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THE STRUCTURAL CHARACTERIZATIONS OF POLYMETHEL(METHAACRYLATE) DOPED NANOPARTICLE METAL (CU,CO,FE) THIN FILM BY USING ND-YAG LASER ABLATION

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ABSTRACT: The structural properties of PMMA doped with (Cu, Co, Fe) nanoparticls prepared by laser ablation were studied. In this research the polymethyl mehtacrylate (PMMA) was dissolved in chloroform with (5%) concentration to form homogeneous solution. PMMA doped with (Cu, Fe, and Co) nanoparticale (NPs) prepared by Nd-Yag(532nm) laser ablation. The X-ray diffraction shows that the structure of pure polymer film have an amorphous nature, but PMMA doped with (Cu, Co, Fe) nanoparticles are polycrystalline structure. The results indicate that there are a shifting and reduction in positions of peak intensity as compared with the pure (Cu, Co, Fe) nanoparticles and there are generated some new peaks appear. The AFM examination reveal to reduction in average nanoparticle diameter after doping with NPs metal (Cu, Co, Fe). The FT-IR examination appear some transmittance band after doping with NPs metal (Cu, Co, Fe)

KEYWORDS: Polymethyl Mehtacrylate (Pmma) ,Doping ,Xrd, Afm,Ftir, Crystal Size, Copper , Cobalt , Iron, Nanoparticle.

المميزات التركيبية لأغشية بولي مثيل ميثاكر لايت المطعم بمعادن نانوية (النحاس،الكوبلت،الحديد) باستعمال الاستأصال بليزر نديميوم – ياك

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الخلاصة:

%) للحصول على محلول متجانس ، ثم طعم بحبيبات 5 في الكلور وفورم بتركيز (PMMAتم في هذا البحث إذابة البوليمر) نانومتر 532نانوية من معادن (نحاس، كوبلت ، حديد) حضرت الأغشية باستخدام القشط الليزري لليزر نديميوم –ياك (وترسيب المحلول بطريقة التغطية المغزلية . بينت نتائج حيود الاشعة السينية أن غشاء البوليمر النقي ذو طبيعة عشوائية ،بينما المطعم بالمعادن النانوية ذات تركيب متعدد التبلور . كما حصل نقصان وزحف بمواقع القمم مقارنة مع قمم الأغشية المعادن النانوية النقية ، وظهور قمم جديدة مقارنة مع مخططات الأشعة السينية للمعدن الحجمية (النحاس ،الكوبلت ، الحديد). المعادن النانوية النقية ، وظهور قمم جديدة مقارنة مع مخططات الأشعة السينية للمعدن الحجمية (النحاس ،الكوبلت ، الحديد). بعد التشويب بجسيمات المعدن المعدن المعدن المعدن المعدن الحميمة (النحاس ،الكوبلت). ويمد النانوية النقية ، وظهور قمم جديدة مقارنة مع مخططات الأشعة السينية للمعدن الحجمية (النحاس ، الكوبلت). ويمد النانوية النوية النقية ، وظهور قمم جديدة معار الذيم معدل قطر الجسيمة النانوية بعد التشويب بجسيمات المعادن النانوية. (Cu,Co,Fe) المعدن المعدن المعدن المعدن المعدن المعدن المعادن النانوية .

INTRODUCTION

PMMA is belongs to industrial polymers family, which is often called (Acrylic), chemical formula ($C_5O_2H_8$). This polymer is thermoplastics obtained by polymerization process of (Methyl Mehtacrylate) [1]. Its widly used as a result of having most of properties such as ; surface hardness, and it can be colored, melted, cut, and formation, with other characteristics that made it suitable for the use of multiple applications [2]. The uses of this polymer in chemical sensors, reflective 3D data storage, separation and extraction of minerals, and pole

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Gelatinous [3] .PMMA have many properties such as high sensitivity and selectivity, stability of long term, low cost, density in range (1.15-1.19) g/cm^3 [4], and high transparency [5].

In the present work the effect of different metals nanoparticle as a dopant on structural properties of PMMA is studied to change some physical properties of polymer such as thermal isolation and its effect on bacteria.

Calculation

To calculate constructively the spacing d between diffracting planes in a few specific directions, determined by Bragg's law [6,7]:

 $2dsin\theta = n\lambda$

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(1)

Where θ is the Bragg angle, n is any integer, and λ is the wavelength of the beam of X-ray, $\lambda=0.15406$ nm. These specific directions appear as spots on the diffraction pattern called reflections. The lattice constant can be finding from the equation[8]:

$$\alpha = \frac{n\lambda \sqrt{h^2 + k^2 + l^2}}{2\sin\theta}$$
(2)

a shape factor is used in X-ray diffraction and crystallography to correlate the size of submicrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. In the Scherer equation [9]:

$$\tau = \frac{\kappa \lambda}{\beta \cos \theta} \tag{3}$$

where K is the shape factor, denoting the ratio of a particle's major dimension to its minor dimension, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM X π /180) in radians, and θ is the Bragg angle; [7] τ is the mean size of the ordered(crystalline) domains, which may be smaller to the crystal size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 µm, which precludes those observed in most metallographic and ceramic graphic microstructures. The strain (ϵ) values are calculated from the relation [10] :

$$\varepsilon = \beta \cos\theta/4$$

The dislocation density (δ) , defined as the length of dislocation lines per volume of the crystal (which represents the amount of defects in the sample), are calculated by the formula [10] :

(4)

(5)

$$\delta = 1.5 \epsilon / a. \tau$$

where (a) is lattice constant.

Experemental

PMMA solution was prepared with weight percentage (5%). by dissolving PMMA in a glass screw cup in (8 ml) chloroform using magnetic stirrer .The solution doped with (2ml) of colloidal nanoparticles (Cu, Co, Fe) .This colloidal solution was prepared by using

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second harmonic generator of Nd:YAG laser (532 nm) with (500) mJ energy and number of pulses is (150). The samples were put on glass substrate to obtain a film by using spin coating technique under (atmosphere pressure and 1000 r/min), the X-Ray Diffractmeter (DX-2700) was used to get the XRD structural properties. Some specimen are cutting in square(1×1)cm² form to use in AFM device, to evaluate the RMS size of particle roughness surface and grain size. Also FTIR device is used to evaluate the binding bonds by adding KBr.

RESULTS AND DISCUSSION

X-ray diffraction:

PMMA thin film

The X-ray diffraction examination describes that the pure PMMA thin film have an amorphous nature, because no peaks were appeared in the diagram as shown in Fig (1).



Fig. (1) The x-ray diffraction of PMMA polymer

PMMA doped Cu NPs polymer thin film

Fig (2) shows the X -ray diffraction of bulk Cu. There are polycrystalline structure in the planes (111) (200) (220) at angles (43.4341) (50.5206) (74.2089) degrees respectively .Fig (3) shows the X -ray diffraction of Cu NPs , that make reduction in intensity and some new peaks appears because of the weak bond coloration and the presence of high surface area, with grain size (54.6215 nm) . Fig (4) shows the X -ray diffraction of PMMA doped with Cu NPs . The doping PMMA polymer with Cu NPs make reduction in grain size up to (5.7460 nm) because of the polymer chians, which served as a barrier to the growth of the grains, which led to decreasing particle size , and then obtain a quantum dots.

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Fig. (2) X-ray diffraction of Bulk Cu.



Fig. (3) The x-ray diffraction of Cu NPs film

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Fig.(4) The x-ray diffraction of PMMA doped with Cu NPs film

X-ray diffraction of doped Co NPs of PMMA polymer thin film

Figs. (5), (6), (7) show the x-ray diffraction of bulk Co , Co NPs and Co NPs doped PMMA. . Peaks were disappeared after doping because of the effect of amorphous structure of polymer after doping and the crystal size is (6.30) nm. The structure becomes polycrystalline with low intensity, There are some new peaks appears because of the bonds that create between the material.



Fig. (5) The x-ray diffraction of bulk Co

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Fig. (6) The x-ray diffraction of Co NPs .



Fig.(7) The x-ray diffraction of PMMA doped Co NPs

X-ray diffraction of doped Fe NPs of PMMA polymer thin film

Figs. (8), (9), (10) show the x- ray diffraction of bulk Fe, Fe NPs and Fe NPs doped PMMA. Peaks were reduced after doping, because of amorphous structure of polymers, and shifted in position for Fe NPs as compared with bulk Fe, because of the structure is in nano size with grain size (88.690nm). After doping the structure become polycrystalline with small grain

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 $(2.7927 \mbox{ nm})$, there some new peaks appears because of the bonds that create between the material.



Fig. (8)The x-ray diffraction of bulk Fe



Fig. (9) The x-ray diffraction of Fe NPs films

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Fig.(10) The x-ray diffraction of PMMA doped Fe NPs

The following table shows the practical results that have been obtained from XRD for PMMA films before and after doping :

BEFORE DOPING			
NPs of metal	τ (nm)	ε	δ
Cu	54.6915	0.00058	0.00063
Со	9.40974	0.0034	0.0250
Fe	88.690	0.00034	0.00022
AFTER DOPING			
PMMA film	τ (nm)	3	δ
doped with NPs of			
metal			
Cu	5.7460	0.0056	0.040
Со	6.3069	0.00508	0.0298
Fe	2.7927	0.01145	0.2145

Atomic Force Microscopy Examination :

AFM of PMMA doped with Cu NPs :

Fig.(11), (12) show that AFM for pure Cu NPs and PMMA doped with Cu NPs respectively. Average roughness is decreased after doping because of decreasing in avg. Diameter as result of doping.

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Fig.(11) AFM of Cu NPs film



Fig.(12) AFM of PMMA doped Cu NPs

AFM of PMMA doped Co NPs

Fig.(13) and (14) show AFM for Co NPs and doped PMMA with Co NPs respectively , because of PMMA doping with Co NPs . The Average diameter of NPs and surface average roughness decreased .

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Fig.(13) AFM of Co NPs film



Fig.(14) AFM of PMMA doped with Co NPs

AFM of PMMA doped Fe NPs

Fig.(15) and (16) show AFM of Fe NPs with PMMA doped Fe NPs . Average diameter after doping is decreasing because of the effect of polymer chain, that served as a barrier to the growth of the grains, which led to decreasing particle size .

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Fig.(15) AFM of Fe NPs film



Fig.(16) AFM of PMMA doped Fe NPs

FT-IR Examination :

Fig.(17) shows FT-IR of pure PMMA film. The results showed presence of transmittance beams for pure PMMA at $(553, 1775, 2239, 2971, 3518)cm^{-1}$. Fig.(18), (19),(20) show FT-IR of PMMA film doped with Cu NPs, Co NPs, Fe NPs respectively. Some new absorption beams appears after doping with NPs of Cu because of doping effect with NPs of Cu.

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Fig.(17) FT-IR of pure PMMA



Fig.(18) FT-IR of PMMA doped Cu NPs

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Fig.(19) FT-IR of PMMA doped Co NPs



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Fig.(20) FT-IR of PMMA doped Fe NPs

CONCLUSIONS

1-It was observed a reduction in XRD peaks after doping with metal NPs (Cu,Co,Fe).

2-Obtaining a shifting in the position peaks.

3-Decreasing in crystal size particle after doping with nanoparticle metals , with NPs diameter between (1 to 10 nm) (Q.Ds).

4-AFM results decreasing in Avg. Diameter and surface roughness after doping with NPs metal (Cu,Co,Fe).

5-FT-IR results appears new transmittance bands after doping with NPs metal (Cu,Co,Fe).

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