EGTRIB Journal
JOURNAL OF
THE EGYPTIAN SOCIETY OF TRIBOLOGY
VOLUME 14, No. 3, July 2017, pp. 66 - 83 ISSN 2090 - 5882
(Received March 15. 2017, Accepted in final form June 28. 2017)

HARDNESS AND WEAR OF POLYMETHYL METHACRYLATE FILLED WITH MULTI- WALLED CARBON NANOTUBES AS DENTURE BASE MATERIALS

Ameer A. K., Mousa M. O. and Ali W. Y.

Department of Production Engineering & Mechanical Design, Faculty of Engineering, Minia University, El-Minia – 61111, Egypt.

ABSTRACT
The main objective of this work is to investigate the influence of multi-walled carbon nanotubes (MWCNTs) on the hardness and wear of polymethyl methacrylate (PMMA) reinforced by MWCNTs of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. % contents. PMMA is prepared at both hot and cold acrylic resins to be used as denture base materials. The hardness of the proposed composites is measured by Shore D Durometer on the surface and side of the composites. Wear of MWCNTs/PMMA composites is measured by weighing the specimens before and after the test on a reciprocating wear tester.

Based on the experiments, it is observed that the hardness of hot cured composites increased while wear decreased by increasing MWCNTs content unlike the cold cured composites,. In addition to that, it is shown that wear of hot cured composites decreased by increasing normal loads also unlike cold cured composites where wear increased by increasing normal loads. From this study, it can be concluded that hot cured composites are better than cold cured composites as denture base materials.

KEYWORDS
Multi-walled carbon nanotubes (MWCNTs), polymethyl methacrylate (PMMA), wear, hardness.

INTRODUCTION
Poly (methyl methacrylate) (PMMA) is one of the most widely used industrial polymeric materials and still remains an active material for research at the cutting edges of science. Because of its good biocompatibility, reliability, dimensional stability, absence of taste, odor, tissue irritation and toxicity, [1], teeth adhesion, [2], insolubility in body fluids, relative ease of manipulation, good aesthetic appearance, [3], and color stability, [4], PMMA based materials are widely used as biomaterials. Nowadays, PMMA finds

applications not only in dentistry but also in areas such as transparent glass substitutes, interior design, transparent dielectric films, [5], acrylic paints, [6], and microcellular foams, [7]. Still, one of the most attractive applications of PMMA based materials is in various biomedical applications such as intraocular lenses, [8], bone cement in orthopedic surgery, [9], and removable partial denture [10].

Carbon nanotubes (CNTs) are tiny tubes with diameters of a few nanometers and lengths of several microns made of carbon atoms. Since the discovery of this form of carbon atoms, [11], in 1991, many attentions have been drawn to use the outstanding physical and chemical properties of CNTs such as high Young's modulus (approximately 1 TPa), tensile strength, and excellent thermal and electrical conductivities, [12]. Carbon nanotubes have been used in various fields of applications in recent years due to their high physical, chemical, and mechanical properties, [13]. One of these fields is composite materials in which CNTs are added to a matrix not only as reinforcement but also to obtain other physical and chemical properties such as electrical conductivity and corrosion resistance. Carbon nanotubes are specially introduced into polymer matrices like epoxy to fabricate polymer matrix nanocomposites which presents a new generation of composite materials, [14 - 18]. Increase in strength and Young's modulus of fabricated double-walled carbon nanotubes/epoxy nanocomposites was reported at nanotube content of 0.1 wt. %, [14] s the resulting nanocomposites. The effect of dispersed multi-walled carbon nanotube (MWCNT) on the enhancement of elastic modulus in an epoxy system was investigated, [15].. The enhancement of strength and Young's modulus of phenolic composites reinforced by single-walled carbon nanotubes was reported, [16].

In recent years, researchers across the globe have focused their attention on tailoring polymer Nano composites by filling Nano dimension materials as filler. This has exhibited better mechanical, thermal, optical and electronic properties as compared to that of macro composite because of molecular level interaction between filler and polymer, [19 - 26]. After the discovery carbon nanotubes (CNTs) in 1991, and its versatile properties, structural dimension and high aspect ratio it has become a natural choice as filler to tailor various amenable properties like electrical, thermal and mechanical, [27, 28]. Keeping in view the requirement of high stiffness strength together with low weight and enhanced mechanical, optical, thermal, dielectric and electrical properties, filler reinforced polymer composites find broad spectrum applications in aerospace and biomedical, [29]. Recently, work has also been done to reinforce bone like hard particles and iron doped hydroxyapatite nanoparticles into a polymer matrix for application as a substrate for hard tissue replacement in tissue engineering domains and for the fabrication of composite scaffold, [30, 31]. Amongst the polymers, we have used polymethyl methacrylate in the present investigation because of its less viscous nature, amorphicity, optical clarity, low cost and miscibility of CNTs in PMMA which is quite good.

In the present work, the influence of multi-walled carbon nanotubes (MWCNTs) on the hardness and wear of polymethyl methacrylate (PMMA) reinforced by MWCNTs is investigated.

EXPERIMENTAL

MATERIALS

The matrix materials used in this study is Polymethyl methacrylate (PMMA) and the fiber is Carbon Nanotubes (MWCNTs) as shown in Fig1. PMMA is used in two types; one as cold cured acrylic reins and the other one as heat cured acrylic reins, as investigated in Figures (2, 3). Table 1 shows the properties of PMMA as acrylic resins, while table 2 shows the details of MWCNTs.

Table 1 Typical Properties of Acrylic PMMA

PROPERTY		VALUE
PHYSICAL	Density (lb/in^3) (g/cm^3)	0.043 1.18
	Water Absorption, 24 hrs. (%)	0.3
MECHANICAL	Tensile Strength (psi)	8000-11000
	Tensile Modulus (psi)	350000-500000
	Tensile Elongation at Break (%)	2
	Flexural Strength (psi)	12000-17000
	Flexural Modulus (psi)	350000-500000
	Compressive Strength (psi)	11000-19000
	Compressive Modulus (psi)	-
	Hardness, Rockwell	M80-M100
	IZOD Notched Impact (ft-lb/in)	0.3
THERMAL	Coefficient of Linear Thermal Expansion(x 10^{-5} in./in./°F)	5 - 9
	Heat Deflection Temp (°F / °C) at 264 psi	150-210 / 65-100
	Melting Temp (°F / °C)	265-285 / 130-140
	Max Operating Temp (°F / °C)	150-200 / 65-93
	Thermal Conductivity (BTU-in/ft^2-hr-°F) (x 10^{-4} cal/cm-sec°C)	3.9 1.2
	Flammability Rating	-
ELECTRICAL	Dielectric Strength (V/mil) short time	400
	Dielectric Constant at 60 Hz	4
	Dissipation Factor at 60 Hz	0.05
OPTICAL	Light Transmission, minimum	92

	(%)	
	Refractive Index	**1.48-1.50**

Table 2 Details of MWCNTs.

Diameter, (nm)	Length, (µm)	Surface area, (m^2/g)	Purity, %
8	**10-30**	**90-350**	**95**

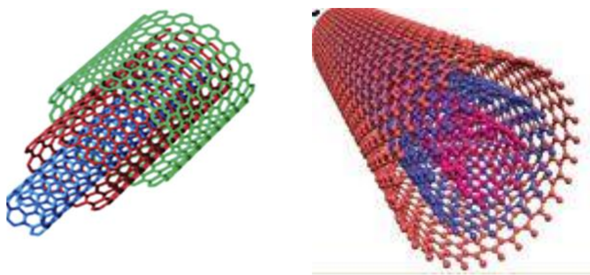

Fig.1 Multi Walled Carbon Nanotubes (MWCNTs), [2]

TEST SPECIMENPREPARATION

Test specimens have been made of PMMA. The MWCNTs were added in different contents of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %. Three specimens have been fabricated from PMMA (as received) and the other specimens have been fabricated by adding the MWCNTs contents to the PMMA powder in a glass beaker, then mixed for 20 second and added to the mold of specimens of cylindrical shape as shown in Figs. 2, 3. The molds were put in water bath at 100°C for 30 second and then ejected and left for bench cooling. Figures 4, 5 show samples of PMMA and PMMA/ MWCNTs composites.

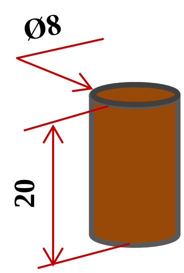

Fig. 2 Test specimen.

TEST METHOD

1-HARDNESS TEST

Shore D Durometer instrument was used. Hardness was measured in three positions. The first one on the surface of the specimens (top and bottom), the second was on the side of the specimens and the third was on the surface in radial distance from center to the edge of all specimens.

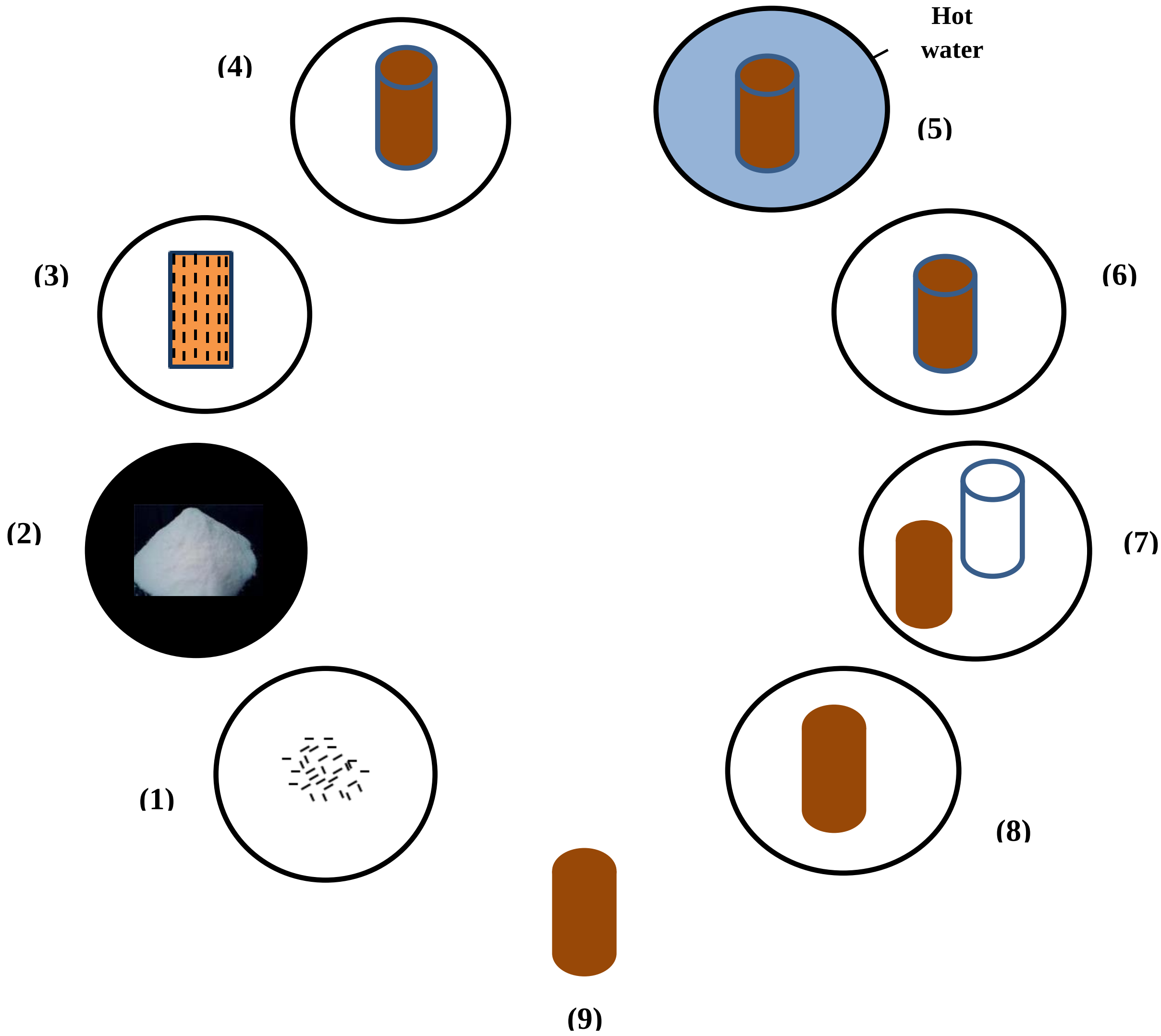

Fig. 3 Preparation steps of test specimens 1. MWCNTs, 2. PMMA, 3. Mixing, 4. Packing, 5. Curing, 6. Bench Cooling, 7. Removing, 8. Grinding, 9. Final Specimen.

2- WEAR TEST

Wear tests were done by weighing the specimens before and after the test to measure the weight loss, where the specimens were tested by making friction between specimens and emery paper (1000 grit size) using reciprocating sliding apparatus as shown in Figure 6.

Fig.4 Sample of PMMA.

Fig.5 Sample of PMMA material reinforced with MWCNTs.

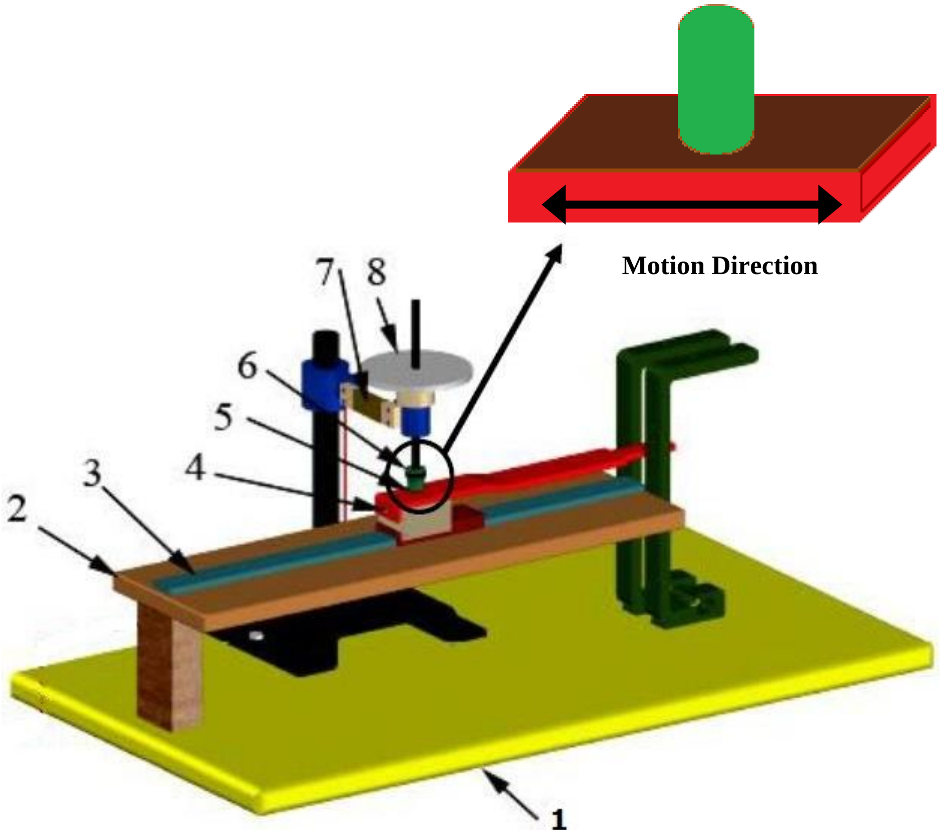

Fig. 6 The reciprocating wear tester; 1. Base, 2. Plate, 3. Linear Bearing, 4. Table, 5. Emery Paper, 6. Sample, 7. Load Cell, 8. Normal Load.

RESULTS AND DISCUSSION

1- HARDNESS

Figures 7, 8 show the effect of MWCNTs contents on the hardness of surface and side of MWCNTs/PMMA composites. It can be noticed that the hardness of the hot composites increased by increasing the content of MWCNTs, this improvement in hardness may be due to the high strength and Young's modulus of the MWCNT reinforcement and the heat treatment that increased hardness values due to an overlap and stacking, which reduced the movement of polymer molecules, which lead to increase the resistance of material to scratch, cut, and become more resistant to plastic deformation.

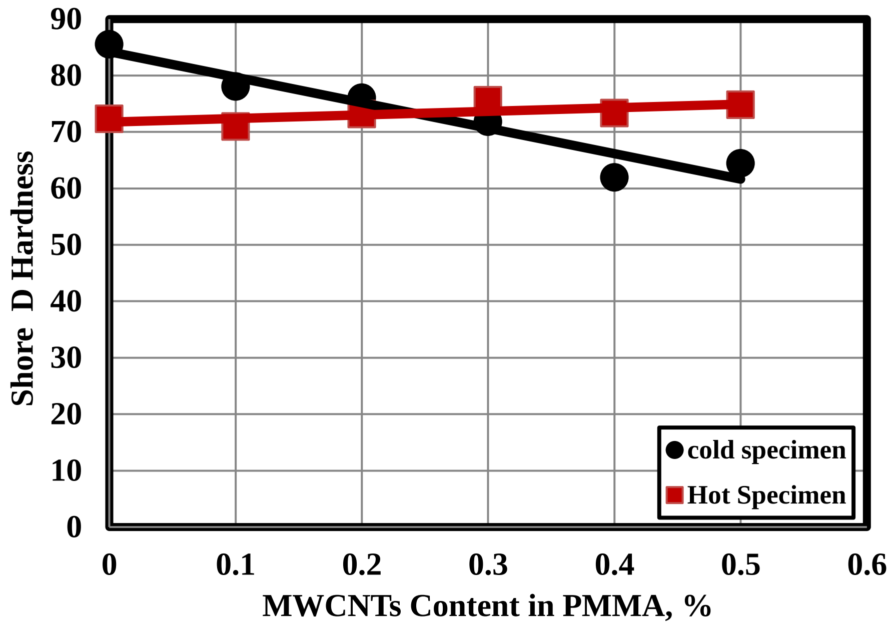

Fig. 7 Effect of MWCNTs contents on the surface hardness of MWCNTs/PMMA composites.

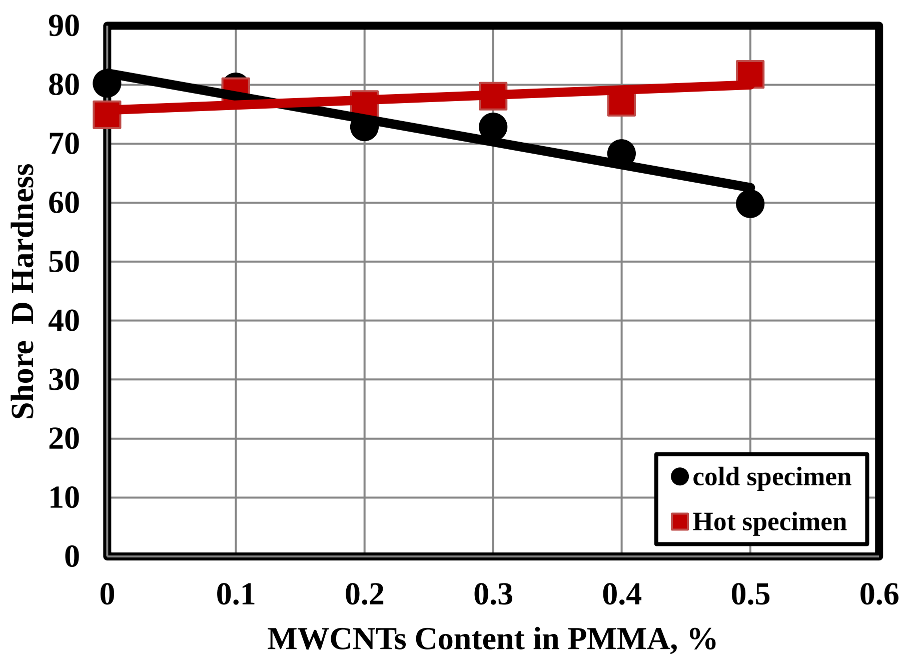

Fig. 8 Effect of MWCNTs contents on the side hardness of MWCNTs/PMMA composites.

Figures 9, 10 show the hardness of the cold MWCNTs / PMMA composites in radial distance from the surface of the composites to the edge, while Figures 11, 12 show the hardness of the hot MWCNTs / PMMA composites in radial distance from the surface of the composites to the edge. It can be seen that the hardness increased at the edge in both hot and cold composites but decreased from the edge to the core of composites where the surface is cooled rapidly than the core of composites. For hot composites the hardness is higher than the cold one because of the reasons mentioned before.

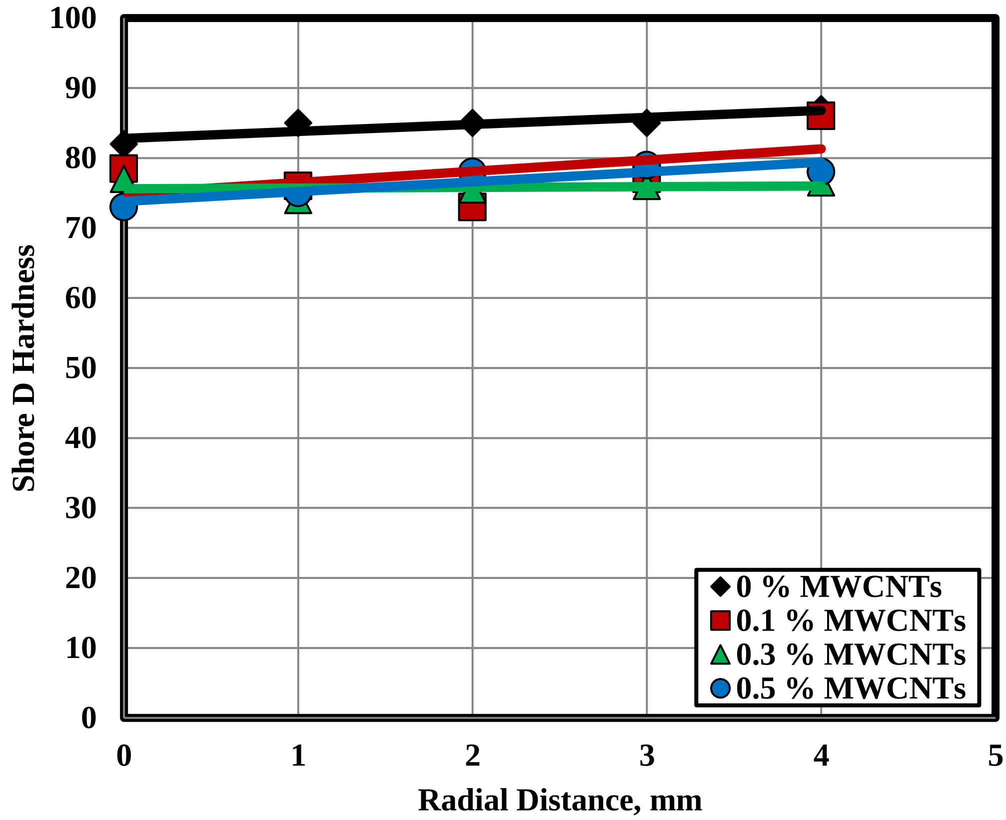

Fig. 9 Hardness of cold MWCNTs/PMMA composites in radial distance from the center of the surface to the edge.

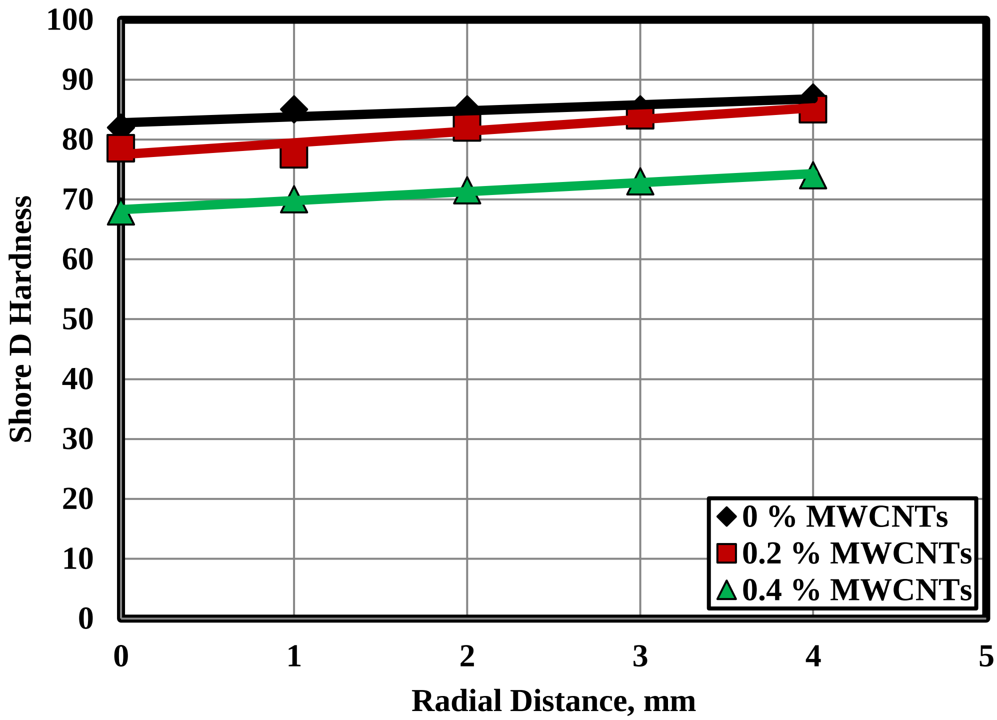

Fig.10 Hardness of cold MWCNTs/PMMA composites in radial distance from the center of the surface to the edge.

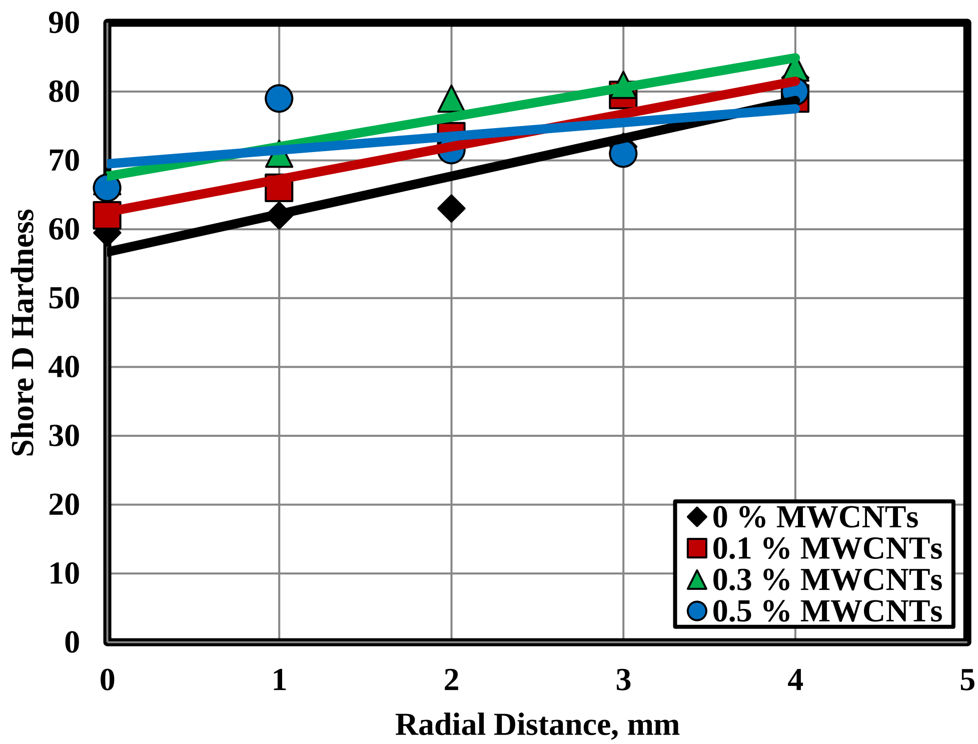

Fig.11 Hardness of hot MWCNTs/PMMA composites in radial distance from the center of the surface to the edge.

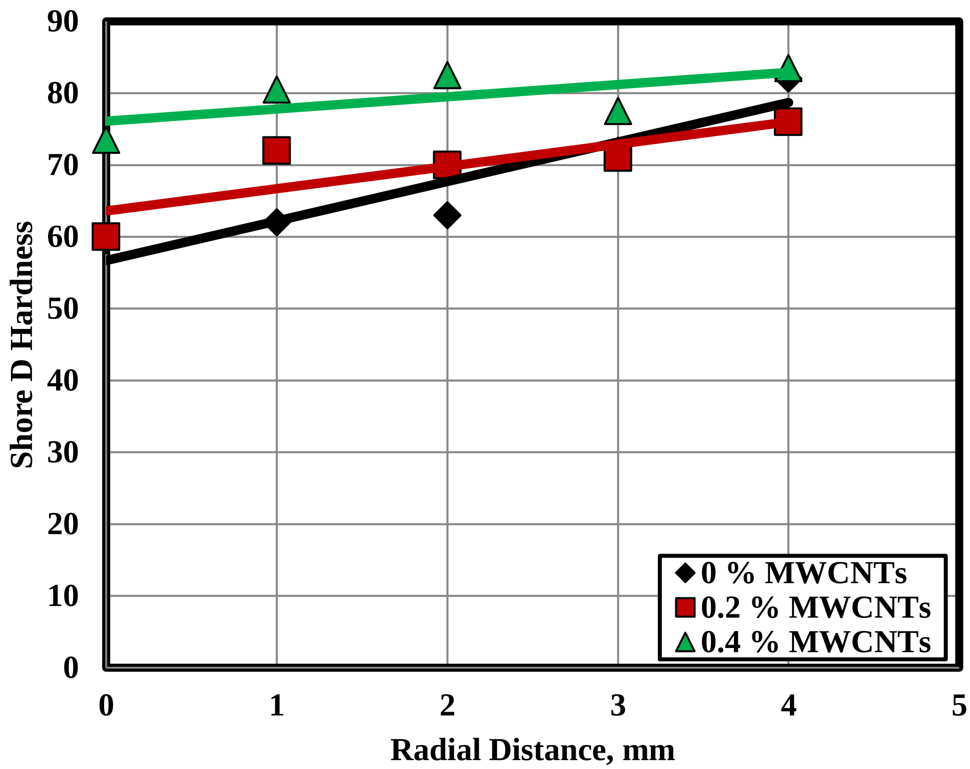

Fig.12 Hardness of hot MWCNTs/PMMA composites in radial distance from the center of the surface to the edge.

2- WEAR

2-1 EFFECT OF MWCNTs CONTENT ON WEAR

Figures 13, 14, 15, 16 and 17 show the effect of MWCNTs content on wear of MWCNTs/PMMA composites for both cold and hot composites under loads 6, 8, 10, 12 14 N. It is noticed that the wear for hot composites decreased by increasing MWCNTs content until of 0.2 and 0.3wt. % content, then wear increased. The decrease of wear may be due to the homogenous dispersion of MWCNTs in PMMA polymer up to 0.3 wt. %, where the strong linkages at the interface phases nanocarbon and PMMA result to increase the coherence of the mixture, while the increase of wear after that content may be due to the inhomogeneous dispersion of MWCNTs in PMMA polymer causing more agglomerations of the carbon nanotubes inside polymer matrix that reduced the reinforcing effects of the MWCNTs by acting as flaws in the resin. On the other side for the cold composites, it can be seen that wear increased by increasing MWCNTs content.

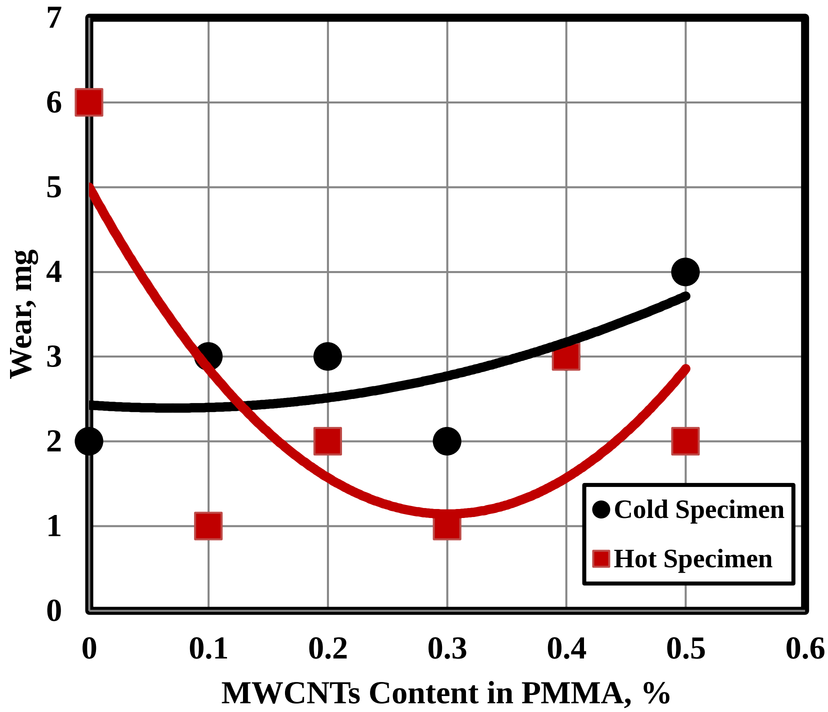

Fig.13 Effect of MWCNTs contents on wear of MWCNTs/PMMA composites at 6 N load.

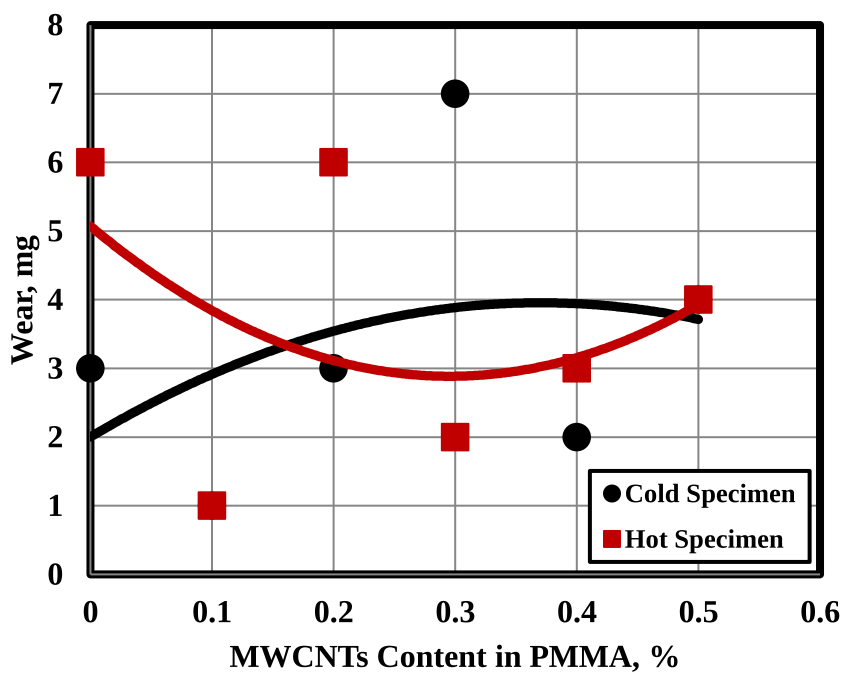

Fig.14 Effect of MWCNTs contents on wear of MWCNTs/PMMA composites at 8 N load.

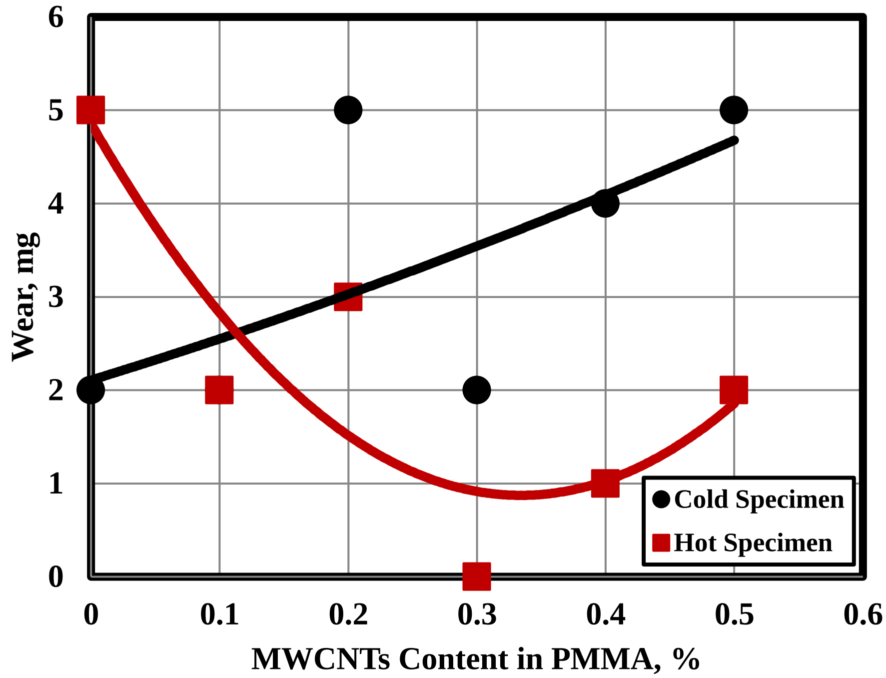

Fig.15 Effect of MWCNTs contents on wear of MWCNTs/PMMA composites at 10 N load.

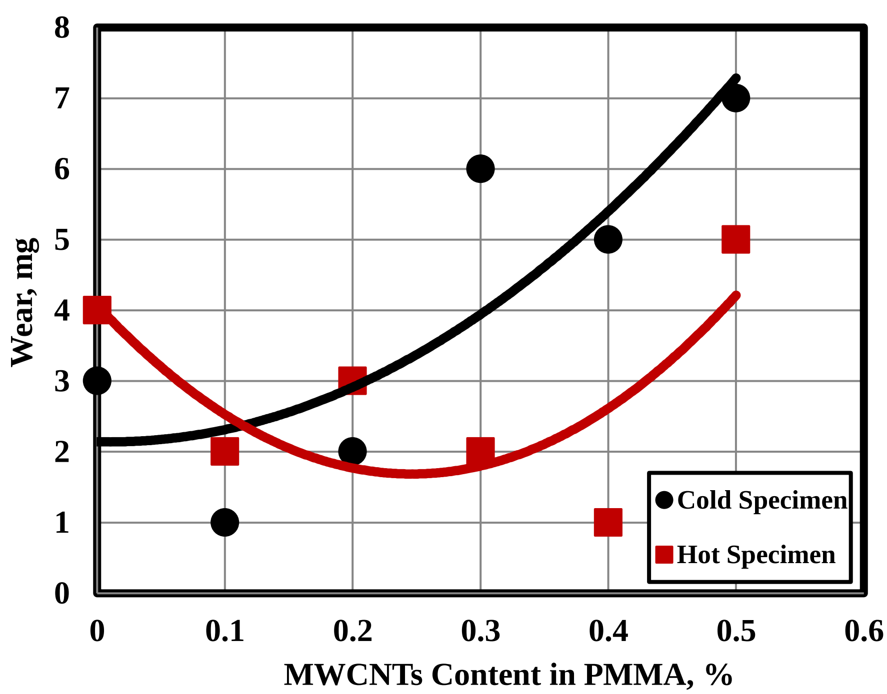

Fig.16 Effect of MWCNTs contents on wear of MWCNTs/PMMA composites at 12 N load.

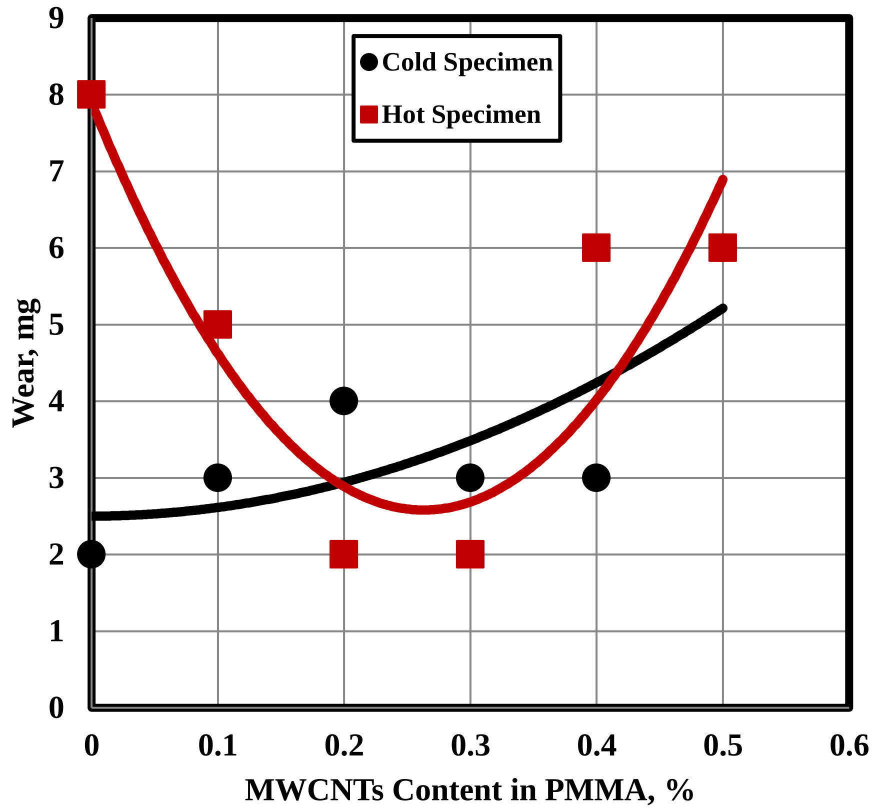

Fig. 17 Effect of MWCNTs contents on wear of MWCNTs/PMMA composites at 14 N load.

2-2 EFFECT OF NORMAL LOAD ON WEAR

Figures 18, 19 show the effect of normal load on wear of cold composites under different contents of MWCNTs, while Figures 20, 21 show the effect of normal load on wear of hot composites. It can be noticed that for cold composites wear increased by increasing normal load. This behaviour may be due to the agglomerates that cannot effectively transfer stress. The local agglomerates formed stress point leads to the generation of fracture source, which increases wear. For hot composites, it can be shown that wear decreases for pure specimen and composites of 0.1, 0.2 and 0.3 wt. %, MWCNTs content, while wear increased for of 0.4 and 0.5 wt. % content because of the agglomeration of MWCNTs inside the PMMA matrix.

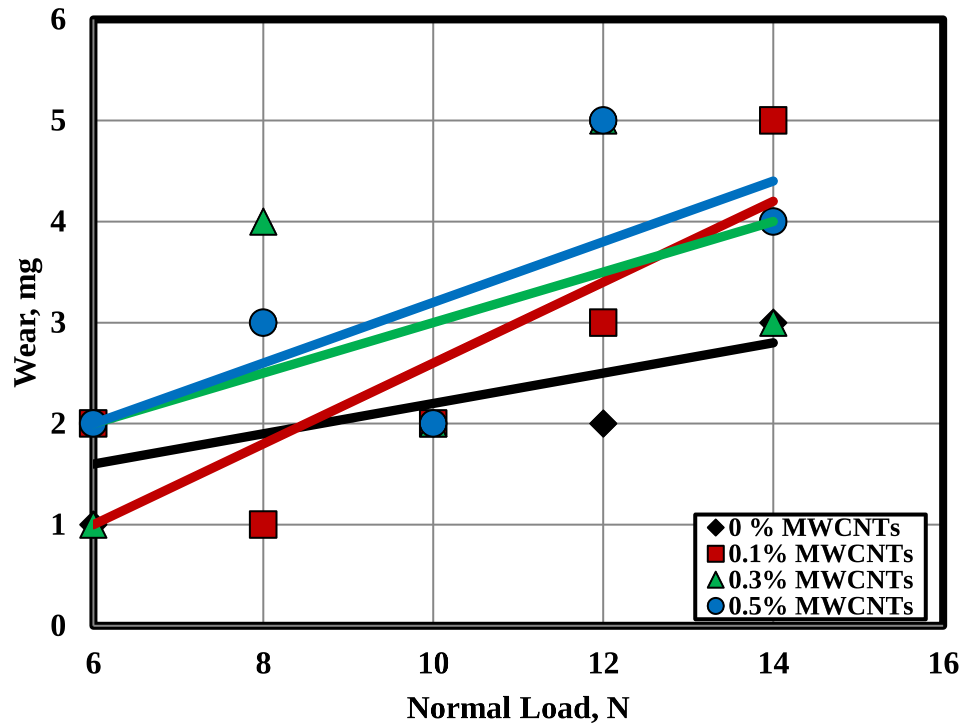

Fig.18 Effect of normal load on wear of cold cured MWCNTs/PMMA.

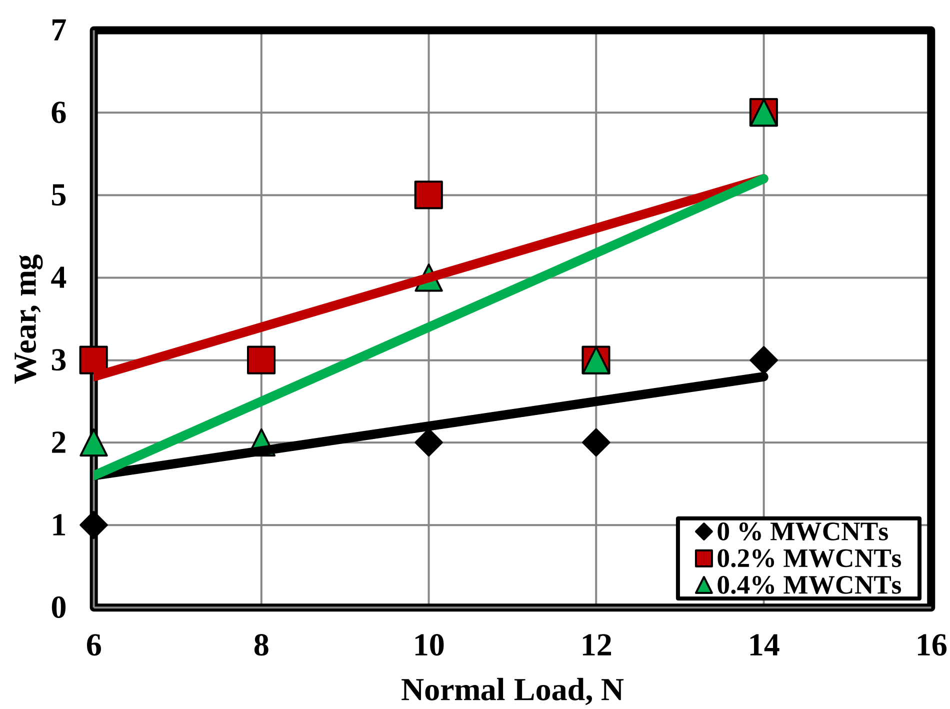

Fig. 19 Effect of normal load on wear of cold cured MWCNTs/PMMA.

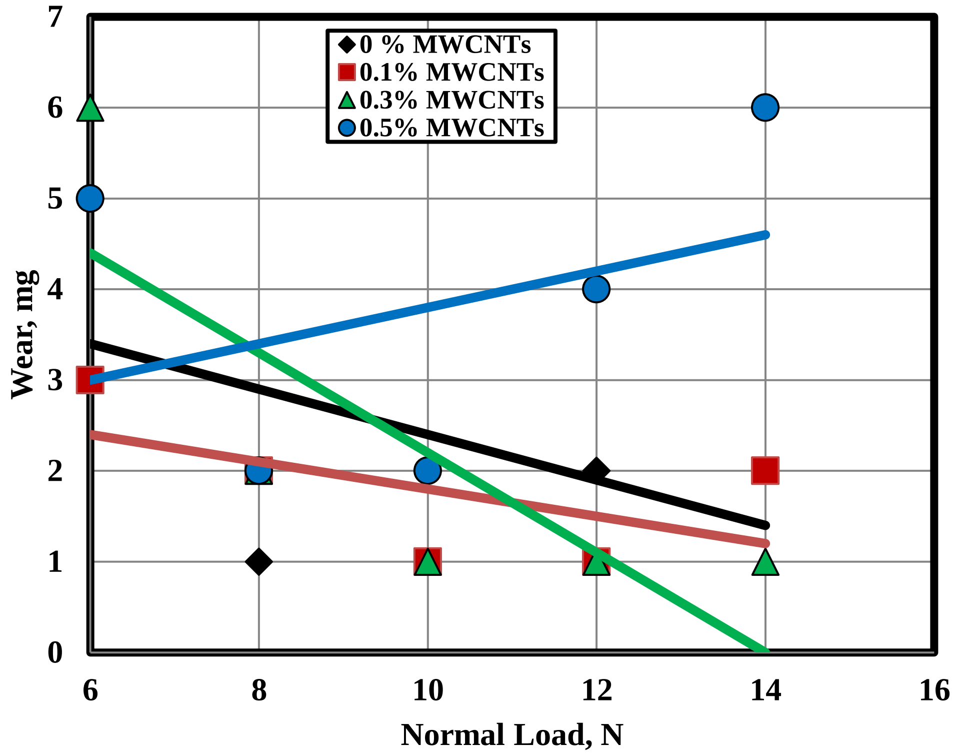

Fig. 20 Effect of normal load on wear of cold cured MWCNTs/PMMA.

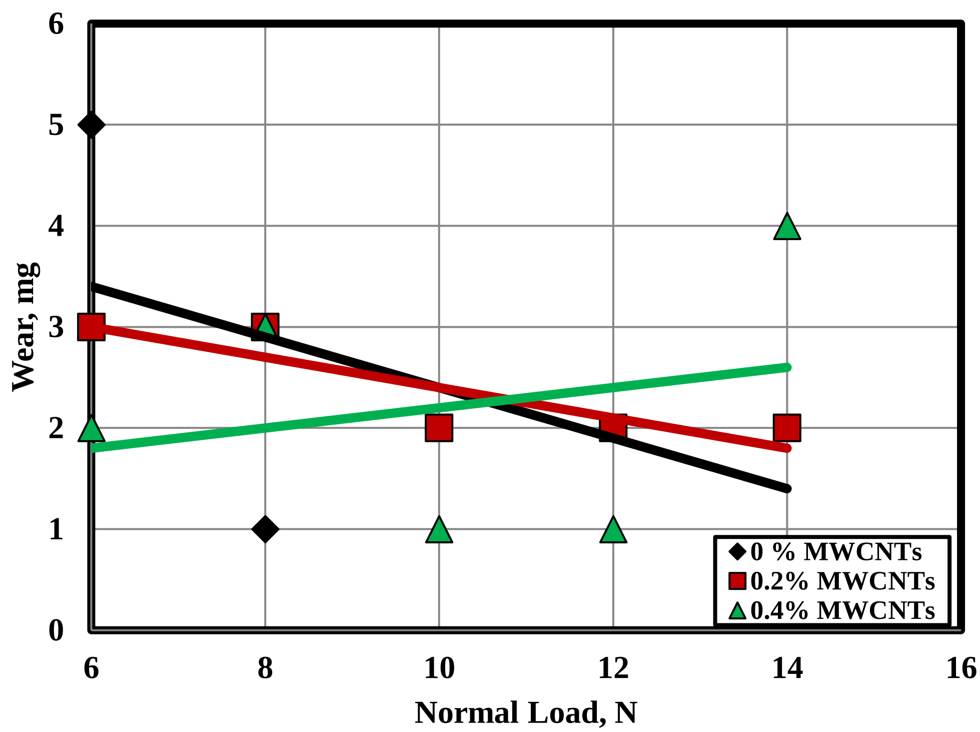

Fig. 21 Effect of normal load on wear of cold cured MWCNTs/PMMA

CONCLUSIONS

From this study the followings can be concluded:

1. Hardness of hot cured MWCNTs/ PMMA composites increases with increasing MWCNTs contents.

2. Hardness of cold cured MWCNTs/ PMMA composites decreases with increasing MWCNTs contents.

3. Wear of hot cured MWCNTs/PMMA composites decreases with increasing MWCNTs content up to 0.3 wt. % content, representing the optimum ones.

4. Wear of hot cured MWCNTs/ PMMA composites increases at MWCNTs contents up to 0.4 and 0.5 wt. %.

5. Wear of cold cured MWCNTs/PMMA composites is relatively higher than unfilled PMMA.

6. Hot cured MWCNTs/ PMMA composites are recommended for medical and engineering applications.

REFERENCES

1. Cooper S., Visser S., Hergenrother R., and Lamba N., "Polymers", in Biomaterials Science: An Introduction to Materials in Medicine," Ratner B., Hoffman A., and Schoen F., Eds., pp. 67– 80, Elsevier Academic Press, SanDiego, Calif, USA, 2nd edition, (2004).

2. Palitsch A., Hannig M., Ferger P., and Balkenhol M., "Bonding of acrylic denture teeth to MMA/PMMA and light-curing denture base materials: the role of conditioning liquids," Journal of Dentistry, vol. 40, no. 3, pp. 210 - 221, (2012).

3. Anusavice J. K., Phillip's Science of Dental Materials, WB Saunders, Philadelphia, Pa, USA, (2003).

4. Bayindir F., Kurklu D., and Yanikoglu N. D., "The effect of staining solutions on the color stability of provisional prosthodontics materials," Journal of Dentistry, vol. 40, no. 2, pp. e41 – e46, (2012).

5. Nagao D., Kinoshita T., Watanabe A., and Konno M., "Fabrication of highly refractive, transparent $BaTiO_3$/poly (methyl methacrylate) composite films with high permittivities, "Polymer International, vol. 60, no. 8, pp. 1180 - 1184, (2011).

6. Rubio E., Almaral J., Ramirez-Bon R., Castano V., and Rodrıguez V., "Organic-inorganic hybrid coating (poly(methyl methacrylate)/monodisperse silica)", Optical Materials, vol. 27, no. 7, pp. 1266 - 1269, (2005).

7. Reglero Ruiz J. A., Saiz-Arroyo C., M., Rodriguez- Perez M. A., and Gonzalez L., "Production, cellular structure and thermal conductivity of microcellular (methyl methacrylate)-(butyl acrylate)-(methyl methacrylate) triblock copolymers," Polymer International, vol. 60, no. 1, pp. 146 - 152, (2011).

8. Shtilman M. I., Polymeric Biomaterials, VSP BV, Utrecht, the Netherlands, (2003).

9. Kuhn K., "What is bone cement?" in The Well-Cemented Total Hip Arthroplasty: Theory and Practice, Breusch S. and Malchau H., Eds., pp. 52 - 60, Springer Medizin, Heidelberg, Germany, (2005).

10. Preshaw P. M., Walls A.W. G., Jakubovics N. S., Moynihan P. J., Jepson N. J. A., and Loewy Z., "Association of removable partial denture use with oral and systemic health," Journal of Dentistry, vol. 39, no. 11, pp. 711 - 719, (2011).

11. Iijima S., "Helical microtubules of graphitic carbon," Nature 354, pp. 56 - 58, (1991).
12. Coleman, J. N., Khan U., Blau W. J. and Gunko Y. K., "Small but strong: a review of the mechanical properties of carbon nanotube–polymer composites", Carbon 44, pp. 1624 - 1652, (2006).
13. Baughman R. H., Zakhidov A. A. and Heer W. A., "Carbon nanotubes—the route toward applications", Science 297, pp. 787 - 792, (2002).
14. Gojny F. H., Wichmann M.H.G., Kopke U., Fiedler B. and Schulte K., "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content," Compos. Sci. Technol. 64, pp. 2363 - 2371, (2004).
15. Martone A., Formicola C. and Giordano M., "Reinforcement efficiency of multi-walled carbon nanotube/epoxy nano composites," Compos Sci Tech 70, pp. 1154 - 1160 (2010).
16. Tai N. H., Yeh M. K. and Peng T. H., "Experimental study and theoretical analysis on the mechanical properties of SWNTs/phenolic composites," Composites: Part B 39, pp. 926 - 932, (2008).
17. Thostenson E. T., Li C. and Chou T. W., "Nanocomposites in context," Compos. Sci. Tech. 65, pp. 491 - 516, (2005).
18. Goadagno L., Vertuccio L., Sorrentiono A., Raimondo M., Naddeo C. and Vittoria V., "Mechanical and barrier properties of epoxy resin filled with multi-walled carbon nanotubes," Carbon 47, pp. 2419 - 2430, (2009).
19. William G. E., Aldo B. A. and Jinwen Z., "Polymer nanocomposites: synthetic and natural filler", a review: Maderas. Cienciay tecnologia; Vol. 7, No. 3, pp. 159 - 178, (2005).
20. Alexandre M. and Dubois P., "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials," Mater. Sci. and Eng., Vol. 28, No.1, pp. 55 - 63, (2000).
21. Pack S., Kashiwagi T., Stemp D., Koo J., Si M., Sokolov J. C. and Rafailovich M.H., "Segregation of Carbon Nanotubes/Organoclays Rendering Polymer Blends Self-Extinguishing", Macromolecules; Vol.42, pp. 6698 - 6709, (2009).
22. Sahoo N. G., Rana S., Cho J. W., Li L. and Chan S. H., "Polymer Nano composites based on functionalized carbon nanotubes," Prog. in Poly. Sci. Vol. 35, pp. 837 - 867, (2010).
23. Jin F. L. and Park S. J., "A review of the preparation and properties of carbon nanotubes-reinforced polymer composites," Carbon Letters; Vol. 12. , No. 2, pp. 57 - 69, (2011).
24. Andrews R., Jacques D., Minot M. and Rantell T., "Fabrication of Carbon Multiwall Nanotube/Polymer Composites by Shear Mixing," Macromol. Mater. Eng. Vol. 287, pp. 395 - 403, (2002).
25. Lasater K. L. and Thostenson E. T., "In-situ thermo resistive characterization of multifunctional composites of carbon nanotubes," Polymer; Vol. 53, pp. 5367 - 5374, (2012).
26. Hu G., Zhao C., Zhang S., Yang M. and Wang Z., "Low percolation thresholds of electrical conductivity and rheology in polyethylene terephthalate through the networks of multi-walled carbon nanotubes", Polymer; Vol. 47, pp. 480 - 488, (2006).

27. Edtmaier C., Janhsen T., Hula R.C., Pambaguian L., Wulz H. G., Forero S. and Hepp F., "Carbon Nanotubes as Highly Conductive Nano-Fillers in Metallic Matrices,"Adv. Mater. Res; Vol. 59, pp. 131 - 137, (2009).
28. Wernik J. M. and Meguid S. A., "Recent Developments in Multifunctional Nanocomposites Using Carbon Nanotubes," App. Mech. Rev. SEPTEMBER; Vol. 63, pp. 1 - 40, (2010).
29. Antonio G., Dante R., Teresa R., Ugo D., Marianna C., Robert D., Luigi N. and Luigi A., "Technical features and criteria in designing fiber-reinforced composite materials," from the aerospace and aeronautical field to Biomedical Applications. J. Appl. Biomaterials and Biomechanics; Vol. 9, No. 2, pp. 151 - 163, (2011).
30. Raucci M.G., Guarino V. and Ambrosio L., "Biomimetic strategies for Bone Repair and regeneration," J. Funct. Biomaterials; Vol. 3, pp. 688 - 705, (2012).
31. Gloria A., Russo T. D., Amora U., Zeppetelli S. D., Alessandro T., Sandri M., Banobre-Lopez M., Pineiro R. Y., Ohlarz M., Tampieri A., Rivas J. Herrmannsdorfer T., Dediu V. A., Ambrosio L. and DeSantis R., "Magnetic Poly(ε-coprolactone)/iron-doped hydroxyapatite nanocomposite substrates for advanced bone tissue engineering," J. R. Soc. Interface; Vol. 10, pp. 20 - 33, (2013).