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INFLUENCE OF MULTI-WALLED CARBON NANOTUBES CONTENT ON THE MECHANICAL PROPERTIES OF COLD AND HOT CURED ACRYLIC RESIN FOR DENTURE BASE.

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ABSTRACT
The main objective of this work is to investigate the effect of multi-walled carbon nanotubes (MWCNTs) on the mechanical properties of polymethyl methacrylate (PMMA) reinforced by MWCNTs of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. % contents. The mechanical properties investigated in the present study are compressive strength, apparent modulus of elasticity, modulus of resilience, modulus of toughness and ductility at yield. PMMA is prepared at both hot and cold acrylic resins to be used as denture base materials. Compression test was considered as a useful tool to describe the mechanical properties of the PMMA/ MWCNTs tested composites. The tests have been carried out on a digital controlled universal testing machine.

Based on the experiments, it is shown that the mechanical properties of the cold PMMA were higher than that measured for the hot at 0 wt. %, MWCNTs, while at 0.1 wt. %, the mechanical properties of the hot MWCNTs/PMMA composites were higher than the cold ones. On the other hand, it was found that after 0.1 wt. %, with increasing MWCNTs content the mechanical properties decreased gradually for both cold and hot composites. The improvement in the strength at 0.1 wt. % may be due to the interfacial shear strength between nanofiller and matrix that was relatively high due to formation of cross links or supra molecular bonding which cover or shield the nanofiller that in turn prevent propagation of crack. From this study, it can be concluded that hot cured composites are better than cold cured composites as denture base materials.

KEYWORDS
Polymethyl methacrylate (PMMA), cold PMMA composites, hot PMMA composites multi-walled carbon nanotubes (MWCNTs), mechanical properties.

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].

There is an ongoing effort to improve the properties of denture base materials. The ultimate goal has been to develop a more biocompatible denture base with better mechanical properties and simpler processing techniques that require shorter time for fabrication, [11]. The incorporation of fibers as impact modifiers into the denture base resin appears to be a good approach to produce stronger and more fracture resistant materials, [12, 13]. It has been studied that the transverse strength of PMMA can be slightly increased by addition of metal strengtheners but they have poor aesthetics. Since the discovery of Carbon Nanotubes (CNTs) by Iijima in 1991 they have been used frequently in experimental studies by incorporation in PMMA to increase their mechanical properties, [14]. Recent experimental studies have suggested that CNT's are 10-100 times higher than the strongest steel at a fraction of the weight when incorporated in PMMA, which results in enhanced properties of the matrix remarkably. CNTs are extremely strong resilient and very light weight, [15]. Different experimental observations on the response of nanotubes under compression by using molecular dynamics simulations showed that CNT's are remarkably flexible and the bending is completely reversible up to angles in excess of 110 degrees, [16, 17].

Recently, researchers across the world have focused their attention on tailoring polymer Nano composites by filling Nano dimension materials as filler. This has showed better mechanical, thermal, optical and electronic properties in comparison with that of macro composite because of molecular level interaction between filler and polymer, [18 - 27] The effect of multi- walled carbon nanotubes (MWCNTs) on the hardness and tribological behavior (friction and wear) of polymethyl methacrylate (PMMA) reinforced by MWCNTs is studied, [28-32]. It can be observed that the tribological properties affect by MWCNTs, where the Friction coefficient for both cold and hot composites decreases gradually by increasing MWCNTs contents and normal load. Hardness of hot cured MWCNTs/PMMA composites increases with increasing MWCNTs contents. Hardness of cold cured MWCNTs/PMMA composites decreases with increasing MWCNTs contents. Wear of hot cured MWCNTs/PMMA composites decreases with increasing MWCNTs content up to 0.3 wt. %

content, representing the optimum ones. Wear of hot cured MWCNTs/ PMMA composites increases at 0.4 and 0.5 wt. % MWCNTs contents. Wear of cold cured MWCNTs/PMMA composites is relatively higher than that observed for unfilled PMMA.

The aim of this study is to reinforce PMMA with MWCNT's. The hypothesis of the study is that the addition of MWCNTs to commercially available cured denture base acrylic resin can significantly enhance its mechanical properties while making them flexible.

EXPERIMENTAL

The Present section presents the experimental work performed to achieve the objectives of the study. The section outline includes the materials used, preparation of specimens, curing of specimens, Mechanical tests.

Materials

The composite matrix used in the present study is polymethyl methacrylate (PMMA) which filled with fiber of multiwall carbon nanotubes (MWCNTs). Practically, PMMA is found in two forms; as cold and heat cured acrylic resins. Table 1 shows the properties of PMMA as acrylic resin which was purchased from (Acrostone Dental & Medical Supplies Company), Cairo, Egypt. Table 2 shows properties for MWCNTs which was purchased from Nanostructured &Amorphous materials, Inc., texas, USA.

Table 1 Typical properties of acrylic PMMA

PROPERTY		VALUE
Physical	Density (kg/m^3)	1180
	Water Absorption, 24 hrs. (%)	0.3
Mechanical	Tensile Strength (MPa)	55-75
	Tensile Modulus (Mpa)	2413-3447
	Tensile Elongation at Break (%)	2
	Fracture Strength (Mpa)	82-117
	Fracture Modulus (Mpa)	2413.16-3447.37
	Compressive Strength (Mpa)	75-131
	Compressive Modulus (Gpa)	2.76-3.30
	Hardness, Rockwell Scale M	M80-M100
	IZOD Notched Impact (KJ/m^2)	1.6

Table 2 Properties of the filler MWCNTs

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

Preparation of Test Specimen

Test specimens have been made of a PMMA matrix. The MWCNTs were added in different contents of 0.1, 0.2, 0.3, 0.4 and 0.5 wt. %. Six specimens have been fabricated from PMMA with 0%wt.of the filler (as received) and the rest 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 Figures 1 and 2. This procedure has been performed for cold and hot cured acrylic resins, where the molds of the hot cured specimens were put in a water bath at 100°C for 30 Minutes and then ejected and left for cooling at room temperature. Test specimens were cut at both ends to flatten the two bases and finished by emery paper of 1000 grain size. Figures 3 and 4 show photographs for specimens of pure PMMA and composite of PMMA with MWCNTs filler respectively.

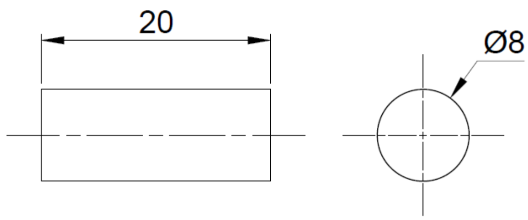
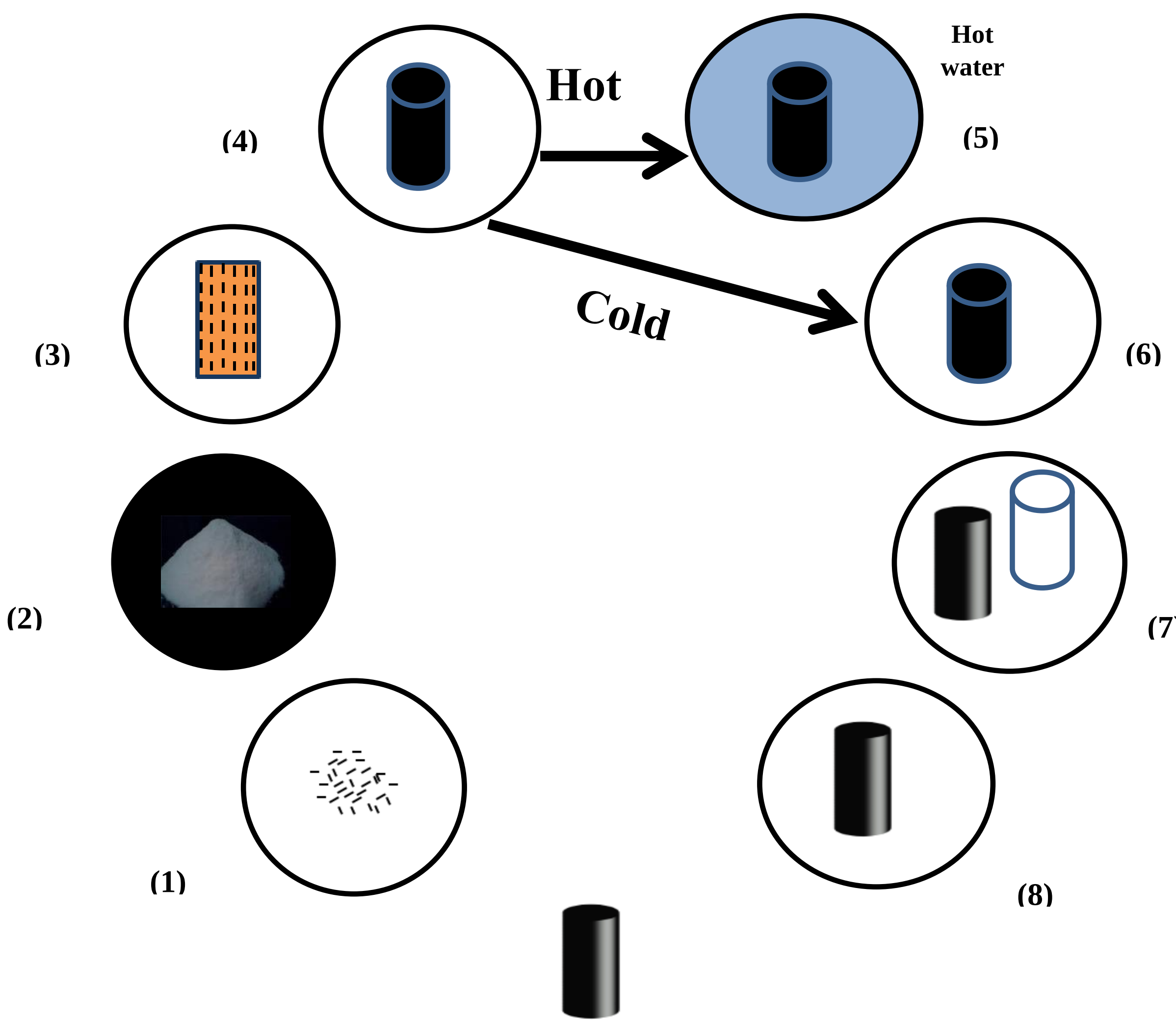


Fig. 1 Wear test specimen.



(9)

1. MWCNTs, 2. PMMA, 3. Mixing, 4. Packing,
5. Curing, 6. Bench Cooling, 7.Removing, 8. Grinding, 9. Final Specimen.

Fig. 2 Preparation steps of test specimens.

Fig. 3 Photograph of specimen of pure PMMA.

Fig. 4 Photograph of specimen of PMMA composite reinforced with MWCNTs.

Mechanical Properties

Compression test was considered as a useful tool to describe the mechanical properties of the PMMA/ MWCNTs tested composites. The compression test was carried out at room temperature using specimen with 8mm diameter and 12 mm height. Fig. 5 shows the test specimen. The tests have been carried out on a digital controlled universal testing machine (Fig. 6) with maximum loading capacity of 30 tons. The universal testing machine has a variable across head speed ranged from 0.1 mm/min up to 50 mm/min. Also, the distance between the cross head and machine base is 800 mm.

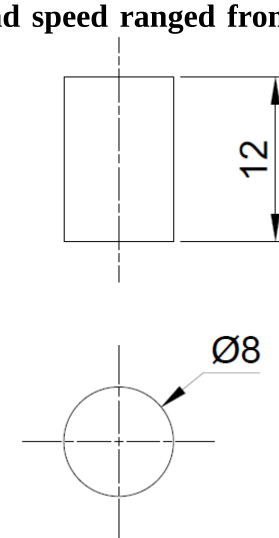


Fig. 5 Compression test specimen

Fig. 6 Universal testing machine.

RESULTS AND DISCUSSION

Compressive Strength

Figure 7 shows the effect of MWCNTs content on the strength of cold and hot MWCNTs/PMMA composites. It is shown that the strength of the cold PMMA is higher than that measured for the hot at 0 wt. %, MWCNTs, while at 0.1 wt. %, the strength of the hot MWCNTs/PMMA composites is higher than the cold composites. On the other hand, it was found that after 0.1wt. %, with increasing MWCNTs content the strength decreased gradually for both cold and hot composites. The improvement in the strength

at 0.1 wt. %, this may be due to the interfacial shear strength between nanofiller and matrix was high due to formation of cross links or supra molecular bonding which cover or shield the nanofiller that in turn prevent propagation of crack and may be due to the use of very fine size nanofillers enable them to enter and fill the space between the chains of polymer , so it restrict the motion of chains and lead to increase rigidity and this will increase the strength. The decrease in strength after 0.1 wt. % may be due to the agglomerations formed in the matrix, where the increase of the amount of nanotubes may lead to the formation of voids and internal cavities, which can negatively impact the mechanical performance of the composite.

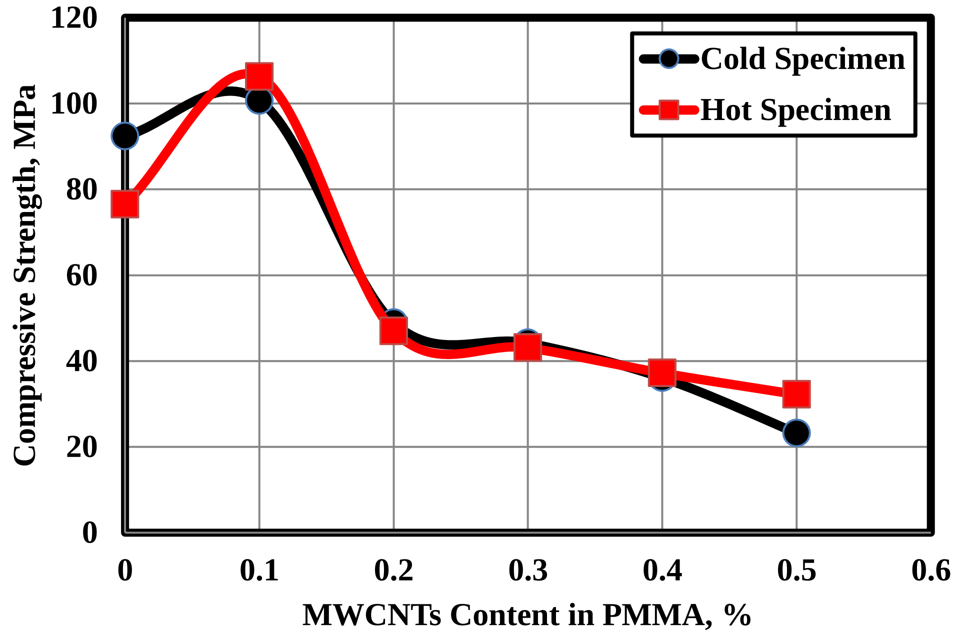


Fig. 7 Effect of MWCNTs content on the compressive strength of cold and hot MWCNTs/PMMA composites.

Apparent Modulus of Elasticity

Figure 8 show the effect of MWCNTs content on the apparent modulus of elasticity of MWCNTs/PMMA composites. It was found that the apparent Modulus of Elasticity of the cold PMMA is higher than that shown for hot at 0 wt., % MWCNTs, while at 0.1 wt., % the apparent modulus of elasticity of the hot MWCNTs/PMMA composites is relatively higher than of the cold composites. On the other hand, it was found that after 0.1wt. %, with increasing MWCNTs content the apparent modulus of elasticity decreased gradually for both the cold and hot composites. The reason for the increase in the modulus of elasticity up to 0.1 wt. % of MWCNTs may be attributable to higher contact surface of nano fillers with the organic matrix, which leads to improve the material strength. The drop in the modulus of elasticity after 0.1 wt. % of MWCNTs may be attributable to an increment the concentration of MWCNTs. It reported that with increasing concentration of nanopfillers, aggregation occurs, which leads to a decrease in the contact area between the nanoparticles and resin matrix and creates defects in the composites. Therefore, the effective interfacial interaction is reduced, and the strength of the films decreases. These results suggest that in order to optimize the

stiffness and bond strength of dental composite, it is important to add a small amount of MWCNTs (0.1 wt. %) to PMMA as denture base material. On other words, it can be said that modulus of elasticity is indicative of bond strength of the material

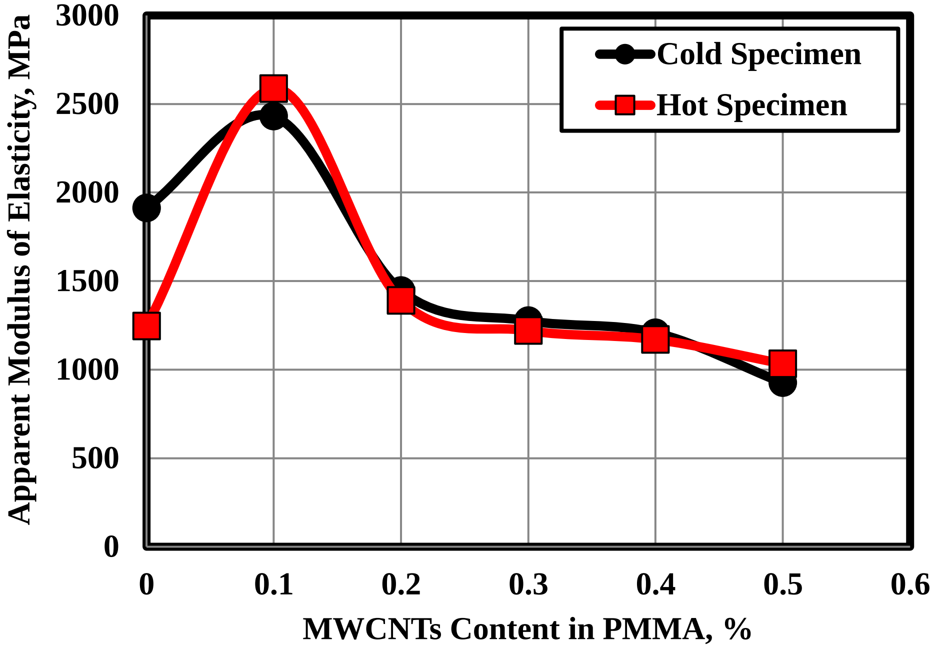


Fig. 8 Effect of MWCNTs content on the apparent modulus of elasticity of cold and hot MWCNTs/PMMA composites.

Modulus of Resilience

Figure 9 indicates the variation of the modulus of resilience against the MWCNTs content. As it is evident in Fig. 9 the modulus of resilience first nearly increased from 1.25 MJ/m^3 for both cold and hot composites to 2.57 MJ/m^3 hot and 2.1 MJ/m^3 cold and then decreased gradually from these values to reach 0.12 MJ/m^3 cold and 0.31 MJ/m^3 hot respectively at 0.5 wt. %, MWCNTs content. The increase in the strength may be responsible for the growth in the modulus of resilience up to 0.1 wt. %, MWCNTs. Over 0.1 wt. % MWCNTs, the agglomeration of MWCNTs in the composites lead to decline the strength and therefore decrease modulus of resilience.

Modulus of Toughness

Figure 10 shows the effect of the modulus of toughness against the MWCNTs content. As it is evident in Fig. 10 at 0 wt. %, MWCNTs the modulus of toughness of cold composites is higher than the hot composites and at 0.1wt. % the modulus of toughness of the hot composites is higher than the cold composites. After the 0.1 wt. %, the modulus of toughness of cold and hot composites decreased gradually up to 0.5 wt. %. The reason of increasing the modulus of toughness up to 0.1 wt. % of MWCNTs may be a result of the increase in the strength, while the reduction of modulus of toughness after 0.1 wt. %, may be due to the agglomerations of MWCNTs formed in the composite which reduce the structure of the composites.

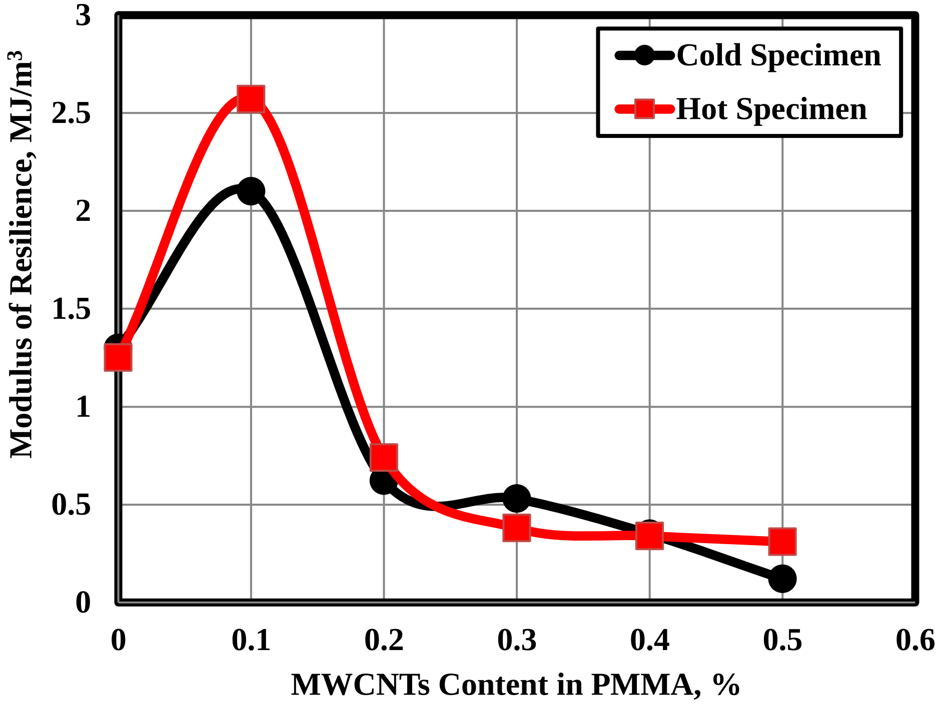


Fig. 9 Effect of MWCNTs content on the modulus of resilience of cold and hot MWCNTs/PMMA composites.

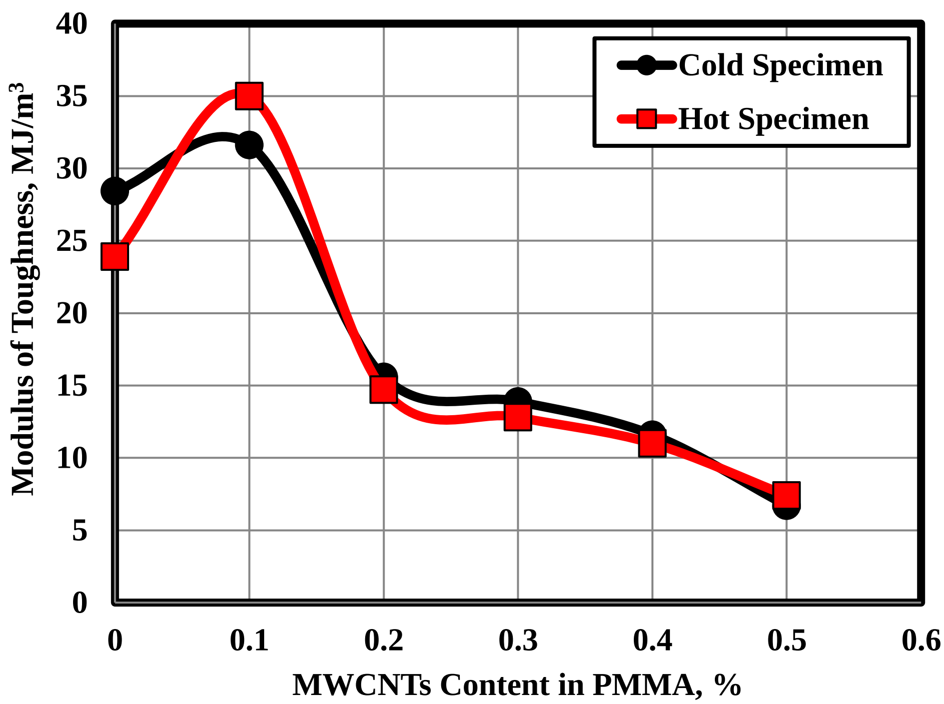


Fig. 10 Effect of MWCNTs content on the modulus of toughness of cold and hot MWCNTs/PMMA composites.

Ductility at Yield

Figure 11 indicates the variation of the ductility against the concentration of MWCNTs. As it is evident in Fig. 11 at 0 wt. %, MWCNTs the ductility of cold composites is higher than the hot composites and at 0.1wt. % the ductility of the hot composites is higher than the cold composites. After the 0.1 wt. %, the ductility of cold and hot composites decreased gradually up to 0.5 wt. %. The major reason of increasing the ductility to of 0.1 wt. % of MWCNTs may be attributed to the increase of yield strength. Over 0.1 wt. %, the aggregation of MWCNTs in the composites leads to decline the strength and therefore decrease the ductility. As indicated in Fig. 11, the concentrations of MWCNTs showed pronounced effects on the ductility at all used contents.

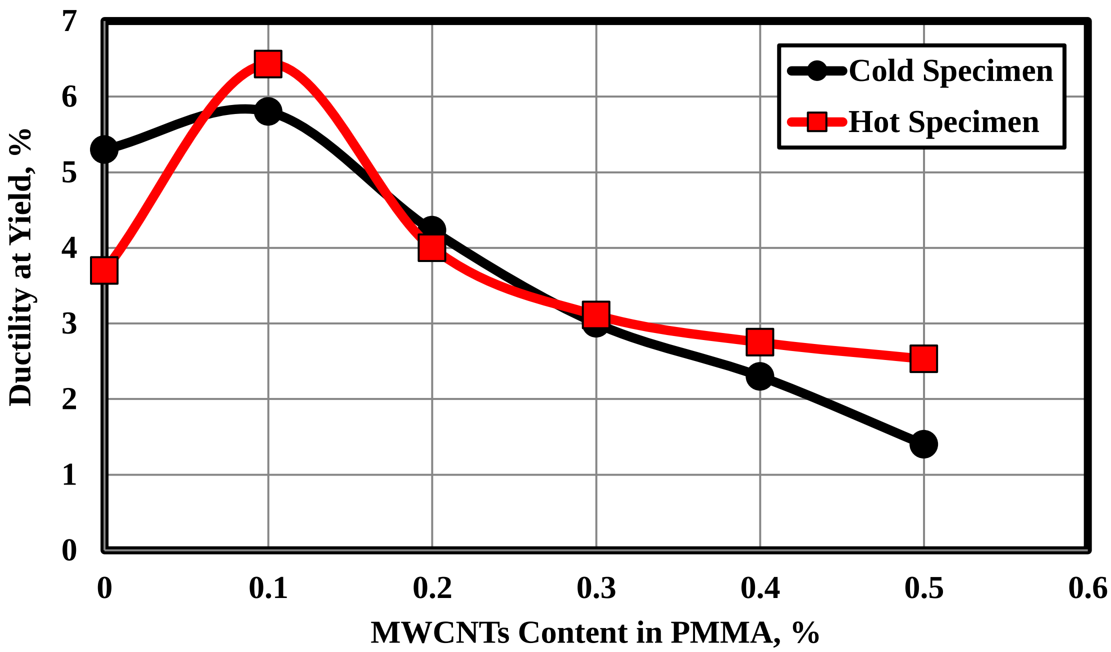


Fig. 11 Effect of MWCNTs content on the ductility of cold and hot MWCNTs/PMMA composites.

CONCLUSIONS

The results showed that, the mechanical properties of PMMA/MWCNTs composites depended on concentrations of MWCNTs in the composites. From the experimental work, the following points can be concluded:

1- Compressive strength, modulus of elasticity, modulus of resilience, modulus of toughness and ductility for pure cold cured PMMA are higher than that observed for the hot cured,

2- Compressive strength, modulus of elasticity, modulus of resilience, modulus of toughness and ductility for hot cured PMMA/MWCNTs composites are higher than that observed for the cold cured composites at 0.1 wt. % content of MWCNTs,

3- The compressive properties after 0.1wt. %, content decreased gradually for both cold and hot MWCNTs/PMMA composites.

4- Hot cured MWCNTs/ PMMA composites are recommended for denture bases applications.

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