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NANO-COPPER COMPOSITE CONSERVATION OF AN EGYPTIAN BRONZE SACRED IBIS BIRD STATUE: CASE STUDY

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ABSTRACT

Bronze was well known in ancient Egypt since the 12th dynasty (1991-1759 B.C). Bronze artifacts endure different types of corrosion due to intrinsic and extrinsic factors before and/or after extraction. This led to various deterioration aspects: corrosion products of several colors, pits, cracks, grooves and lost parts. Nanometerials and nanocomposites were widely used for the inhibition of micro – organisms, consolidation, and protection of artifacts. But very few studies were concerned with the completion of lost parts, which is considered a challenge in the conservation of cultural heritage. This research focused on finding out a suitable nanocomposite for this purpose. Three polymers: Paraloid B-66, Plexisol P-550, and thermoplastic polyurethane were evaluated through mechanical properties before and after exposure to artificial ageing (ultraviolet radiation). Nan-copper and nano-silver particles were added in three concentrations 0.25. 0.5, 1% w/v to plexisol P-550, which donate the best results to form nanocomposites. Shear strength and color change of nanocomposites were determined. Transmission electron microscope TEM was utilized for characterization of nano-particles. Whereas stereomicroscope SM, polarizing microscope PLM, scanning electron microscope SEM, attached with energy dispersive X- ray unit EDX, and portable X-ray fluorescence p-XRF spectrometer were used to diagnose deterioration phenomena, to determine microstructure and to analyse chemical composition of the studied statue's alloy. Data declared that 1% nano- copper plexisol P-550 composite was the best one for improving mechanical properties without effect on color. It was applied for the completion of lost parts in an ancient Egyptian bronze sacred Ibis bird statue, Late Period (664 -332 B.C), from the Grand Egyptian museum, Giza, Egypt.

KEYWORDS: Nanocomposites, bronze, corrosion, completion, mechanical properties, color change

1. INTRODUCTION

In ancient Egypt, bronze alloy was used for manufacturing several artifacts, such as statues, beads, stoves, surgery tools, coins, mirrors, daggers, weapons, and house tensiles. Bronze is an alloy consists essentially from copper and tin, in addition to intended metals such as lead. This alloy is harder and more durable than copper, has lower melting point, and better mechanical properties (Figueiredo, 2010; Scott, 2002; Selwen, 2004; Smith, et al., 2011; Wang. et al., 2009). Metallic artifacts whenever were found, they were covered by encrustations of metallic compounds known as corrosion products. There is no difference between these compounds and their corresponding prototype minerals in the earth's crust: mineralization process of ancient metals). This process was occurred due to internal and external factors. The 1st concerns essentially with chemical composition of metallic objects and their manufacturing methods. Whereas the 2nd one includes the surrounding environment (physical, chemical, and biological effects (Robbiola, et al, 1998; Scott, 2002; Scott, et al., 2000; Selwen, 2000; Tylecota, 1979; Robbiola et al., 1996).

All these deterioration factors caused distortion and consuming the constituting metals of artifacts. In serious cases this may led to a loss of some parts. The completion process of these lost parts in metallic objects is very important and urgent for their protection and preservation. In the past, it was carried out either by soldering a metal or using adhesive polymers with addition of coloring materials, glass fibers, and, metallic powder. These previous materials, have disadvantages such as distortion, presence of fine cracks and decreasing of compressive strength (Odgan, 2000).

Nowadays, nanomaterials and nanocomposites attracted the attention of scientists to apply them for conservation and pretection of cultural heritage, (Fedel, 2010; Joseph, et al. 2013; Langrodi, 2009; Pothak, et al., 2012; Riad, et al., 2015; Tsirita, 2012; Vassilioui, 2008; Wang, et al., 2004; Yan, et al., 2010). This is due to their excellent properties (physical, chemical, electrical, and antibiological activity. In the present study it is the 1st time to apply nanocomposites for the completion process of metallic artifacts. The aim of the present work is to evaluate nano copper and nano silver composites for protection of bronze artifacts.

2. MATERIALS AND METHODS

2.1. MATERIALS

2.1.1 Nanoparticles

Copper and silver nanoparticles Cu NP_s & Ag NP_s were used. The 1st one was prepared by the national research center, Egypt, and the 2nd one was supplied by Sigma Aldrich chemical company, Germany.

2.1.2 Polymers

Three polymers: Paraloid B-66 (polymethyl butyl methacrylate ($C_8H_{14}C_{12}XC_5H_8O_2$), plexisol P-550 (Polybutyl methacrylate ($C_2H_{14}O_2$), and thermo plastic polyurethane (based on isocyanide and alcohol) were used. They were evaluated through mechanical properties to select the best one for preparing nanocomposites. The 1st two polymers were supplied by Italian CTS company, whereas the 3rd one was purchased from pharaonic Egypt company.

Fig. 1 Deteriorations in the statue. (A)& (B) Missing parts in the metal and internal core, (C) Corrosion Products.

2. 1.3 Nanocomposites

Two nanocomposites were prepared by adding copper and silver nanoparticles in three concentrations: 0.25, 0.5, 1.0% w/v to the selected polymer plexisol P-550, which gave the highest values of mechanical properties.

2.1.4 Bronze statue

Sacred ibis bird statue is referred to the late period (664 – 332 B.C.) from the grand Egyptian museum in Cairo was picked to apply the best nanocomposite for the completion process (see Fig. 1).

2.1.5 Bronze strips

Bronze strips were manufactured by the central metallurgical research development institute, Egypt. They had similar chemical composition of the statue's alloy, to carry out the experimental study. Their dimensions were 10 x 2x 2.5 cm^3.

3. METHODS

Transmission electron microscope TEM using Jeol JEM, 2100 Model was used and copper and Silver nanoparticles Cu NP_s & Ag NP_S were characterized.

Zeiss stereomicroscope, Discovery V.20 Model was utilized for declaring deterioration aspects of the statue.

Zeiss PLM, model Imager was used for determination the type of the statue's alloy, and its corrosion products.

Examination of the statue surface by SEM model FEI Quanta 3D 2001 was realized to investigate its morphology, and to measure the thickness of the remaining metal in micrometers. EDX analysis was accomplished to determine the constituting elements of the statue's alloy.

Thermo scientific Nitron portable x-ray fluorescence type, model XLT_3 Golded x-ray analyzer was used for characterization the chemical composition of the alloy.

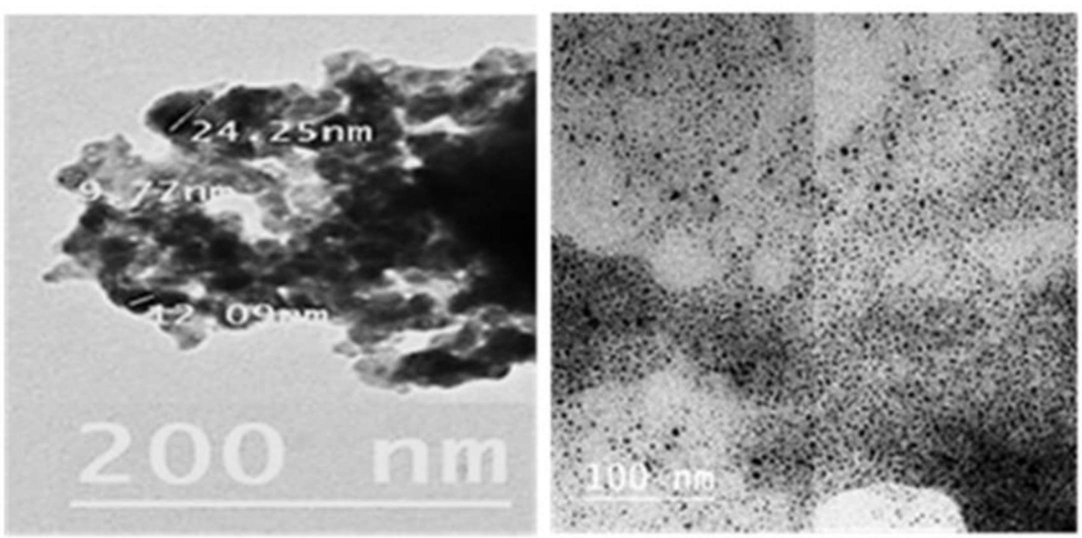
Shear, tensile, and compressive strengths of the selected three polymers were determined before and after exposure to artificial ageing (ultraviolet radiation) λ 312 nm till 168 hrs) according to ASTM D 1002 – 10.

The change of bronze strips' color was evaluated after application of nanocomposites.

4. RESULTS

4.1 NANOPARTICLES

TEM images showed that the grain size of copper nanoparticles $CuNP_s$ is between 12.09-24.25 nm, and those of silver nanoparticles is between 10.38 – 13.62 nm as given in Fig.2.



A B

Fig. 2. TEM images of nanoparticles. (A) Nano copper (200 nm scale), (B) Nano silver (100 nm scale)

4.2 CHARACTERIZATION OF THE STATUE'S ALLOY

Stereomicroscopic examination Figs. 3, 4 indicated that hollow cast technique was used for manufacturing the statue as well as corrosion products.

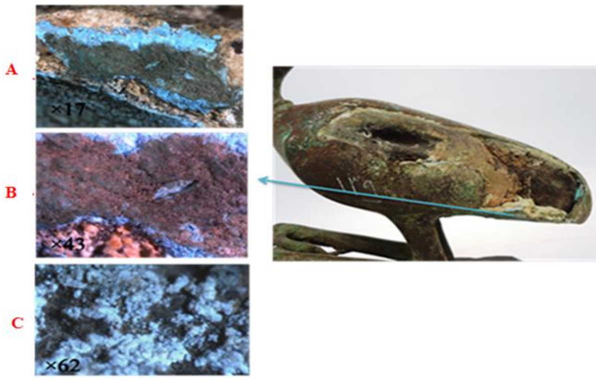


Fig. 3 SM Images of Blue Corrosion Products with different magnifications, (A) 17X, (B) 43X, (C) 62X.

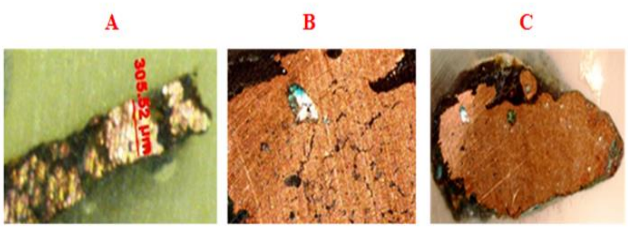


Fig. 4 SM Images of the thickness of metal statue with different magnifications, (A) 17X, (B) 39X, (C) 58X.

Polarizing microscopic investigation revealed that cold hammering. technique was utilized as clear from twinning of crystals in Fig.5.

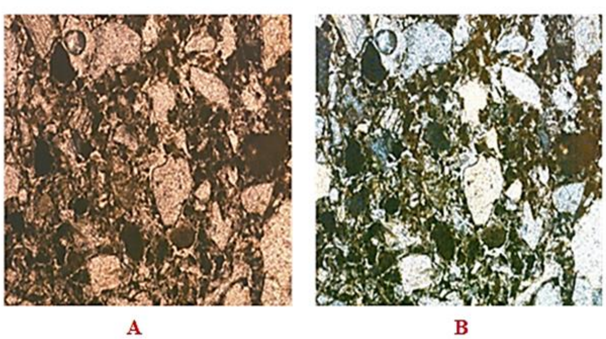


Fig. 5 PLM Images of the statute's bronze alloy, (A) Under PL, (B) Under CN.

SEM micrographs showed morphology of the statue's surface and corrosion layers (see Fig.6).

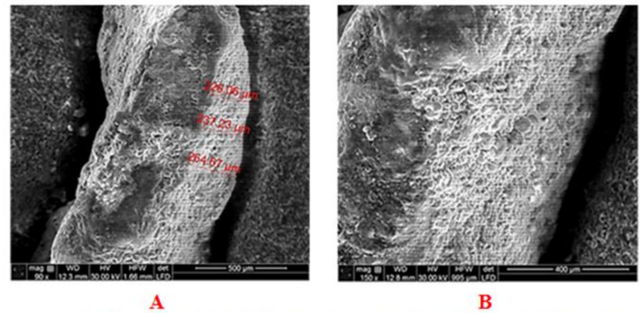
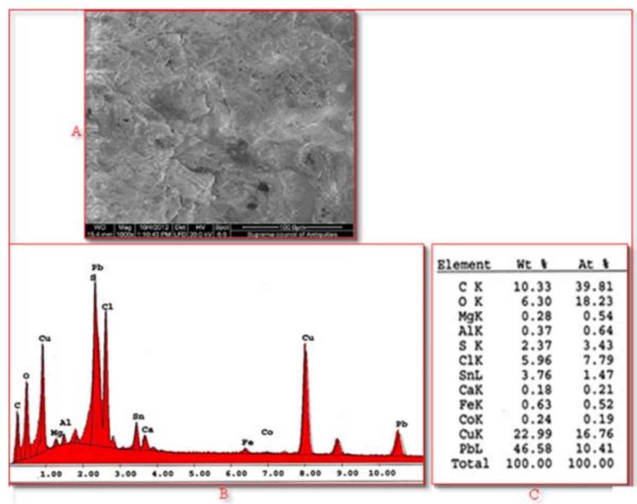


Fig. 6 SEM Photomicrograph of the statute's bronze alloy with large field detector, (A) thickness of bronze sample 90X, (B) layers of corrosion products150X.

Whereas EDX analysis visualized that the statue was made from lead tin bronze alloy Cu: 22.99%, Pb: 46.58%, Sn: 3.76% as shown in Fig.7. The internal core of the statue constitutes mainly of silica Si: 23.79% and Al: 8.02% .

Fe: 9.48 %, (see Fig8). Portable x-ray fluorescence pXRF data confirmed the previous EDX results of the alloy (Fig. 9).



Element	Wt %	At %
C K	10.33	39.81
O K	6.30	18.23
MgK	0.28	0.54
AlK	0.37	0.64
S K	2.37	3.43
ClK	5.96	7.79
SnL	3.76	1.47
CaK	0.18	0.21
FeK	0.63	0.52
CoK	0.24	0.19
CuK	22.99	16.76
PbL	46.58	10.41
Total	100.00	100.00

Fig. 7 SEM photomicrograph of the statute's bronze alloy (A) 1000X, (B) EDX spectrum, (C) Percentages of elements.

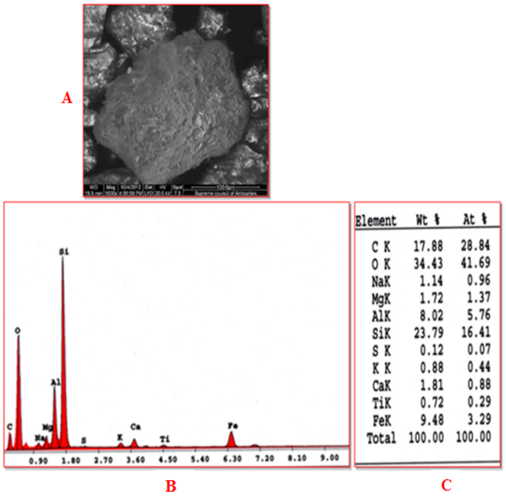


Fig. 8 SEM photomicrograph of the statute's internal core (A) 1000X, (B) EDX Spectrum, (C) Percentages of elements.

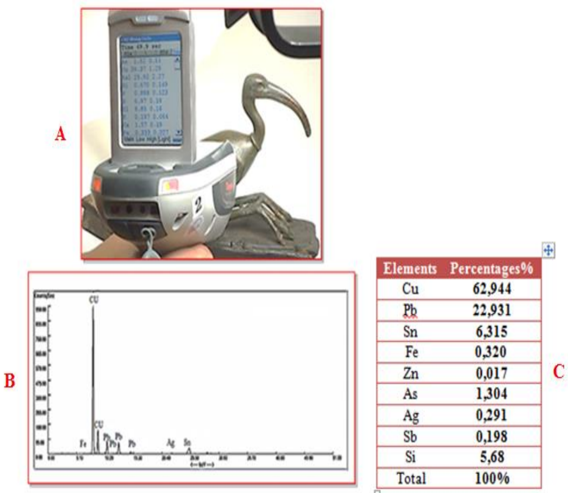


Fig. 9 Portable XRF analysis of the statute's bronze alloy. (A) During analysis, (B) XRF Spectrum, (C) Percentages of elements.

4.3 MECHANICAL PROPERTIES OF POLYMERS

4.3.1 Shear strength (i.e. adhesion force)

Data showed that plexisol P-550 polymer is the best one, comparing with paraloid B-66 and thermoplastic urethane ones after exposure to artificial ageing . It gives higher values and in the meantime a lower decrease in values after exposure to artificial ageing. Before ageing the value was 77.85, after 48 hrs ageing was 66.98 and reached to 62.78 after 168 hrs ageing. Concerning paraloid B-66 polymer there is a sharp decrease in its values as follows: before ageing :21.1, after 48 hrs ageing: 7.22, and after 168 hrs: 7.11. For thermoplastic polyur-ethane gives the following values: before ageing: 10.29, after 48 hrs ageing : 9.32, and after 168 hrs ageing: 8.98, (see Fig.10).

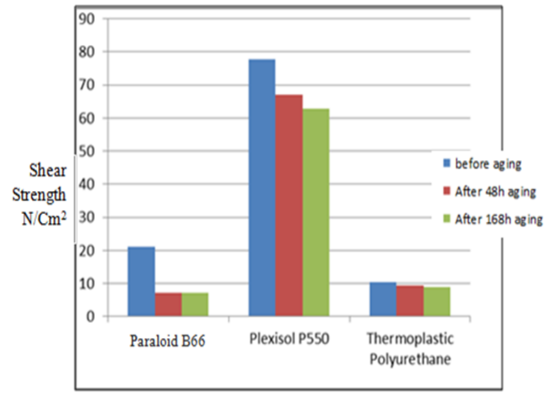


Fig. 10 Effect of artificial ageing on shear strength of the three polymers.

4.3.2 Tensile strength

Results declared that Polyurethane polymer has high flexibility, value: 630%. It Kept this flexibility after exposure to 48 hrs ageing, but it decreased to 573% after 168 hrs ageing. On the other hand paraloid B-66 Polymer was completely destructed and became fragile after dryness. So, this test could not be continued. Plexisol P-550 polymer gives the same tensile strength value: 250% before and after exposure to ageing for 168 hrs (see Fig.11).

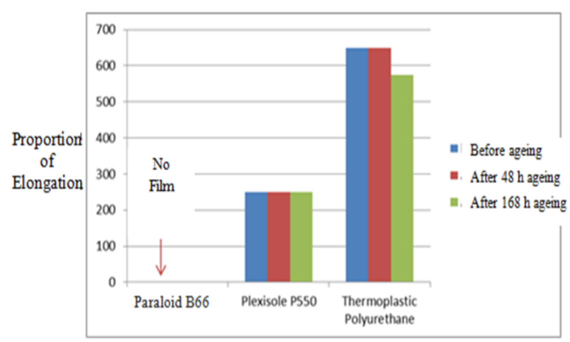


Fig. 11 Effect of artificial ageing on tensile strength of the three polymers.

4.3.3 Compressive strength

Thermoplastic polyurethane polymer demonstrated deformation and changes in its dimensions after exposure to compressive forces as follows: before ageing: 49.76 N/cm² after ageing 34.64 N/cm². Also paraloid B-66 polymer was fractured during exposure to small compressive forces, before ageing : 68.32

N/cm² and after ageing 168 hrs. 52.6 N/cm² .On the other hand plexisol P- 550 polymer showed high resistance to large compressive forces, before ageing : 1399 N/cm² and after ageing for 168 hrs: 1018 N/cm² as shown in Fig.12.

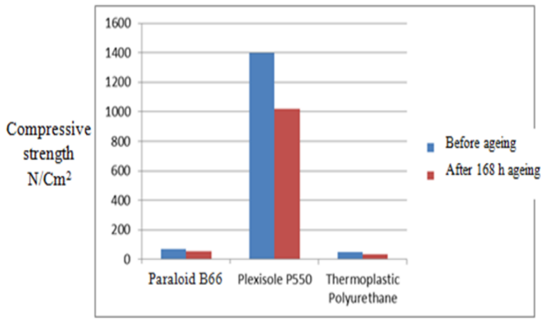


Fig. 12 Effect of artificial ageing on Compressive strength of the three polymers.

5. ASSESSMENT OF NANOCOMPOSITES

5.1 NANOCOPPER PLEXISOL P- 550 COMPOSITE

Data declared that addition of nano-copper particles $CuNP_s$ to plexisol P- 550 polymer ameliorates shear strength, values, (see Fig.13). It increases parallely by increasing the percentage of the added nano Cu particles from 0.25% to 1%, values as follows:

Concentration of Cu NPs %	Shear strength N/cm²
0.25	85.23
0.50	124.02
1.00	182.31

It was found that 1% nano – Cu plexisol P-550 composite had the lowest change in color after exposure to artificial ageing for 168 hrs. ΔE value: 2.54 as given in Table 1.

5.2 Nano silver plexisol P-550 Composite

By increasing the percentage of the added nano silver particles $AgNp_s$ from 0.25% to 1% there was a decrease in shear strength values as follows (see Fig. 13).

Concentration of Ag NPs %	Shear strength N/cm²
0.25	139.00
50.0	126.87
1.00	60.00

With respect to color change test, there was a large change in color. Its ΔE value is 7.52 (see Table 1).

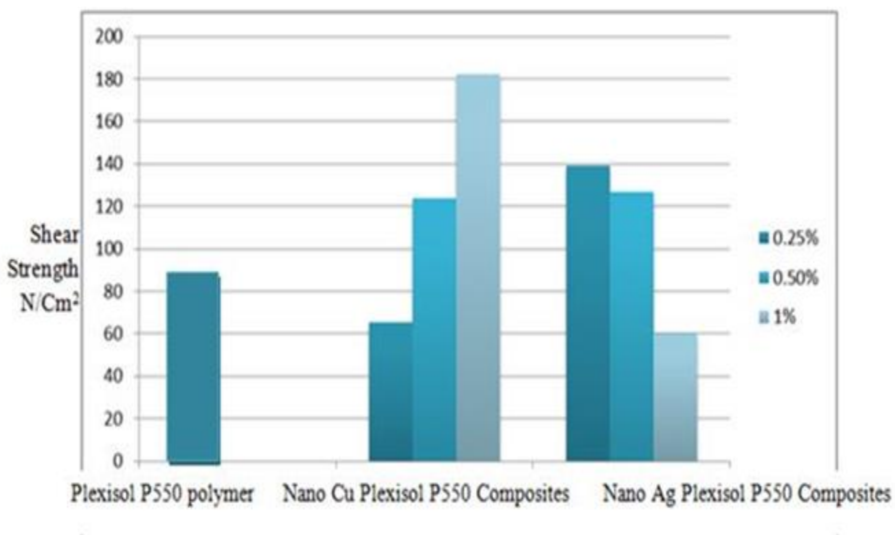


Fig. 13 Shear Strength results of Plexisol P-550 Polymer , Nano Copper & Nano Silver Plexisol P-550 Composites.

Table 1. Color Change of Plexisol P-550, Nano Copper&Nano Silver Plexisol P-550 Composites before and after artificial aging processes.

Sample	before artificial aging			after artificial aging			Color change			
	L	a	b	L	a	b	ΔL	Δa	Δb	ΔE
Plexisol P-550 polymer.	89.38	0.62	-7	87.99	0.28	-5.89	-1.39	-0.34	1.11	1.81
0.25% Nano Cu Plexisol P-550 Composite.	78.43	1.06	-4.22	71.75	0.75	-3.04	-6.68	-0.31	1.18	6.79
0.5%Nano Cu Plexisol P-550 Composite.	75.01	1.15	-4.48	70.48	1.57	-3.52	-4.53	0.42	1.32	4.74
1%Nano Cu Plexisol P-550 Composite.	69.75	1.7	-4.09	67.34	1.14	-3.51	-2.41	-0.56	0.58	2.54
0.25%Nano Ag Plexisol P-550 Composite.	62.45	0.57	-3.49	48.3	2.67	-1.55	-14.15	2.1	1.94	14.44
0.5%Nano Ag Plexisol P-550 Composite.	33.56	0.88	-1.37	26.67	2.56	4.62	-6.89	1.68	5.99	9.2
1%Nano Ag Plexisol P-550 Composite.	25.58	0.5	0.02	19.81	2.22	4.53	-5.77	1.72	4.51	7.52

L : Brightness, a: Change of color from red (+value) to green (-value), b : Change of color from yellow (+value) to blue (-value), ΔE: Total chromatic change

6. DISCUSSION AND CONCLUSION

In the current study, three polymers were assessed: Paraloid B-66, plexisol P-550, and thermo- plastic polyurethane copolymer, through mechanical properties (shear, tensile, and compressive strengths). Plexisol P-550 polymer donates the best mechanical properties after exposure to artificial ageing (UV radiation).

Nano-copper and Nano-silver particles $CuNP_s$ & $AgNP_s$ were added in three concentration 0.25, 0.5, 1.0 w/v to plexisol P-550 polymer to form polymer nanocomposites. Evaluation of nanocomposites was carried out by determining shear strength (i.e. adhesion force), and change in color.

The properties of polymer nanocomposites PN_c depend to a great extent on the polymer type (i. e. chemical composition) matrices, nature of nanoparticles (size/shape), and loading method in which they were prepared. There is an influence of the nano-particle type on the mechanical properties of the obtained polymer nanocomposite, (Aki Kutvanon, et al., 2012; Ciprati., 2004; Ciprati, et al., 2006; Tjung, 2006, Koo, 2016; Grosby, et al., 2007).

The success of 1% nanocopper plexisol P-550 composite for enhancing shear strength is due to strong polymer–nano copper particle intera-ctions. The formation of polymer network (cross links) has a predominant role on the PN_c reinforcement (Dinari, at al., 2014). Nano – copper particles have small nano size, and sherical shape, which are compatible to that of the polymer monomers, more effective at toughening the polymer nanocomposite, and uniform dispersion in the polymer matrices (Tjong, 2006; Aki Kutvanon et al., 2012)

It is found that shear strength values of the nano–copper plexisol P-550 composite were increased parallely by increasing the conc-entration of nano-copper particles from 0.25 to 1% . It reaches its highest value: 182.31 N/ cm^2. Moreover, data declared that it gives the lowest change in color Δ E : 2.54.This character is urgent and essential in restoration and conservation field of artifacts.

On the other hand, data of nano – silver plexisol P-550 composite showed that there is an increase of shear strength value at 0.25% concentration of $AgNP_s$ only. But there is a continuous decrease by increasing the concentration of Ag NPs from 0.5 to 1%. It reaches its lowest value: 60.00 N/ cm^2 This refers to agglomeration areas of nano-silver particles in the polymer matrix (Riad et al., 2015). This nano- composite gives the highest change in color Δ E: 7.72, which is refused in cultural heritage field.

In conclusion, 1% nano-copper plexisol P-550 composite is recommended for the completion of lost parts in ancient bronze artifacts. It enhanced the adhesion force of the Polymer, conserved the alloy's color, and precluded distortion caused by utilizing conventional materials.

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REFERENCES

Aki Kutvanon, A., Rossi, G., Puisto, S.R., Rostedt, N.K.J., and Ala- Nissla, T., (2012) Influence of nanoparticle size, loading and shape on the mechanical properties of polymer nanocomposites, *Journal of chemical physics* 137, issue 21, 214901- 214908.

Cheng Ma, P., Kim, J.k., Tang, B.Z., (2007) Effects of silane functionalization on the properties of carbon nano tube / epoxy nanocomposites, *Composites science and technology*, Vol.67, issue, 14, 2965 – 2972.

Ciprati, D.L., (2004) Mechanical characterization of polymer nanocomposites, and the role of interfase. Master thesis of science in materials science and Engineering, Georgia Institute of Technology.

Ciprati, D.L., Jacob, K, and Tannenbaum, R., (2006) Characterization of polymer nanocomposite interphase and its impact on mechanical properties, *Macromolecules*, Vol. 39, 19. 6565-6573.

Davis, J., (2000) Corrosion: Understanding the basis Library of Congress ASM International.

Dinari, M., Reza Raja, A., (2017), Structural thermal and mechanical properties of polymer nanocomposites based on organo soluble polyamide with naphtyl pendent group layered double hydroxide high performance, *Polymer journal,* vol. 29, issue 8, 951-959.

Fedel, M., (2010) Environmentally friendly hybrid coatings for corrosion protection : Saline based pre – treatmenrs and nano structured waterborne coatings, Department of materials engineering and Industrial technologies, University of Torento, Italy, 7- 10.

Feretti, M. O Miazzo, L., Moioli, (1997) The applicalicin of non – destructive XRF method to identify differents alloy in the bronze statue of the Capitoline horse, *Studies in conservation*, Vol. 42, No. 4, pp 241- 246.

Figueiredo, E., (2010) Study of metallurgy and corrosion of ancient copper based artifacts from the portuguese territory, Universidad Nova de Lisboan, Faculdade de cienciase Technologia.

Grosby, A. F., Young Lee, J., (2007) Polymer nanocomposites: The nano effect on mechanical properties, *Journal Polymer reviews*, Vol.47, issue 2, 217 – 229.

Helmi, F.M., (2016) Study of color conversion by time in ancient Egyptian faience artifacts, SCIENTIFIC CULTURE, Vol. 2, No.3, 17- 23.

Ingo, G.M., De carro, T., Riccucci, C., , khos Roff, S., (2006) Uncommon corrosion phenomena of archaeological bronze alloys, *Applied physics journal* A 83, 581-588.

Ingo, G.M., (2009) Large scale investigation of corrosion agents and mechanism of metallic archaeological artifacts from the Mediterranean basin, in 4th Intern. Congress on science and technology for safeguard of cultural heritage in the Mediterranean Basin, Cairo, Egypt .

Joseph, R., Dorothy, R., (2013) Corrosion resistance of nano-particle incorporated nano coatings, *European chemical Bulletin*, Vol.2 No. 12, 965 – 970.

Karydas, A., (2008) Mobile micro – XRF and LIBS spectrometer for diagnostic micro – analysis of ancient metal objects, chapter 6, in Metals and museums in the Mediterranean, Edited by B. Argyropoulos, Department of conservation of Antiquities works of art, Technological Institute of Athens, Greece, 154 – 164.

Kiran, M.S.R.N, Raidongia Ramamurty, U., Rao, C.N.R., (2011) Improved mechanical properties of polymer nanocomposites, incorporating graphene – like BN: Dependence of the number of BN layers, *Scripta Materialia*, Vol .64, issue 6, 592-595.

Koo, J.H., (2016) Mechanical properties of polymer nanocomposites, chapter 7, publisher Cambridge University Press, 273 – 331.

L. Roy Xu, L., Vikram Bhamidipati, Wei – Hong Zhong, Jiang Li, Charles M. Lukehart, Edgar Lara – Curzio, Kenneth, e.Liu, Michael, J.Lance, (2004) Mechanical property characterization of a polymeric nanocomposite reinforced by Graphitic nanofibers with reactive linkers, *Journal of composite materials*, Vol. 38, No.18, 1563 – 1582.

Langrodi, E., (2009) Synthesis and characterization of nanosilica based coatings for protection of antique articles, *Intern. Journal of Nanotechnology*, Vol .6, no, 10, 10 – 11.

Lifu, Q., Ling, X., (2012) Preliminary study of corrosion sratues on bronze excavated from Qin dynasty tombs at Xinfeng town in china, Intern. *Journal of Corrosion*, Vol. 2012, 1-6

Lucas, A., Harris, J.R., (1962) Ancient Egyptian materials and Industries, 4th edition, Edward Arnold, London.

Ogdan, J., (2000) Metals. Ancient Egyptian materials and technology, (Eds. P. T. Nicholson and Show, I., Cambridge University Press.

Pathak, S., Khanna, A., (2012) Sol – Gel nanocoating for corrosion protection, in corrosion protection and control, edited by, Cock, Indian Institute of technology Bombay, © wood head publishing limited, India.

Pawelic, z., Bakar, M., (2013) Shaping, mechanical and thermal properties of polymer nanocomposites, *Maintenance problems*, 159 – 168.

Riad, M., Harhash, A., Elhiny O., Salem, G., (2015) Evaluation of the shear bond strength of orthodontic adhesive system containing antimicrobial silver nanoparticles on bonding of metal brackets to Enamel, *Life Science Journal*, Vol. No.12, cumulated No.59, 32 - 35.

Robbiola, L., Blengino, J.M., and Fiaud, C., (1998) Morphology and mechanism of formation of natural patina on archaeological Cu-Sn alloys, *Corrosion Science Journal*, 40, Vol. 40, Issue 12, 2083 – 2111.

Scott, D.A., (2002), Copper and bronze in art: Corrosion, colorants conservation, Los Angeles, Getty Conservation Institute, 392- 396.

Scott, D.A., Dodd, L.S., (2002), Examination, conservation and analysis of a gilded Egyptian bronze Osiris, Journal of cultural Heritage, 3(4), 333- 345

Selwen, L., (2004) Metals and Corrosion: A handbook for the conservation professional, Ottawa, Canada, Canadian Conservation Institute.

Smith, A., Botha, H., de Beer, F., Ferg, E., (2011) The examination, analysis and conservation of a bronze Egyptian Horus statuette, *Nuclear Instrument and Methods, in Physics Research* A, No. 651, 221-228.

Stevens, R., Garside, P., Russell, E., (2011) A review of current and recent practice in the use of adhesives by the conservation Department at the British library, Proc. symposium in adhesives and consolidants for conservation, Research and applications, Canadian conservation Institute.

Tjung, S.C., (2006) Structural and mechanical properties of polymer nanocomposites, *Materials science and Engineering: Reports,* Vol. 53, issue 3-4, 73-197.

Tsirita, k., (2012), The selection of the gap-filling material for the conservation of a Chinese Shang dynasty bronze vase, Technological Educational Institute of Athens, Department of conservation of antiquities and works of art.

Tylecota, R.F., (1979) The effect of soil condition on the long term corrosion of buried tin-bronzes and copper, *Journal of Archaeological Science*, Vol.6, issue 4, 345 – 368.

Vassiliou, P., (2008) Copper alloy and silver artifacts protection by coating with nano-alumina pigments, School of chemical Engineering, National Technical University of Athens, 132 – 137.

Wang, J., Wu, Y., Zhang, S., (2014) A new coating system modified with nano-sized particles for archaeological bronze protection, *Studies in Conservation*, Vol. 59, No.4, 268- 275.

Wang, Q., Huang, H., Shearman F., (2009), Bronzes from the sacred animal Necropolis at Saqqara, Egypt, A study of the metals and corrosion, *The British Museum Technical Research Bulletin* 3, 73- 82.

Wenjie Zhao, Tong Li, Yupeng Li, Daniel, J., O' Brien, Mauricio Terrones, Bingping wei, Jonghwan suhr, Lucas Lu, (2018) Mechanical Properties of nanocomposites reinforced by carbon nanotube sponges, *Journal of Materiomics*, Vol. 4, issue 2, 157 – 164.

Yan, X., Xu, G., (2010) Corrosion and mechanical properties of Epoxy- polyurethane/Bronze composite coating with low infrared emissivity, College of material science and technology, Nanjing university of Aeronautics and Astronautics, China.

Zvi, G., (1980) Archaeological chemistry (Chemical analysis), Ph.D, Nuclear Research center, published by John Wiley and Sons, 2nd edition.