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Study of the Morphological, Optical, and Thermal Properties of the Polymeric Blend CMC/PEG Reinforced by Various Concentrations of Au NPs

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Abstract

Using an environmentally friendly and inexpensive method, AuNPs gold nanoparticles (AuNPs) were prepared using pulsed laser ablation technique (PLAL) 600,700mJ different ablation energies of a gold target immersed distilled water (DW). The size and shape of the nanoparticles were verified by examining the morphological characteristics, as they showed the value of diameters between 30-75 nanometers with almost regular spherical shapes. Solution casting technique was used to prepare CMC/PEG composite polymeric films prepared in equal weight ratios 50:50% supported with different ratios of 5,10,15 ml of AuNPs. UV-vis spectroscopy was used to calculate some optical constants such as absorbance, absorption coefficient, energy gap, and properties as thermal conductivity coefficient k for polymeric films CMC/PEG-NPs. The results showed an increase in the thermal conductivity coefficient with an increase in AuNPs, and optical examinations showed a decrease in the value of the energy gap. With the increase in the nanomaterial concentration due to the presence of voids between the polymer chains or the lack of electron transfer contribution with the accumulation of AuNPs. We notice a decrease in the energy gap by increasing the concentration of nanoparticles until it reached a value of 3.21eV at 700mJ

Keywords: Pulsed Laser Ablation in Liquids, Gold Nanoparticles, Thermal Conductivity.

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دراسة الخصائص المورفولوجية والبصرية والحرارية للمزيج البوليمري CMC / PEG المدعم بتراكيز مختلفة من جسيمات الذهب النانوية Au NPs

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الخلاصة

باستخدام طريقة صديقة للبيئة وغير مكلفة، تم تحضير جزيئات الذهب النانوية (AuNPs) باستخدام تقنية الاستئصال بالليزر النبضي (PLAL) باستخدام طاقات مختلفة (6000-7000mJ) لقطعة معدنية مغمورة في محلول الماء المقطر (DW). تم التحقق من حجم وشكل الجسيمات النانوية من خلال فحص الخصائص المورفولوجية، حيث أظهرت أحجام أقطار بين (30-50nm)) نانومتر بأشكال كروية منتظمة تقريبًا. تم استخدام تقنية الصب بالمحلول Solution Casting لتحضير أغشية بوليمرية (CMC/PEG) محضرة بنسب وزن متساوية 50:50% مدعومة بنسب مختلفة من جسيمات الذهب النانوية (AuNPs) 5،10،15ml.

تم استخدام التحليل الطيفي للأشعة فوق البنفسجية لحساب بعض الثوابت البصرية مثل الامتصاصية ومعامل الامتصاص وفجوة الطاقة ومعامل التوصيل الحراري(k) للأغشية البوليمرية النانوية (CMC/PEG-Au) أظهرت النتائج زيادة في معامل التوصيل الحراري مع زيادة نسبة (AuNPs)، وأظهرت الفحوصات البصرية انخفاضًا في قيمة فجوة الطاقة مع زيادة تركيز المواد النانوية بسبب وجود فراغات بين سلاسل البوليمر أو نقص مساهمة نقل الإلكترون مع تراكم وجود (AuNPs). نلاحظ انخفاض في فجوة الطاقة بزيادة تركيز الجسيمات النانوية حتى وصلت إلى قيمة 3.21eV عند الطاقة 700mJ.

الكلمات المفتاحية: الاستئصال بالليزر النبضي في السائل، جسيمات الذهب النانوية، التوصيل الحراري

Introduction

Recent years, metal NPs and Polymer composites have sparked a lot of research curiosity the inclusion of inorganic nanoparticles embedded in a polymeric matrix. The new nanomaterial exhibits unique properties that are completely different from those of materials which are conventional [1]. These nanocomposites have unique optical or electrical properties, making them useful in sectors such as batteries, optical imaging, and optics, as well as antimicrobial coatings and photosensitive sensor design. [2]. Because of their superior chemical and physical capabilities, nanoparticles (NPs) have recently attracted attention in a variety of sectors including medicine, physics, chemistry, materials science, and photonics [3]. NPs are a form of material having a high surface-to-volume ratio and other characteristics. The "quantum volume effect" is used to infer characteristics [4]. AuNPs are particularly important among these metals because of their ability to efficiently interact with light via surface plasmon resonance (SPR). are the collective oscillations of conduction electrons in a metal at a wavelength substantially bigger than the size of the nanoparticles [5,6]. It also exhibits catalytic activity due to its large surface area to lose atom ratio. With the advancement of nanotechnology, AuNPs have the potential to serve as building blocks for future plasmonic, photonic, and optical systems. [7].

Method of combining two or more polymer matrices It was utilized to create novel polymeric materials quickly and easily by utilizing favorable features found in virgin polymers[8]. Polyethylene glycol (PEG) is a linear polymer with high crystallinity. Thus, different types of salts can be dissolved by PEG. The responsiveness is extremely restricted by CeO, CeC and CeH [X]. Polyethylene glycol or polyethylene is used in a variety of applications due to its chemical structure. The concentration of the crystalline phase within the limits of the PEG polymer is high conductivity [9]. Carboxymethyl cellulose (CMC) is a cellulose derivative created by reacting sodium hydroxide with chloroacetic acid. Sodium carboxymethyl (CH_2COONa) is included in a variety of groups. A type of cellulose molecule that aids in water solubility [10]. It is environmentally safe and clean due its amorphous nature, and it uses a natural polymer CMC in the mixing process to aid in many applied fields such as food and industry. Phase separation, such as CMC, can be decreased by increasing the amorphous percentage of PEG in the blending process. Due to the presence of OH groups in its composition, it is also soluble in ionic water and can react with other polymers by forming hydrogen bonds. Papermaking, pharmaceuticals, electrical equipment, paper, and packaging are just a few of the applications for this polymer. Because of this, as well as hygiene and printing supplies. Characteristics [11].

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Researchers have recently employed novel composite to carry out specialized and one-of-a-kind tasks, such as water treatment, optical and electrochemical devices [12,13]. Nowadays, smart technologies rely on sustainability and cost-effectiveness are receiving increasing attention [14]. Scientists use porous materials to Identification and extraction of trace or heavy elements of metal ions. Thus, the present work aims to present the synthetic properties for AuNPs particles and knowing the effect of the prepared particle sizes and shapes using PLAL techniques with different laser energies 600,700mJ and supporting them on a polymer mixture of polyethylene glycol/ carboxymethyl cellulose, studying some optical constants and calculating the thermal conductivity coefficient K.

Experimental

Material

A sheet of high purity 99.9% 24 carat gold was used, with dimensions (8.7 * 0.2 * 4.6) nanometers and weight (0.5 g). Also, two types of hydrophilic polymers were used as polymeric mixture, carboxymethyl cellulose polymer (CMC) and was in the form of a white powder. (PEG) Polyethylene glycol with a molecular weight of 6000 manufactured in Russia, 6472 Darmstadt Merck KGaA. It was in the form of white scales molecular formula (C_2H_4O) OnH Ho.

Preparation of gold nanoparticles and films of pure CMC/PEG polymeric blend by gold nanoparticles with different volume ratios

In this work, (PLAL) technique was used to prepare (Au NPs) of different energies 600,700mJ to a piece of pure gold metal, washed with ethanol and liquid alcohol and water several times to remove impurities, then it is irradiated by Nd:YAG device that has wavelength (1064 nm)), the total number of pulses was 500 and the value of frequency was 1 Hz, immersing the metal target in 5ml of distilled water as shown in Figure (1) .

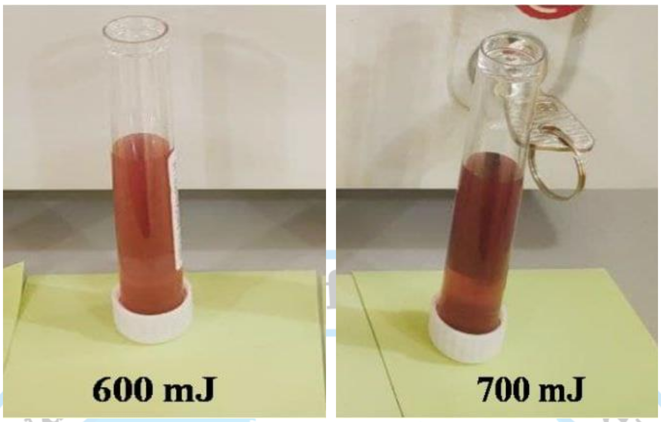

Figure 1: Solution of gold particles nanoparticles

The polymeric CMC/PEG mixture is dissolved in 15ml of DW solution, Mix with equal weights 50:50% and stir for 1 hour with a magnetic mixer at Heat 27°C, then added different volume ratios of AuNPs (5, 10, 15 ml) to the mixture reaching an energy of (600,700)mJ and continued stirring for another hour until the mixture became homogeneous and its color changes from white to pink by increasing the addition of AuNPs within the polymeric mixture (CMC/PEG). To perform the required checks. Figure 2 , 3 demonstrates preparation steps.

Figure 2: CMC/PEG Polymeric Mixture Film

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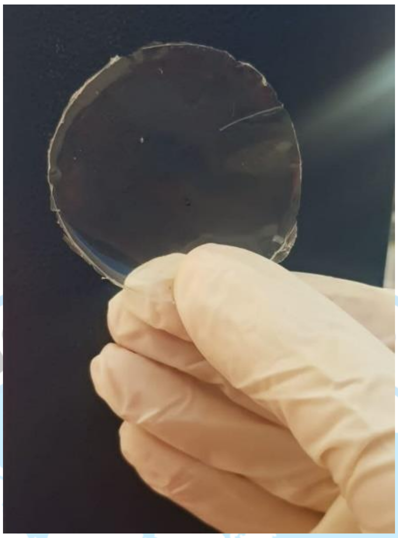

Figure 3: CMC/PEG Pure Blend Film

Characterization techniques

The surface morphology was examined to study the size and the shape of AuNPs which was prepared by PLAL method using Field-Emission scanning electron microscopy (FE-SEM) with energies of 600,700mJ. The device specifications as follow:

Brand : ZEISS
Model : MERLIN
Resolution : 0.8nm @ 15 kV / 1.4nm @ 1 kV / 0.6nm @ 30 kV (STEM mode)
Magnification : 20.000-50.000kx

Ultraviolet absorption spectra of polymeric mixture compounds samples were measured within a wavelength range of 300_1200 nm. The thermal conductivity of the CMC/PEG composite films was tested by using pouring solution method. The device specifications as follow:

UV-Visible:1800 double beam spectrophotometer
Company Name: Shimadzu Japanese
Wave Length (90-1200nm)

Result and discussion

Field-Emission Scanning Electron Microscopy

The particle size and shape and morphology were studied by FE-SEM images of different energies (700, 600) mJ and there histograms are presented in Figure (4, 5). From the figures, the assay results show the formation of Au NPs with different sizes and their appearance as spherical in most of the samples. The aggregation is not clear and noticeable and with the increase of the ablation energy leads to an increase in the average size of the spherical Au NPs particles and the result agrees with the result of the researcher [15]. The increase in the size of the particles is due to the increase in the concentration of particles when the energy of ablation increases due to the frequent collisions between the generated nanoparticles, so the temperature rises and the nucleation process begins, and then the particles merge to produce particles of larger diameters.

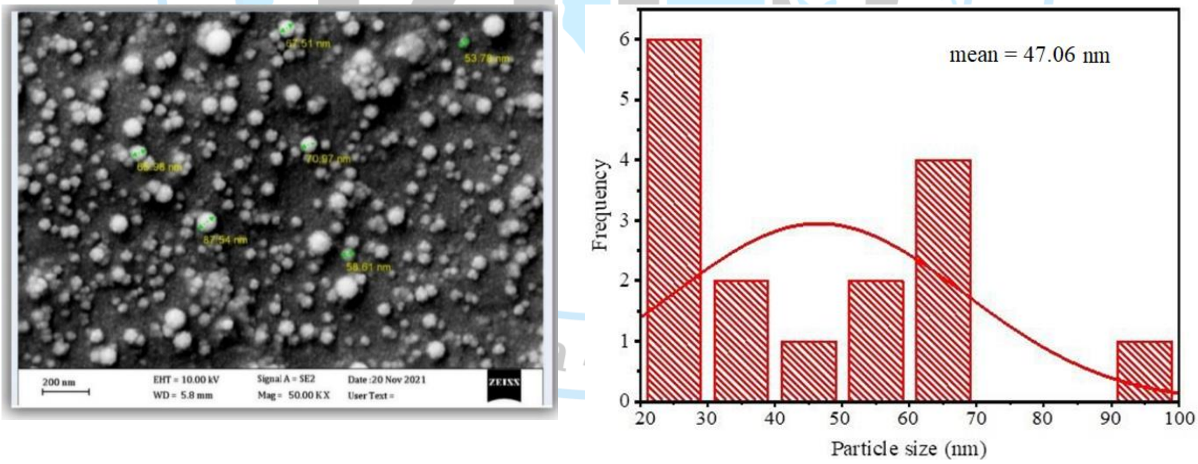

Figure 4: FE-SEM images of gold nanoparticles at 600mJ

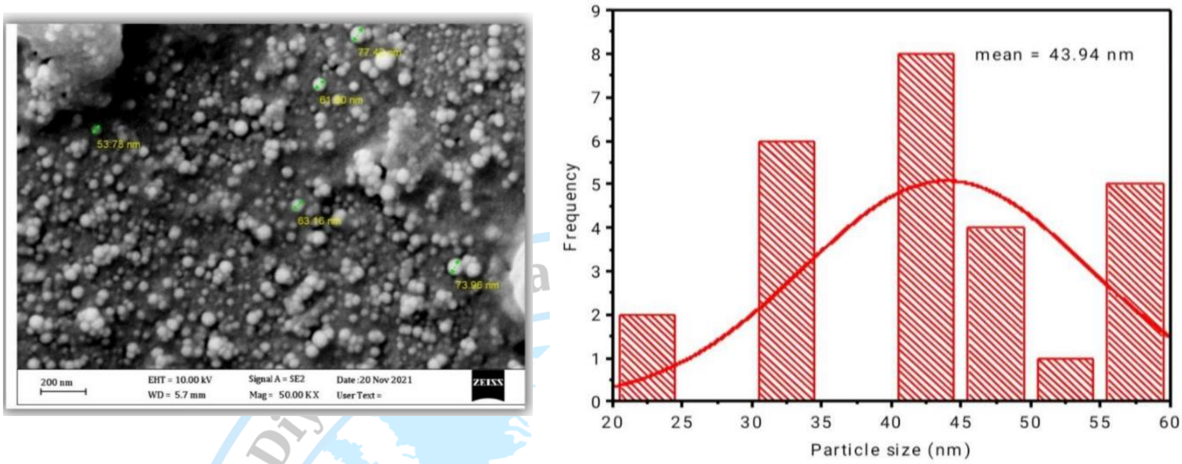

Figure 5: FE-SEM images of gold nanoparticles at 700mJ

UV Visible Spectrophotometer for CMC/PEG-Au

The absorption coefficient of the pure polymeric mixture films supported by gold nanoparticles with different volume ratios was calculated as 5,10,15ml and prepared with 600,700MJ energies. The absorption coefficient was calculated using the next equation:

$$I = I_o \, Exp(-\alpha \, t) \quad (1)$$

Where:

I: The intensity of the transmitted radiation

I_o: Incident

α: absorption coefficient

t: time

Figure 6 shows that the absorption coefficient increases with the increase in the laser energy, because of the increase in the granular volume of the particles, in the little concentration the absorption coefficient decreases because the photon energy is not sufficient to transfer the electron from the parity beam to the connection beam [16,17].

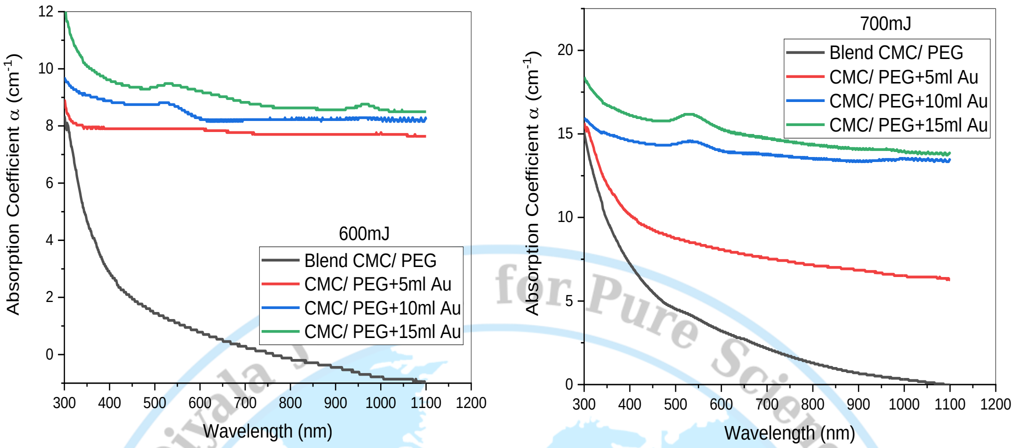

Figure 6: Absorption Coefficient of CMC /PEG-Au Polymeric Composite Films with Different Laser Energies and Concentrations

The absorbance of all samples has high values, as can be observed in the figures(7). The absorption diminishes with rising wavelength and decreasing quantity of gold supplied at the wavelength at the edge of the initial absorption. As a result, the absorption in the visible infrared band is minimal. The interaction between the photon and the incoming matter occurs as the wavelength decreases, and absorption increases. [18]. In other words, the free electrons absorb the incident light [19].

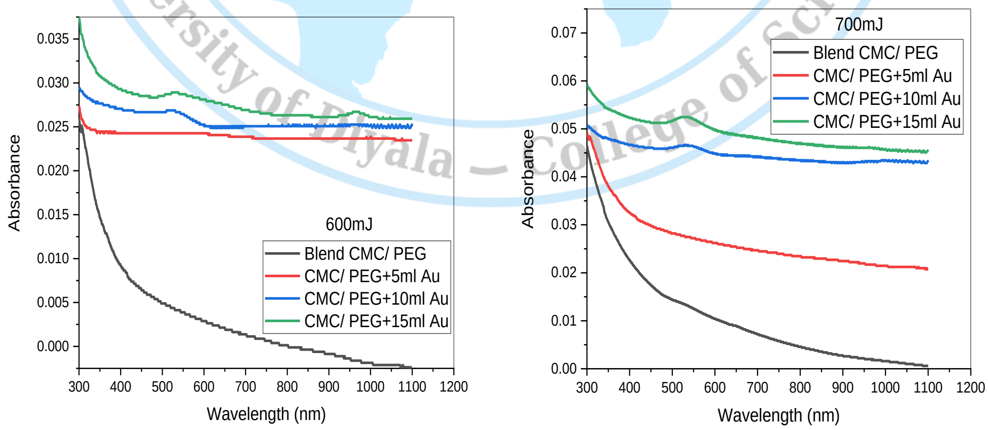

Figure 7: UV-Visible Absorption Spectrum of CMC/PEG-Au Polymer Compound Films with Different Laser Energy and Concentrations

Allowed Direct transition gap. Calculated Using equation 2, when the value of r = 0.5, direct transition is allowed the bandgap to be calculated. The figure (8), figure (9) shows the relationship between the absorption edge (αhv) 0.5 for (CMC/PEG-Au) and (CMC/PEG) nanocomposites as a function of photon energy, when plotting a straight line from the top of the curve toward the (x) axis at the value (αhv) 2 = 0. The values that are obtained in figure (8), figure (9) as well as Table (1), shows that the energy gap values decrease by increasing the weight ratios of the AuNPs. The transition in this case occurs in two stages, which includes the transition of the electron from the valence band to the local levels to the conduction band As a result of the increased weight ratio of AuNPs. This is indicated by the fact that nanocomposites with heterogeneous electronic conductivity depend on the gold concentration. With the increase of AuNPs, pathways are available in the polymer that allow the transfer of electrons from the valence band to the conduction band [20,21].

$\alpha\, h\nu = B(h\upsilon - Eg)^{r}$ ....(2)

where:

β: is a constant called the band tailing parameter,

Eg: is the energy of the optical band gap

hυ: Gives a straight line in a certain region

r: Power

α: absorption coefficient

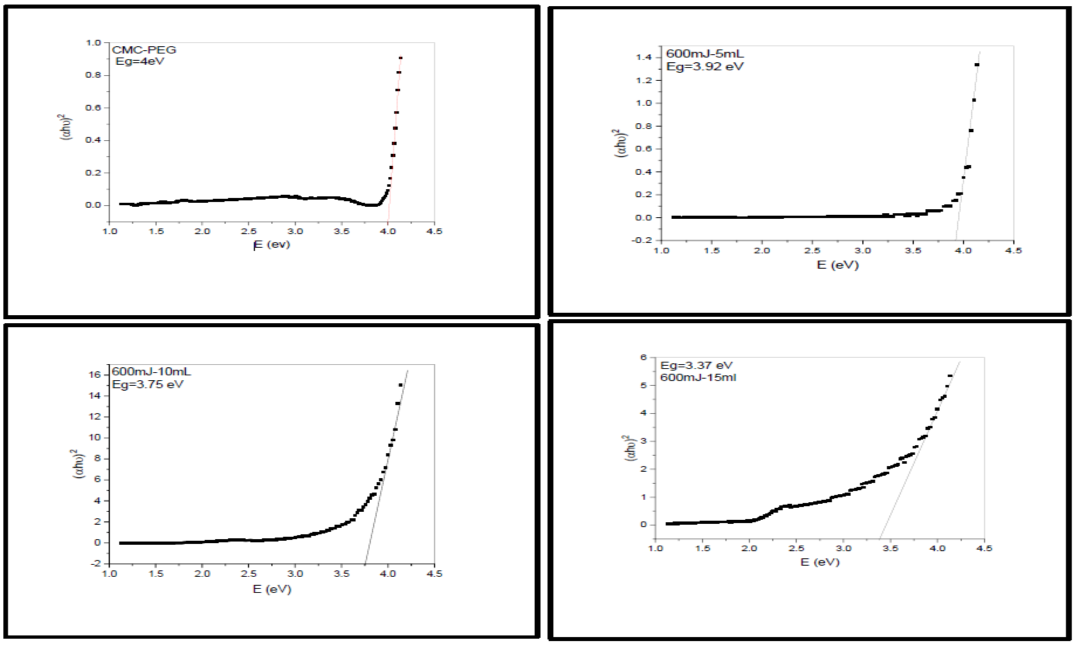

Figure 8: The energy gap of the nanocomposite for 600 mJ

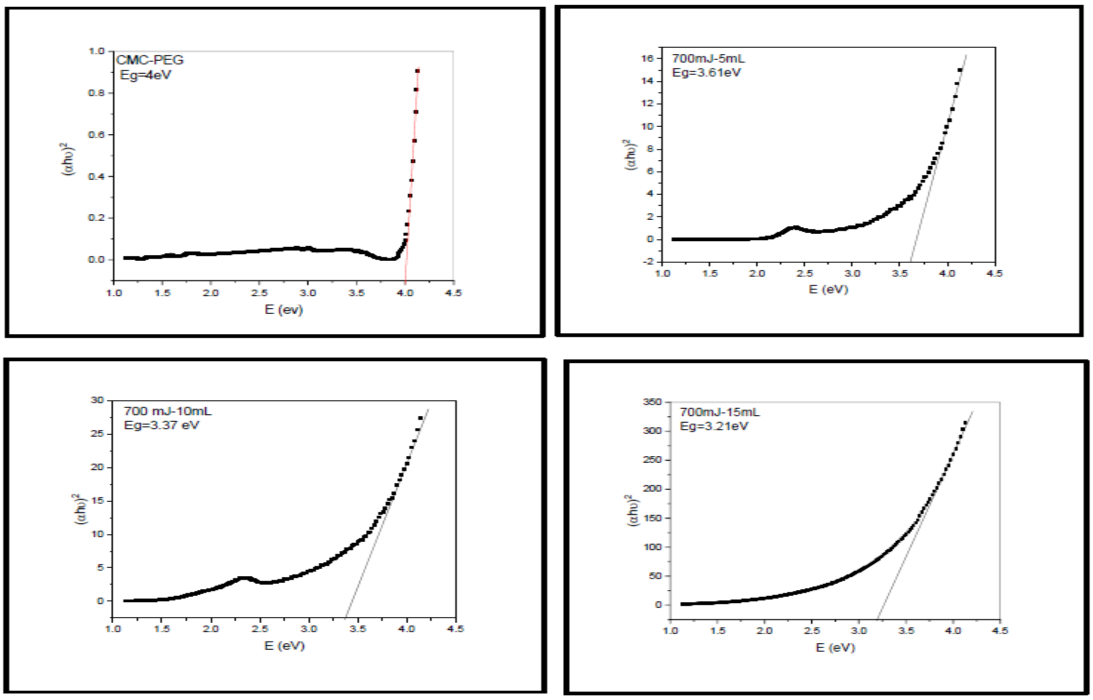

Figure 9: The energy gap of the nanocomposite for 700 mJ

Table 1: Optical energy gap values

Blend CMC/PEG	Concentration of AuNPs	600mJ Eg(eV)	700mJ Eg(eV)
15 ml	Pure	4 eV	4 eV
	5 ml	3.92eV	3.61eV
	10 ml	3.75eV	3.37eV
	15 ml	3.37eV	3.21eV

Thermal conductivity of pure CMC/PEG polymeric composite films supported by gold nanoparticles

Thermal energy is transferred within the films prepared by pouring the solution in two ways, namely by free electrons in the conductor or vibrations in the insulator that occur from one atom to another by phonons, the other way is heat transfer through the conductor This is due to the presence of gold because it contains an abundance of Electrons play a major role in the transfer of thermal energy. The direct behavior of the particle size is proportional to the thermal energy transferred through the model [22-24] According to the results of the study, the films are supported by Au NPs. The energy increased 700mJ because the number of NPs is large and crystalline, and this means that the atoms are periodically regular, and the higher the crystallization, the greater the number of particles, and this leads to an increase in thermal conductivity as in the figure (10) and table (2).

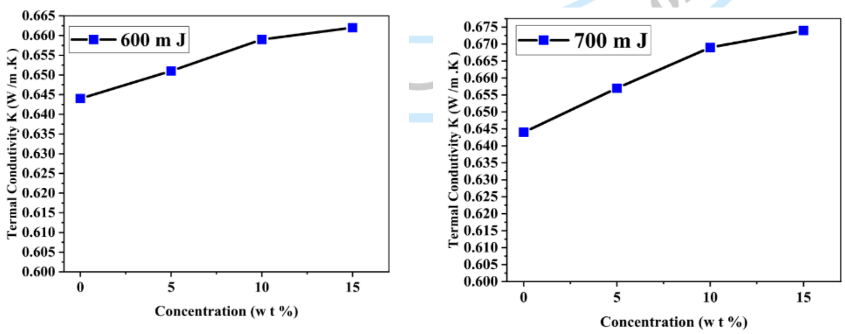

Figure 10: Thermal conductivity coefficient of the films of the pure CMC/PEG polymeric mixture supported by gold nanoparticles

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Table 2: Thermal conductivity coefficient values

	700MJ	600MJ
Blend (CMC + PEG)	0.644 W/m.K	0.644 W/m.K
5 ml Au	0.677 W/m.K	0.649 W/m.K
10 ml Au	0.678 W/m.K	0.650 W/m.K
15 ml Au	0.684 W/m.K	0.651 W/m.K

Conclusion

Various concentration of Au NPs were successfully mixed for polymeric mixture CMC/PEG with solution molding technology, visual inspection results confirmed that The surface plasmon resonance peak and absorption spectra appeared as the compounds indicated a clear shift in The absorption edge is towards longer wavelengths, and this confirms the presence of AuNPs within polymeric films. Nanomaterials lead to potential future for multiple applications of Optoelectronics, filters and thermoelectric devices. The inert polymer material is improved by Addition of gold metal to increase the value of the coefficient of thermal conductivity. Tests were performed on these samples only, without applications.

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