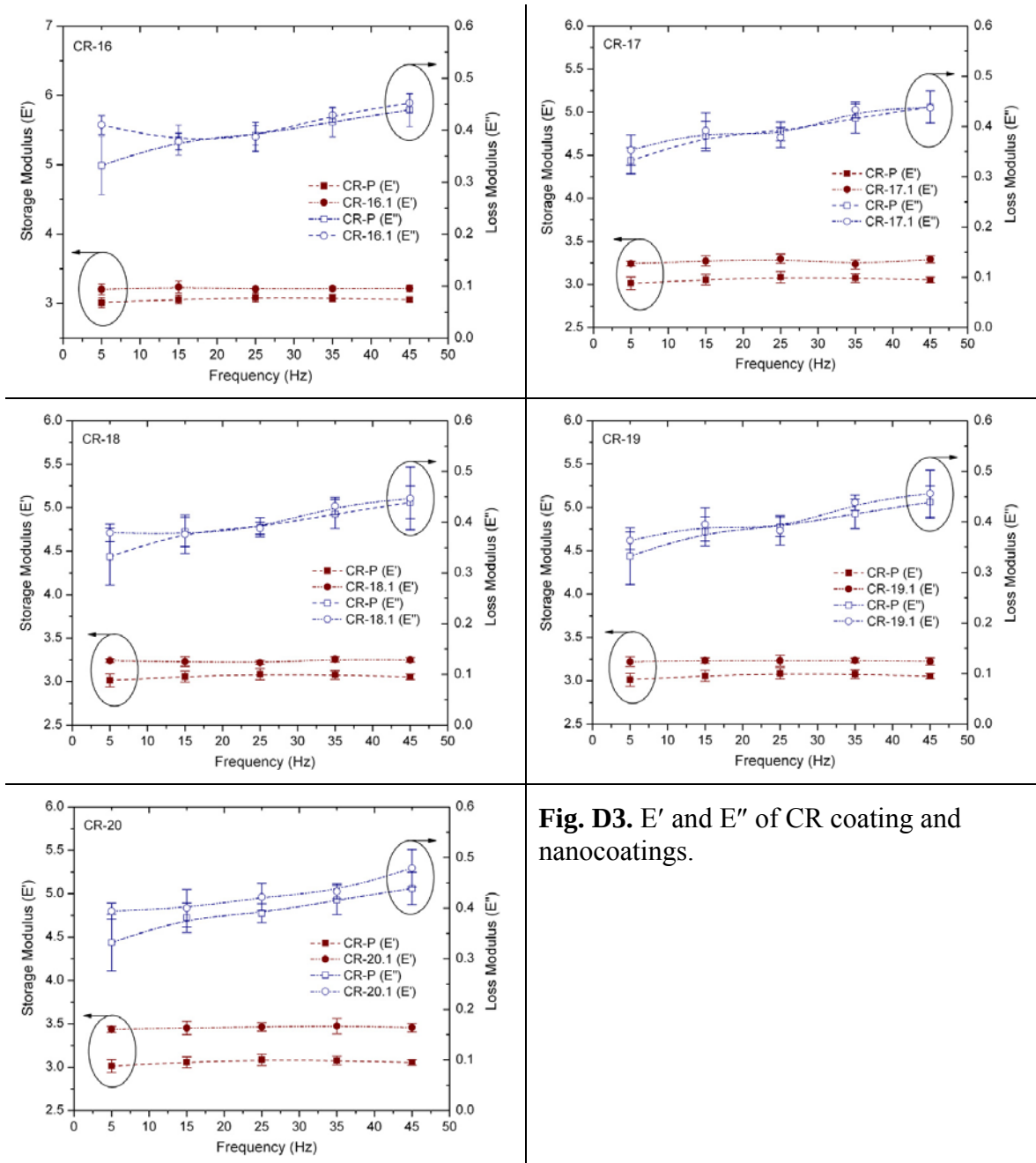


Fig. D3. E' and E'' of CR coating and nanocoatings.

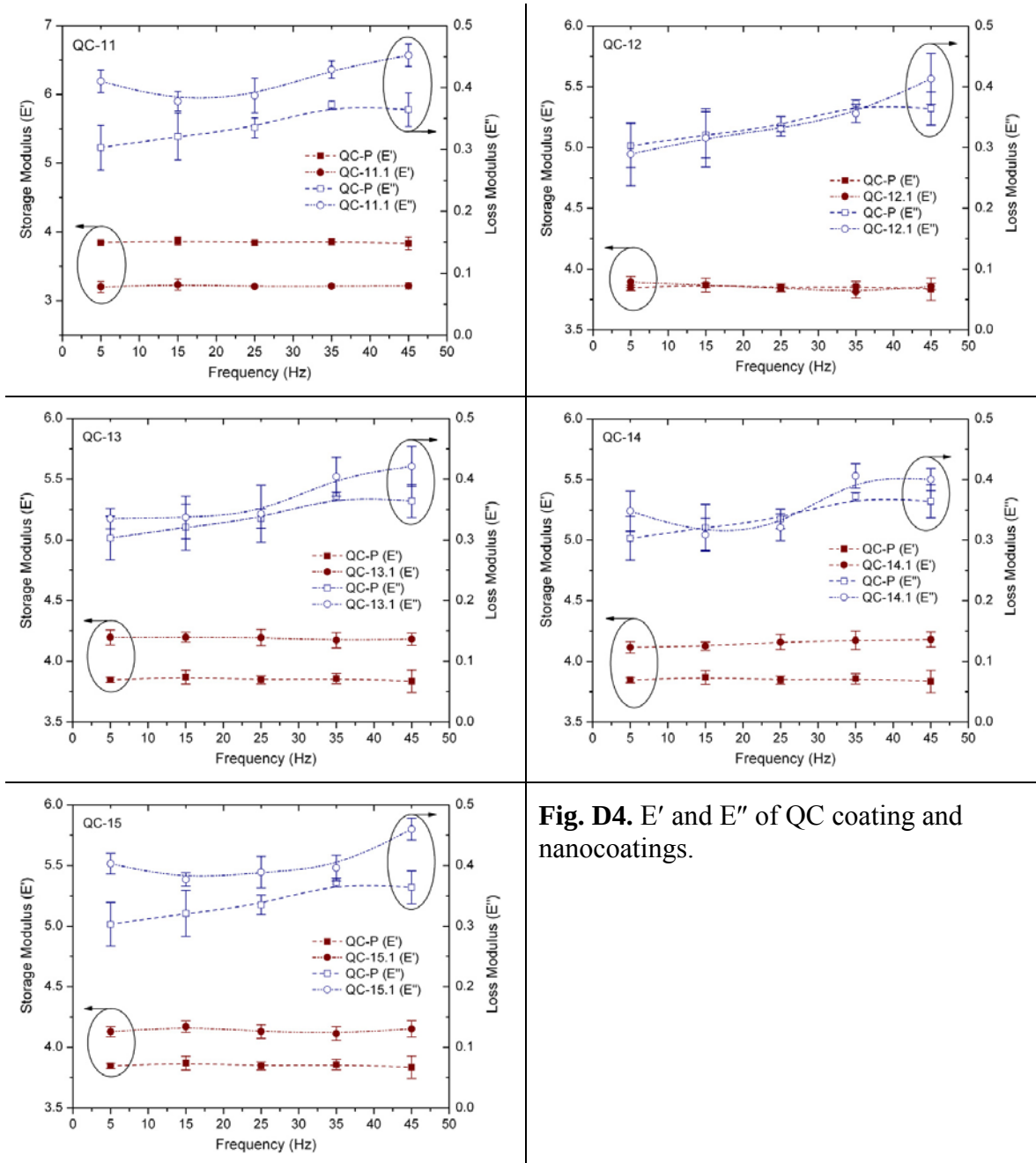


Fig. D4. E' and E'' of QC coating and nanocoatings.