



## Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-PMMA Bio-Composite Coating Via Electrostatic Spray Technique

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### KEY WORDS

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Bio-composite coating,  
electrostatic deposition  
technique.

### ABSTRACT

*This work aims preparation of polymer-based biocomposite coating by electrostatic spray method onto 316L stainless steel substrate, the present work will compare the effects of incorporation of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> particles at a different percentage of (10,15 and 20 % wt. from Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> with (90,85 and 80% wt. PMMA - based electrostatic deposition coating is studied. The structure and chemical composition of composite coatings were studied by using (SEM) & (EDS) and mechanical properties (Microhardness and adhesion strength) of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-PMMA composite coating. The SEM&EDX result showed that the composite coating to be dense with uniform dispersants and continuous with a well homogenous mixture within coating exhibits a much-increased Microhardness and remarkably improved adhesion strength.*

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### 1. INTRODUCTION

Ceramics is an inert biological ceramic material with high mechanical properties and hardness, fracture toughness, wear & corrosion [1] with have several advantages that have generated much interest in recent years because of its superior properties and potential applications including biomedical application, electrochemical capacitor electrodes and optical devices, synthetic photocatalysts fuel cells and advanced ceramics [2 and 3]. Powder spray coating was used for many applications such as paint decoration and protection against corrosive environments. The electrostatic spray method is used to lower the manufacturing cost and the environmental effect during the production process [4 and 5]. It is done by electrostatic device and sprays gun to create a layer on the substrate to play a protective role due to its capability to produce high corrosion & wear-resistant

surface, and its newly the electrostatic composite coatings have acquired wide currency in tribology, biomedical aerospace applications [6 and 7]. A polymer electrostatic matrix biocomposite coating represents a general technique achieve to coatings on the various materials (substrates) with a high thickness of the coating, including any complex surface dimensions and edge geometry. Electrostatic spray deposition (ESD) has been used in the paint industry, and it can be used to fabricate composite materials like SiC, ZrSiO<sub>4</sub>, B<sub>4</sub>C, Al<sub>2</sub>O<sub>3</sub>, TiN, and TiB<sub>2</sub> carried out [3]. ESD has been applied for different particle size composite materials, and it gives good fluidity and can be deposited on large surfaces with uniform particle distribution [8]. The present work aims to study the effects of reinforcement of Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> particles with different percentages on the structure, chemical composition and mechanical properties of PMMA- matrix Biocomposite coatings by using the electrostatic method.

## 2. EXPERIMENTAL METHODS

316L Stainless steel with dimensions (2mm x 2 mm x 1mm) is used as substrate. The sample surface is grinding process with emery paper 400, 500, 600 grades. After that, the substrate surface is cleaned from any rust or products of oxidizing then washing with distilled water and acetone. All powders mixture with (50  $\mu$ m) in particle size were deposited by electrostatic spray deposition (ESD), The specimens coated with different compositions of composite materials were prepared as shown in Table I. The ESD system consisted of a stainless-steel capillary nozzle connected to high voltage supply COLO CL668W/30kV/PN switched to positive polarity, and a grounded metal collector on which a substrate was placed. The high voltage was 15 KV. The diameter of the capillary nozzle was 0.8 mm, and the distance between the nozzle tip and the substrate was about 20 cm. The samples were cured at 140 °C for 2 hours. SEM and EDX as well as microhardness and adhesion strength were used to characterize the deposited composite coatings.

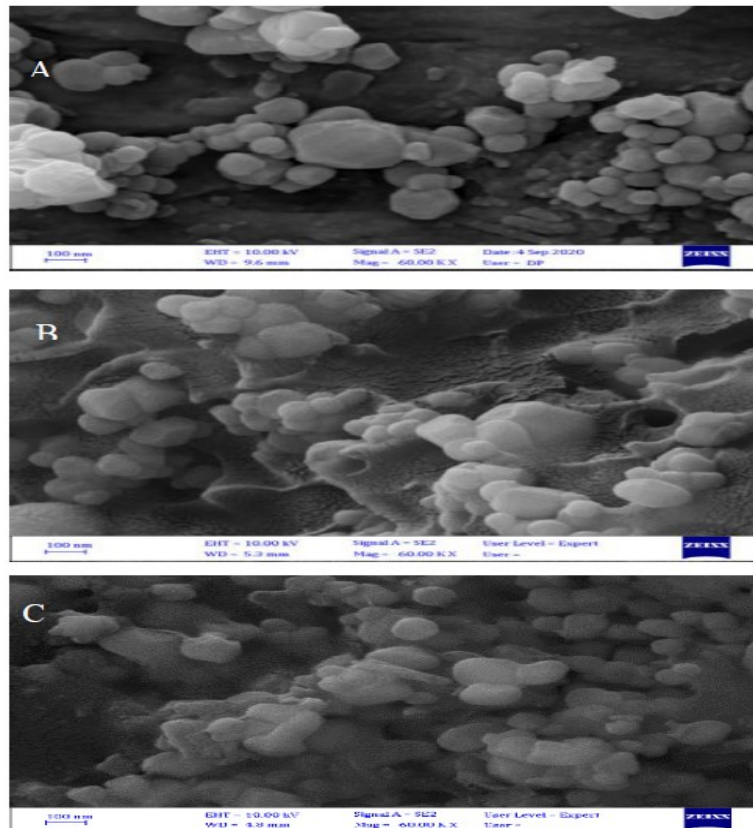
**TABLE I: Groups of coating specimens at different compositions of PMMA composite material that prepared in this study**

Group no.	Mixing Ratio	Weight Percentage (wt%) of Cold Cure PMMA	Weight Percentage (wt%) of Reinforcing Materials	Substrate Type
G 0	A0	100 %	Pure PMMA	316L stainless steel
G A	A1	90 %	2 % Al <sub>2</sub> O <sub>3</sub> + 8 % TiO <sub>2</sub>	
	A2	90 %	4 % Al <sub>2</sub> O <sub>3</sub> + 6 % TiO <sub>2</sub>	
	A3	90 %	6 % Al <sub>2</sub> O <sub>3</sub> + 4 % TiO <sub>2</sub>	
	A4	90 %	8 % Al <sub>2</sub> O <sub>3</sub> + 2 % TiO <sub>2</sub>	
	A5	90 %	10 % Al <sub>2</sub> O <sub>3</sub> + 0 % TiO <sub>2</sub>	
	A6	90 %	0 % Al <sub>2</sub> O <sub>3</sub> + 10 % TiO <sub>2</sub>	
G B	B1	85 %	3 % Al <sub>2</sub> O <sub>3</sub> + 12 % TiO <sub>2</sub>	316L stainless steel
	B2	85 %	6 % Al <sub>2</sub> O <sub>3</sub> + 9 % TiO <sub>2</sub>	
	B3	85 %	9 % Al <sub>2</sub> O <sub>3</sub> + 6 % TiO <sub>2</sub>	
	B4	85 %	12 % Al <sub>2</sub> O <sub>3</sub> + 3 % TiO <sub>2</sub>	
	B5	85 %	15 % Al <sub>2</sub> O <sub>3</sub> + 0 % TiO <sub>2</sub>	
	B6	85 %	0 % Al <sub>2</sub> O <sub>3</sub> + 15 % TiO <sub>2</sub>	
G C	C1	80 %	4 % Al <sub>2</sub> O <sub>3</sub> + 16 % TiO <sub>2</sub>	316L stainless steel
	C2	80 %	8 % Al <sub>2</sub> O <sub>3</sub> + 12 % TiO <sub>2</sub>	
	C3	80 %	12 % Al <sub>2</sub> O <sub>3</sub> + 8 % TiO <sub>2</sub>	
	C4	80 %	16 % Al <sub>2</sub> O <sub>3</sub> + 4 % TiO <sub>2</sub>	
	C5	80 %	20 % Al <sub>2</sub> O <sub>3</sub> + 0 % TiO <sub>2</sub>	
	C6	80 %	0 % Al <sub>2</sub> O <sub>3</sub> + 20 % TiO <sub>2</sub>	

## 3. RESULTS AND DISCUSSION

Figure 1 (A, B and C) presented the SEM micrographs images of various polymer base composite coatings when electrostatic feed powders with different weight percentages (10, 15, and

20%) from ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) to PMMA resin. Figure 1 shows the morphology of the formation of polymer-coated specimens that are homogenous structures beside ceramic microparticles (alumina and titania) specimens to still have some agglomeration on this coating. Some particles, of larger diameter, have been cracked, maybe due to thermal pinch effect/fragmentation of polymer resin at some places coagulation of particles is also observed in those figures.



**Figure 1: Surface morphology (SEM micrograph) of PMMA- based composite coating: A (6% $\text{Al}_2\text{O}_3$  and 4% $\text{TiO}_2$  with 90%PMMA, B (9% $\text{Al}_2\text{O}_3$  and 6% $\text{TiO}_2$  with 85%PMMA and C (12% $\text{Al}_2\text{O}_3$  and 8% $\text{TiO}_2$  with 80%PMMA**

The Surface morphology has consisted of variation flattened particles with heterogeneous lamellar structure, Figure 1 B and C at (9 and 12% wt  $\text{Al}_2\text{O}_3$  or (6 and 8% wt  $\text{TiO}_2$ ) with (85 and 80% PMMA) does not demonstrate a perfect layered electrostatic spray structure but show a higher wetting degree PMMA molten as a matrix. The images of SEM appeared the formation of clusters in composite materials films is identical to the powder-filled polymer composite materials reported in the literature [5 and 9]. The surface morphology of the composite thin films showed that the ceramic particles are embedded in the polymer resin surface from  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  clusters of particles are distributed within the coating surface. However, there are agglomerates and not molten from ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) powders founded in the deposit. In addition, to some of the porosity is somewhat dark gray in color.

The electrostatic sprayed coating average coating thickness of  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$ -PMMA composite coating obtained at different weight percentages are presented in Figures 2 and 3 and Table II.

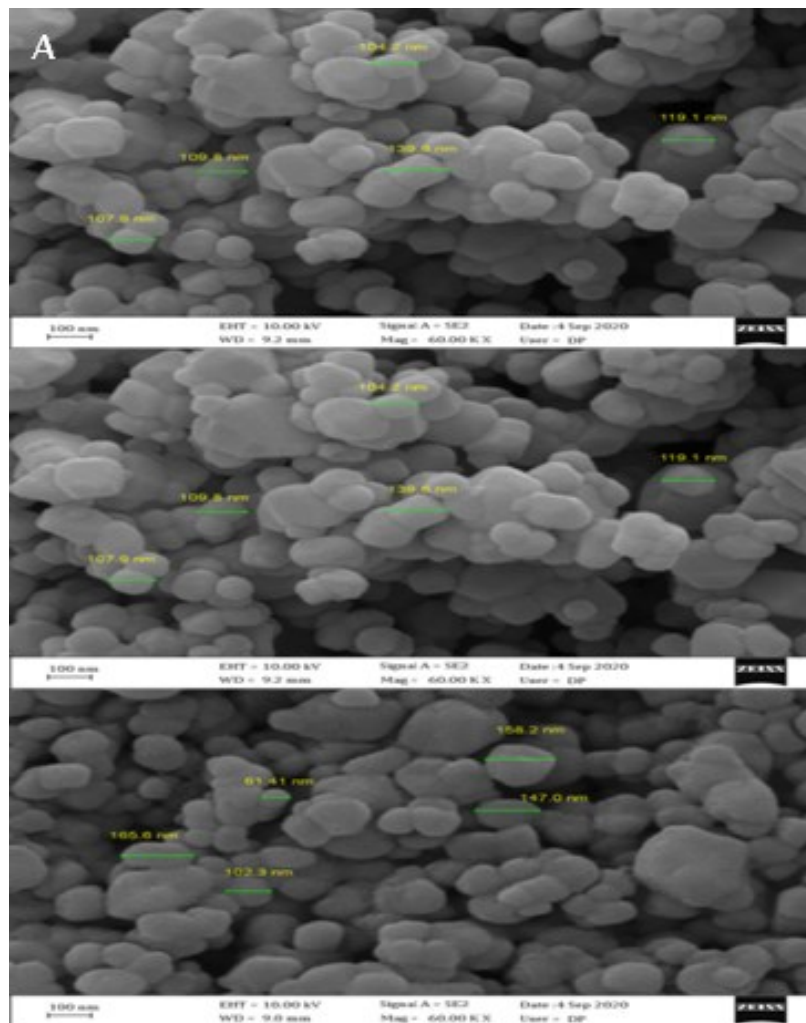


Figure 2: SEM micrograph shows the average diameter of PMMA- based composite coating by electrostatic technique: A (6%Al<sub>2</sub>O<sub>3</sub> and 4%TiO<sub>2</sub> with 90%PMMA), B (9%Al<sub>2</sub>O<sub>3</sub> and 6%TiO<sub>2</sub> with 85%PMMA) and C (12%Al<sub>2</sub>O<sub>3</sub> and 8%TiO<sub>2</sub> with 80%PMMA)

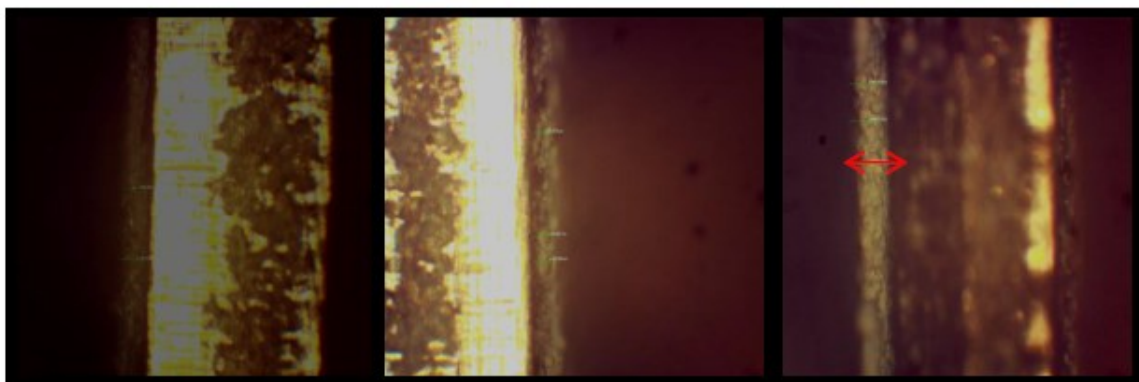


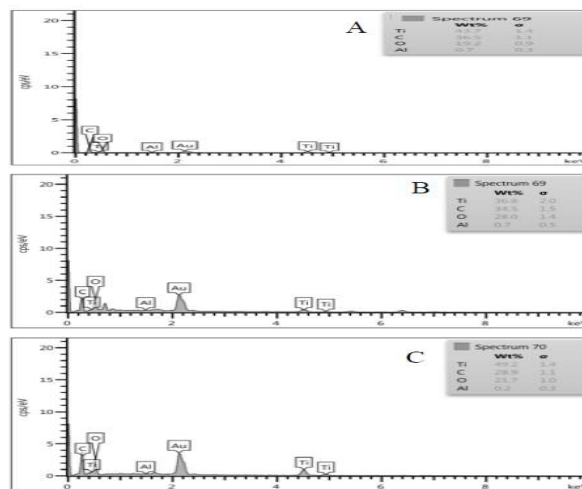
Figure 3: Computerized optical microscope measurement shows the coating thickness at the interface of PMMA- based composite coating by electrostatic technique: A (6%Al<sub>2</sub>O<sub>3</sub> and 4%TiO<sub>2</sub> with 90%PMMA) B (9% Al<sub>2</sub>O<sub>3</sub> and 6% TiO<sub>2</sub> with 85%PMMA) and C (12% Al<sub>2</sub>O<sub>3</sub> and 8% TiO<sub>2</sub> with 80%PMMA), at magnification 40X

**TABLE II: Average diameter and average coating thickness by SEM images and computerized optical microscope measurement of PMMA-based composite coating.**

Group no.	Mixing Ratio	Weight Percentage (wt%) of Cold Cure PMMA	Weight Percentage (wt%) of Reinforcing Materials	Average Diameter (nm)	Average thickness of coating ( $\mu\text{m}$ )
G 0	A0	100 %	Pure PMMA		
G A	A1	90 %	2 % $\text{Al}_2\text{O}_3$ + 8 % $\text{TiO}_2$	100.298	46.068
	A2	90 %	4 % $\text{Al}_2\text{O}_3$ + 6 % $\text{TiO}_2$		
	A3	90 %	6 % $\text{Al}_2\text{O}_3$ + 4 % $\text{TiO}_2$		
	A4	90 %	8 % $\text{Al}_2\text{O}_3$ + 2 % $\text{TiO}_2$		
	A5	90 %	10 % $\text{Al}_2\text{O}_3$ + 0 % $\text{TiO}_2$		
	A6	90 %	0 % $\text{Al}_2\text{O}_3$ + 10 % $\text{TiO}_2$		
G B	B1	85 %	3 % $\text{Al}_2\text{O}_3$ + 12 % $\text{TiO}_2$	128.589	44.55
	B2	85 %	6 % $\text{Al}_2\text{O}_3$ + 9% $\text{TiO}_2$		
	B3	85 %	9 % $\text{Al}_2\text{O}_3$ + 6 % $\text{TiO}_2$		
	B4	85 %	12% $\text{Al}_2\text{O}_3$ + 3 % $\text{TiO}_2$		
	B5	85 %	15 % $\text{Al}_2\text{O}_3$ + 0 % $\text{TiO}_2$		
	B6	85 %	0 % $\text{Al}_2\text{O}_3$ + 15 % $\text{TiO}_2$		
G C	C1	80 %	4 % $\text{Al}_2\text{O}_3$ + 16% $\text{TiO}_2$	107.418	43.33
	C2	80 %	8 % $\text{Al}_2\text{O}_3$ + 12 % $\text{TiO}_2$		
	C3	80 %	12 % $\text{Al}_2\text{O}_3$ + 8 % $\text{TiO}_2$		
	C4	80 %	16 % $\text{Al}_2\text{O}_3$ + 4 % $\text{TiO}_2$		
	C5	80 %	20 % $\text{Al}_2\text{O}_3$ + 0 % $\text{TiO}_2$		
	C6	80 %	0 % $\text{Al}_2\text{O}_3$ + 20% $\text{TiO}_2$		

From Table II observed, the higher average thickness was about (46.068) at A grope, whereas the lower value is (43.333) C grope for composite coating on 316L substrates.

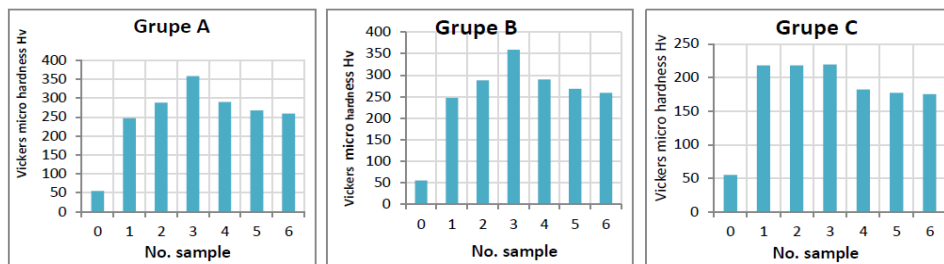
The chemical analysis of the composite coating by using EDS shows the presence of mainly C (73.6 %) on stainless steel substrate after applied electrostatic coating according to Figure 4 A, B, and C are illustrated the examinations of PMMA- composite coatings on the stainless steel 316L substrate compared with pure ceramic powders ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) as shown in Figure 4, EDS result shows the presence of mainly Al and Ti along with a considerable amount of C and O in the coating. Higher amounts of Al and Ti (0.7% and 49.2%) respectively, were detected along with C (36.5 %), correspondingly that provided the direct evidence of the existence of ceramic particles in a polymer matrix.



**Figure 4: EDS electron image for PMMA- based composite coating by electrostatic technique on 316L SS substrate: A (6% $\text{Al}_2\text{O}_3$  and 4% $\text{TiO}_2$  with 90%PMMA) B (9% $\text{Al}_2\text{O}_3$  and 6% $\text{TiO}_2$  with 85%PMMA) and C (12% $\text{Al}_2\text{O}_3$  and 8% $\text{TiO}_2$  with 80%PMMA)**

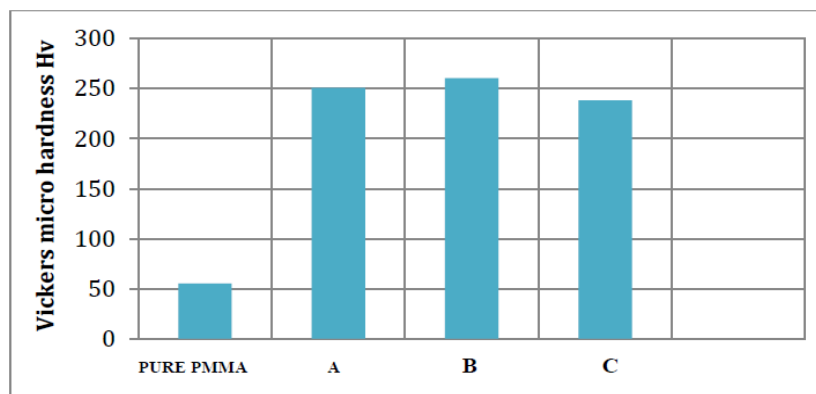
It is obvious from the EDS results also that the C % diminished a lot this can be attributed to the increased depletion of the ceramic powders this will give enough space to diffuse and create more coupling with PMMA particles, which provide the coating with the necessary protection but also lead to increase cracking sometimes because of generating compressive stresses at the coating layer.

The Vickers microhardness test of pure PMMA and  $\text{Al}_2\text{O}_3/\text{TiO}_2$ -PMMA composite coating samples on 316L SS substrate was performed at three different positions and an average of the measurements was reported. The composite coating showed a comparatively high hardness value of HV Figure 5, the pure PMMA coating was found to be soft due to its polymeric structure nature with a pure PMMA average hardness value of 55 HV [10]. Generally, the microhardness composite coatings have a wider range of values, Figure 5. Additionally, the microhardness values of the  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  with PMMA composite coatings increase with an increase in ceramic powders contented in the composition of the polymer coating. With the addition of (6,9 and 12%wt of  $\text{Al}_2\text{O}_3$  and 4,6 and 8 % wt of  $\text{TiO}_2$  with 90, 85 and 80% wt of PMMA) by electrostatic technique composite composite coatings.



**Figure 5: Variation of Vickers microhardness of pure PMMA and all group preparation composite coating samples on 316L SS substrate by electrostatic technique.**

At the lower weight percentage of alumina and titania in base polymer composite coating, the average hardness value is lower, but after increasing the content of the ceramic particles in the coated sample the average hardness value was increased. From Figure 6, notice the existence of ceramic particles  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  particles improved the hardness with superior mechanical properties composite coating by forming a strong bonding between ceramic and polymer due to perfect wetting from the polymer matrix to additive powders, addition to best top coupling between individual coating layers with fewer content of defect (pores, cavities and voids) compared with pure ceramic practical additive. Higher ceramic particles ( $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ ) concentration with PMMA encourages producing a structure with beads in composite coating within the polymeric matrix. It has low wetting with low coupling make it difficult to adhesive, these structures gradually disappeared when increasing the pure  $\text{Al}_2\text{O}_3$  especially for additions (10%  $\text{Al}_2\text{O}_3$  +0%  $\text{TiO}_2$ + 90% PMMA), (15%  $\text{Al}_2\text{O}_3$  +0%  $\text{TiO}_2$ + 85% PMMA) and (20%  $\text{Al}_2\text{O}_3$  +0%  $\text{TiO}_2$ + 80% PMMA), then converted to more interconnectedness with homogenous distribution in composite coating. Moreover, a decrease grain size of the additive within the structure of the coating could be another reason for the enhanced microhardness of composite coatings is due to the strengthening state of the dispersion resulting [11].



**Figure 6: Variation of Vickers microhardness of pure PMMA and  $\text{Al}_2\text{O}_3/\text{TiO}_2$ -PMMA composite coating samples on 316L SS substrate by electrostatic technique**



The tension load was applied to the adhesive two pieces with and without the coated section by using an adhesive epoxy type (REP-15-0104) with a rate of (1mm/min) until the failure of the specimen. Figure 7 shows the adhesion strength of all composite coated specimens prepared by electrostatic spray coating on 316L SS. Actually, the values are not the values of dislocating the coating film from the metal surface, but they are for higher adhesion strength of the epoxy only due to good adhesion between the polymer -base coat and 316L SS substrate which has a higher surface roughness ( $3.487\mu\text{m}$ ) leads to enhance overlying coating interlocking with the surface. The higher adhesive bonding strength was (C grope) and the best fracture is at the contact layer between coating and surface of 316L SS alloy. The higher hardness and adhesion strength when less porosity can be accrued at a lower coating thickness such as (B) groups. Greatest adhesion value (100 MPa) was achieved by C group (9%  $\text{Al}_2\text{O}_3$  + 6 %  $\text{TiO}_2$  +85% PMMA) as compared lower ceramic percentage A grope (6%  $\text{Al}_2\text{O}_3$  + 4 %  $\text{TiO}_2$  +90% PMMA) which has a lower value of adhesive bonding strength (70 MPa).

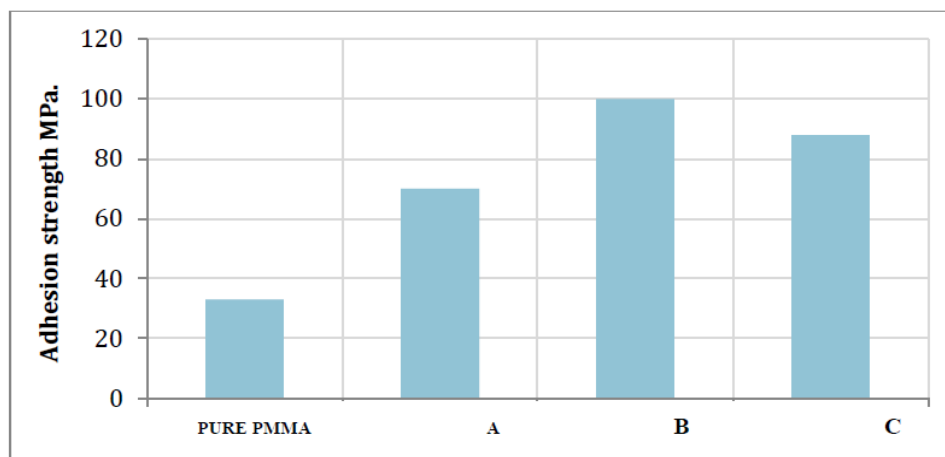


Figure 7: Variation of adhesion strength of pure PMMA and  $\text{Al}_2\text{O}_3/\text{TiO}_2$ -PMMA composite coating samples on 316L SS substrate by electrostatic technique

#### 4. CONCLUSIONS

- 1) Using an Electrostatic spray technique may be synthesis ceramic particles reinforced polymer resin-matrix biocomposite coating successfully.
- 2) The SEM&EDX result, showed that the deposited composite PMMA-  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  coating is well distributed in PMMA base coating to be dense with uniform desparation, and high hardness, adhesive strength and continuous with the well homogenous mixture. However, there are agglomerates and not molten from ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) powders founded in the deposit. In addition, to some of the porosity is somewhat dark gray in color.
- 3)  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  particles improved the hardness with superior mechanical properties composite coating by forming a strong bonding between ceramic and polymer due to perfect wetting from the polymer matrix to additive powders, in addition to topmost interlocked coupling between layers of PMMA resin.
- 4) The adhesion strength increase with increasing ceramic ( $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ ) concentration phase reinforced particles the higher adhesion strength gets it when the  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$  powders arrive at the surface in the fully polymer molten condition.

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