INFLUENCE OF PISTACHIO SHELL POWDER REINFORCEMENT ON FTIR AND DSC BEHAVIOR OF PMMA ACRYLIC RESIN

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ABSTRACT

Although, the PMMA have good advantages made it appropriate to denture base applications. But its low impact and fracture strength represent the main drawbacks of it.so many studies had been done in order to overcome these problems. In this study Pistachio Shell powder was added in different weight fractions of about (3, 6, 9 and 12 wt. %) and different average particle sizes of about (53µm, 106µm, 150µm and212µm) to (heat-cure) PMMA that is popularly utilize in denture base applications and study the Fourier transform infrared spectroscopy (FTIR) and Differential Scanning Calorimeter (DSC) behavior of this bio composite. The results were as the following: the FTIR results demonstrated that there are no new peaks appeared after the reinforcing by Pistachio Shell powder. Also there was no shifting in any of these peaks. While the DSC test showed that the glass transition temperature (Tg) increased as the particle size of Pistachio Shell powder increased. The highest value of Tg (126.9°C) was obtained for composite specimen reinforced with 12% of Pistachio Shell powder with average particle size of about (212µm).

Key Words: Denture Base, PMMA, Pistachio shell powder, FTIR, DSC.

تأثير التقوية بمسحوق قشور الفستق على سلوك اختبار الاشعة تحت الحمراء (FTIR) و اختبار المسعر الالكتروني الماسح (DSC) لراتنج البولي مثيل ميثا اكريليت

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الخلاصة

بالرغم من ان راتنج البولي مثيل ميثا اكريليت المعالج حراريا يمتلك مزايا جيدة جعلته ملائما لتطبيقات قاعدة طقم الاسنان. لكن مقاومة الصدمة ومقاومة الكسر المنخفضة تمثل المشكلة الرئيسية له. لذلك العديد من الدراسات اجريت من اجل التغلب على هذه المشاكل. في هذه الدراسة مسحوق قشور الفستق تم اضافته بكسور وزنية مختلفة (3%, 6%, 9% و12%) وبمعدلات حجوم حبيبية مختلفة (53, 106, 150 و 212) مايكرون لراتنج البولي مثيل ميثا اكريليت المعالج حراريا المستعمل بشكل واسع في تطبيقات قاعدة طقم الاسنان ودراسة سلوك الاشعة تحت الحمراء (FTIR) و سلوك المسعر الالكتروني الماسح (DSC) لهذه المتراكبة . النتائج كانت كالتالي: اختبار الاشعة تحت الحمراء (FTIR)

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اوضحت عدم ظهور قمم جديدة, كذلك لم يحدث انتقال او ازاحة لاي قمة من القمم الخاصة براتنج البولي مثيل ميثا اكريلت بعد التقوية بمسحوق قشور الفستق. بينما اختبار المسعر الالكتروني الماسح (DSC) اظهر ان درجة حرارة الانتقال الزجاجي سوف تزداد بزيادة الحجم الحبيبي لمسحوق قشور الفستق, وان اعلى قيمة لدرجة الانتقال الزجاجي (126,9م°) تم الحصول عليها في العينة المتراكبة المقواة ب(12%) من مسحوق قشور الفستق وبمعدل حجم حبيبي (212) مايكرون.

INTRODUCTION

The tooth loss resulted from many causes such as dental trauma, periodontitis, tooth decay and others [C. Upadhyaya and M. Humagain, 2009]. Denture which is also called false teeth is a manufacturing device that is made to replace the missing teeth. It is dating from 3500 years ago. Human used many materials to prosthetic the denture (partial or complete) starting from wood, animals' teeth, ivory, gold …etc. in order to help the patient through mastication, aesthetic, pronunciation and self-esteem [S. K. Khindria et. al., 2014]. It's worth mentioning that, dentures must be prepared from biomaterial, which can be released on any synthetic or natural materials that can be used to replace or restore function of the body tissue that is in continuous or intermittent contact with body fluid [J. K. Oleiwi et. al., 2017]. W. Abbas et. al., [2010] studied the effect of adding (low cost materials biocompatible antibiotic materials) Genuine Nigella sativa and Thyme as oil to heat cure acrylic resin in different weight fraction by (0.5, 1, 1.5, and 2 wt. %), and estimated the changes that may occur to transverse strength, indentation hardness, color property, residual monomer, dimensional accuracy, porosity, measurement of IR spectra, and anti–microbial–sensitivity test. The results of the study illustrated that there was a significant difference (S) where (P= 0.05). Moreover, there were an increasement in transverse strength and hardness of the denture base materials, no porosities, an increase in residual monomer elution at first day. J. Xu et.al., [2013] studied the effect of adding short Ramie fibers with different length of (1.5µm and 3µm) by volume fraction of (4 and 10 vol.%) on the flexural strength and flexural modulus. They concluded that the specimens that reinforced with fibers of (1.5mm) length showed an increasing in the flexural modulus while the flexural strength declined steadily with increasing the fibers content. Whereas, the 3mm fibers showed an increasing in flexural modulus in 4%vol. of fiber content then it dropped at (10% vol.) of fiber content**.** H. A. Khalaf, [2016] prepared composite specimens of heat cure denture base resin (PMMA) reinforced by salinized mixture of siwak and poly propylene fibers, and evaluated the (impact strength, transverse strength, shear bond strength, thermal conductivity, (Shore D) hardness, surface roughness and water sorption). The results were statistically analyzed by using one-way ANOVA, and the overall results showed that the addition of salinized mixture of siwak and polypropylene fibers into heat cure PMMA improve the tested physical and mechanical properties. S. I. Salih et. al., [2017], determined the mechanical properties (tensile, impact and hardness) in addition to the infrared test (FTIR) of the denture base resin (PMMA) reinforced by Siwak fibers of different lengths (2, 6 and 12 mm) and different concentration of (3, 6 and 9 wt. %) by weight. The results of this study illustrated an improvement in the tensile strength, young modulus, fracture toughness and hardness of the reinforced specimens as the weight fraction and fiber length increased. S. I. Salih et, al., [2018] assessed the effectiveness of adding the natural powder of pomegranate peels(PPP) and seed powder of dates Ajwa (SPDA) in individual form, in nanometer size and different weight fraction of (0.4, 0.8, 1.2 and 1.6 wt. %) on the mechanical and some of physical properties of denture base resin. The results showed that there was a considerable improvement in the properties for both groups, but the specimens reinforced with pomegranate peels powder in nanometer size that showed the highest properties as compared with the bio composite specimens strengthened by nano seed powder of dates. J. K. Oleiwi et, al., [2018] estimated the effectiveness of adding, Bamboo and Rice Husk powders on the heat behavior of heat cure PMMA resin. The powders were added in different weight fraction (2, 4, 6 and 8 wt. %), and different particle size (25µm and 75µm).

The thermal tests showed that the thermal conductivity and thermal diffusivity of the PMMA reinforced with these powders will increase with increasing the weight fraction of the reinforcing material. The main aim of this research is to study if the FTIR and DSC behavior of (heat-cure) PMMA resin will be or will not be affected by the presence of Pistachio Shell powder after reinforcing with it.

MATERIALS USED

In this study the (heat- curing) Poly (Methyl Methacrylate) PMMA resin, which is produced by (Spofa dental) company used as a matrix, while the Pistachio Shell which is used as cellulose agricultural waste material, was used as reinforcing material, in different average particle sizes of about (53µm, 106µm, 150µm and 212µm), and different weight fraction of about (3, 6, 9 and12 wt. %). This powder has been added to PMMA acrylic resin to produce bio composite specimens of prosthetic denture base.

ALKALI TREATEMNT

Pistachio Shell powder was treated by (5%) (weight \volume) alkaline solution of (NaOH) at (25 ˚C) for (24 hr). [H. C. Obasi et. al., 2014], and maintained the ratio of natural powder to liquor as 1:30(w/v). Additionally, after the mentioned period the treated powder was rinsed by distilled water for lot of times in order to remove the remaining alkali solution, until the neutralize (PH-7) was reached. After previous steps, the powder was dried at room temperature for 5 days. Eventually it put in the furnace at (50-60˚C) to emphasize the drying process.

SPECIMENS PREPARATION

By using the (Hand lay-up) method, all the PMMA and PMMA composite specimens of denture base material were prepared. According to particle size and weight fraction of Pistachio Shell powder the PMMA composite specimens were be prepared. Table (1) gives an indication about the specimens grouping of this study.

RESULTS and DISCUSSIONS

FTIR Test

Figure (1) demonstrated the infrared spectrum of PMMA where the structure of, PMMA is – [–CH2–C (CH3) (COOCH3)–]n. The infrared spectrum, of PMMA results from the group, frequencies of the (C–C) and (C–H) groups of backbone chain, the (C–C) (C=O) and (C–O) units, of the ester group and C–H units of the methyl substituent [T. E. Motaung et.al.,2012 and Paul W.et.al., 1999]. The infrared spectrum obtained to neat PMMA as the following: The distinctive vibration bands (υ) of PMMA, at (1722.10) cm^{-1} υ, is related to (C = O), and (1434.27) cm^{-1} υ correspond (C– O). The bands at (2949.25and 2920.55) cm^{-1} υ match the (C–H) stretching of the methyl group (CH3), while the bands at (1386.38) cm^{-1} υ are corresponding (C– H) symmetric and asymmetric stretching modes, respectively. The torsion of the methylene group CH2 is represented at (1239.28) cm^{-1} υ band. The peak at (1189.69) cm^{-1} υ for the band corresponds to vibration of the ester group (C–O), while (C–C) stretching band are at (985.97 and 840.09) cm^{-1} υ [Chen F. et. al.,2002 and Niranjan P. et. al., 2009]. The FTIR results of PMMA and PMMA composite those were reinforcing with different percentages of Pistachio Shell powder of (3, 6, 9 and 12 wt. %), with an average particle size of about (53µm, 106µm, 150µm and 212µm) are clarified in figures (2),(3),(4) and (5) respectively. All the characteristics vibration bands of PMMA composites are reserved in the infrared spectrum (FTIR) of group's composites specimens in these figures. It can be noticed from these figures that there are no new peaks appeared after the reinforcing by the Pistachio

Shell. Also, there was no shifting in any of these peaks. This behavior refers to find Physical bonds composite constituents, this is giving good indication of improvement the miscibility state between composite constituents, and absence any residual monomer or by product that may cause toxicity, allergic and inflammation of human body. Figure (2) illustrates the FTIR spectrum for PMMA specimens that reinforced by Pistachio Shell particles with different weight fractions at average particle size (53µm). Moreover, it shows that there is an increase in the peak intensity for all of characteristics peak of PMMA composite to raise peak intensity of neat PMMA with increasing the weight fraction of Pistachio Shell powder for all percentages, and it reaches the maximum value at (12 % wt.). Figure (3) illustrates FTIR spectrum for the PMMA composite specimens reinforced by average particle size (106µm) of Pistachio Shell powder with different percentages. The peaks intensity of PMMA composite decreases to lower than the peaks intensity of neat PMMA at weight fraction (9%) and (12%) of Pistachio Shell powder. While the peaks intensity, of PMMA composite increase, to higher than the peaks intensity of neat PMMA, when the weight fraction of Pistachio Shell is (3%) and (6%), and it reaches its maximum value at (3% wt.). Figure (4) illustrates the Infrared Spectrum of PMMA composite specimens reinforced by average particle size of (150µm) of Pistachio Shell powder in different percentages. Furthermore, the peaks intensity of PMMA composite increase to higher, than the peaks intensity of neat PMMA with increasing the weight fraction of Pistachio shell powder for all percentages and it reaches to the maximum value at (9%wt.). Figure (5) which is clarifying the FTIR spectrum of PMMA composite specimens reinforced by average particle size of (212µm) with different concentration of Pistachio Shell powder. The figure illustrated an increasing in the peak's intensity of PMMA composite to higher than the peaks intensity of neat PMMA with increasing the weight fraction of Pistachio Shell for all percentages and reaches its maximum value at (6% wt.) except at (3%wt.) the peak intensity had been decreased.

DSC Test

The purpose of this test is to estimate the thermal behavior of pure PMMA and PMMA composite specimens; it depends on the rate at which the composite specimens absorb the energy comparing with the pure PMMA specimen. This technique depends on the changes involved in different phase transition of certain polymer composite, such as glass transition temperature, crystallization temperature, melting temperature and degradation temperature as well as miscibility. The glass transition temperature (Tg) represents the most important one, [David Farrelly, 1984. and J. Goldstein, et. al., 2017]. The values, of glass transition temperature, crystallization temperature, and degradation temperature for PMMA material before and after the addition of constant percentage (12%wt.) of Pistachio Shell powder with different average particle size are listed in table (2). It can be noticed from this table and figures (6), (7), (8), (9)and (10) that the Tg, Tm, Td and T_C of neat PMMA and PMMA composites were obtained in the temperature range from (20 to 600) ^oC the PMMA composites behavior depends on changes in nature and type of reinforcing material in composite. Figure (6) shows the DSC test result for neat PMMA, where the Tg of pure PMMA is observed at 120.6 ^oC Table (2) and figures (7), (8),(9) and (10) show that there are an increasing in Tg values for (PMMA-Pistachio Shell) composites as compared to the Tg value of neat PMMA. Additionally, it has been noticed that the glass transition temperature increased with increasing the particle size of Pistachio Shell powder. The highest value of Tg (126.9℃) was obtained for composite specimen reinforced with 12% of Pistachio Shell powder with average particle size of about (212µm) and this is shown in figure (10). The glass transition temperature of neat PMMA increased from 120.6 ℃ to 123.6 ℃ when adding 12% Pistachio Shell powder of average particle size of about (53µm) and (106µm) to PMMA as shown in figures (7) and (8) . Whereas, when adding12% Pistachio Shell powder of average particle size of about (150μm) to PMMA led to increasing in Tg value of PMMA composites to 123.8℃ as shown in figure (9). Furthermore, the DSC scans of PMMA composite specimens were reinforced with Pistachio Shell powder of different average particle size in the PMMA matrix showed an increase of (Tg), due to the nature of natural powders (Pistachio Shell), which is acting as an agent caused restriction and limited in the PMMA chain mobility, Finally, that leads to increase the molten state viscosity and rise the glass transition temperature for all composite specimens, [Carola Esposito Corcione 2012, Chow Wen Shyang. et. al., 2008. and Benjamin J. Ash. et. al., 2002]. It was observed from these figures that the addition of Pistachio Shell powder to PMMA resulted in emergence only one value of Tg. All that promote to a good interfacial reaction, as well as it gives good indication to effective compatibility and strong bonding or interaction between reinforcing materials and PMMA resin in composite specimens. Furthermore, these figures and table (5-3) showed no significant change in the heat flow behavior values (melting temperature, crystallization temperature and degradation temperature) for neat PMMA and PMMA composite specimens.

CONCLUSIONS

According to the above mentioned FTIR and DSC results of neat PMMA and bio composite specimens of prosthetic denture base resin, it can be concluded that:

1- The FTIR results FTIR results had been showed that, there were no new peaks, appeared after the reinforcing by the Pistachio Shell. Also, there was no shifting in any one of these peaks, and this behavior refers to the physical bond between the matrix and the reinforcing material, and there was no new material formed.
2- The DSC scans of PMMA composite specimens were reinforced with Pistachio Shell powder of different particle size in the PMMA matrix showed an increase of (Tg). The highest value of Tg (126.9℃) was obtained for composite specimen reinforced with 12% of Pistachio Shell powder with average particle size of about (212μm).
3- So it can be concluded that it is safe and useful to use the pistachio shell powder as reinforcing material to the denture base material.

Table (1): Shows the Groups of neat PMMA and PMMA Composite Material that Prepared in this Study.

Type of Composite	*Weight Fraction of Pistachio Shell Powder (wt. %)*	*Average Particle size of Pistachio Shell Powder*	*Acrylic Resin*	*No. of specimens*
First Group	0	………	PMMA (Heat-cure)	**3**
Second Group	3	53**µm**	PMMA (Heat-cure)	**3**
		106 **µm**		**3**
		150 **µm**		**3**
		212 **µm**		**3**
Third Group	6	53 **µm**	PMMA (Heat-cure)	**3**
		106 **µm**		**3**
		150 **µm**		**3**
		212 **µm**		**3**
Fourth group	9	53 **µm**	PMMA (Heat-cure)	**3**
		106 **µm**		**3**
		150 **µm**		**3**
		212 **µm**		**3**
Fifth group	12	53 **µm**	PMMA (Heat-cure)	**3**
		106 **µm**		**3**
		150 **µm**		**3**
		212 **µm**		**3**

Table (2): Extract the Important Characterization of DSC Curves of PMMA Composites Before and After Addition of Pistachio Shell Powder.

Specimen	T_g °C	T_c °C	T_m °C	T_d °C
Pure PMMA	120.6	320.4	415	423.549
PMMA- 12% of 53 µm	123.6	376.5	412.6	452.172
PMMA- 12 % 106 µm	123.6	377.6	411.9	442.132
PMMA- 12 % 150 µm	123.8	377.8	418.7	424.37
PMMA- 12 % 212 µm	126.9	370.9	413.2	432.925

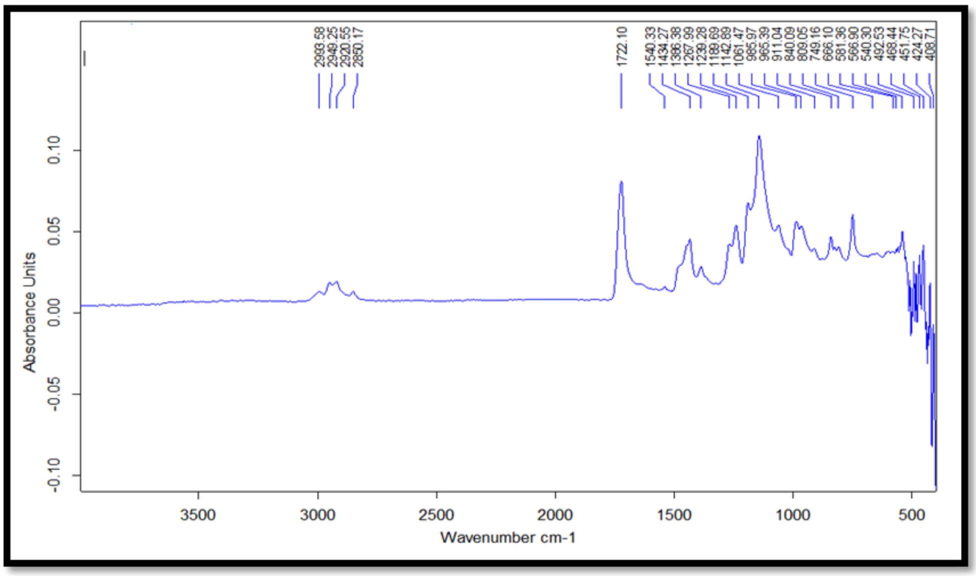

Fig. 1 : FTIR Spectrum for Heat Polymerizing PMMA Specimen.

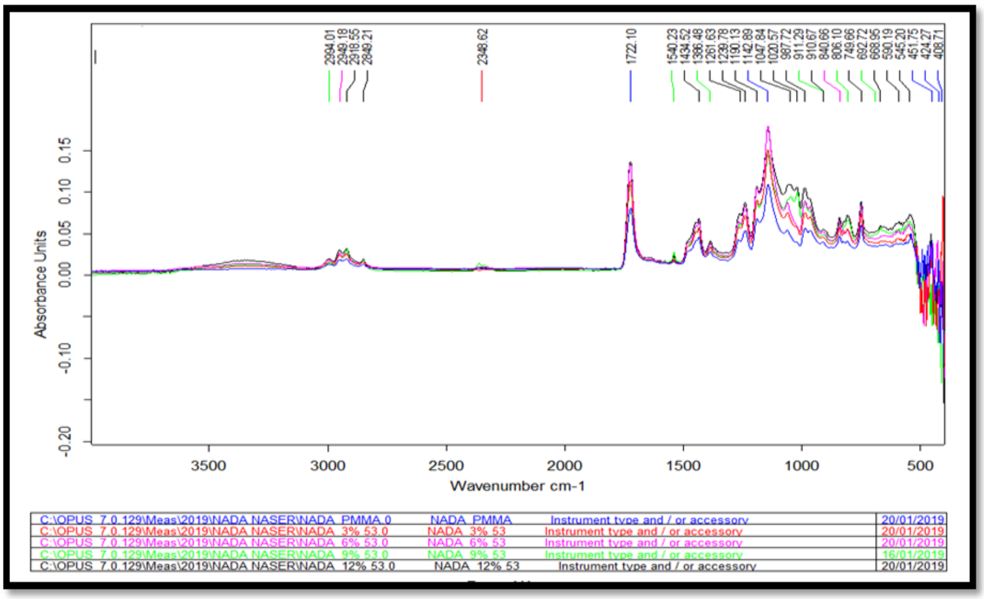

Fig. 2 : FTIR Spectrum of PMMA Composite Reinforced with Pistachio Shell Powder (wt.%) at Average Particle Size of (53µm.).

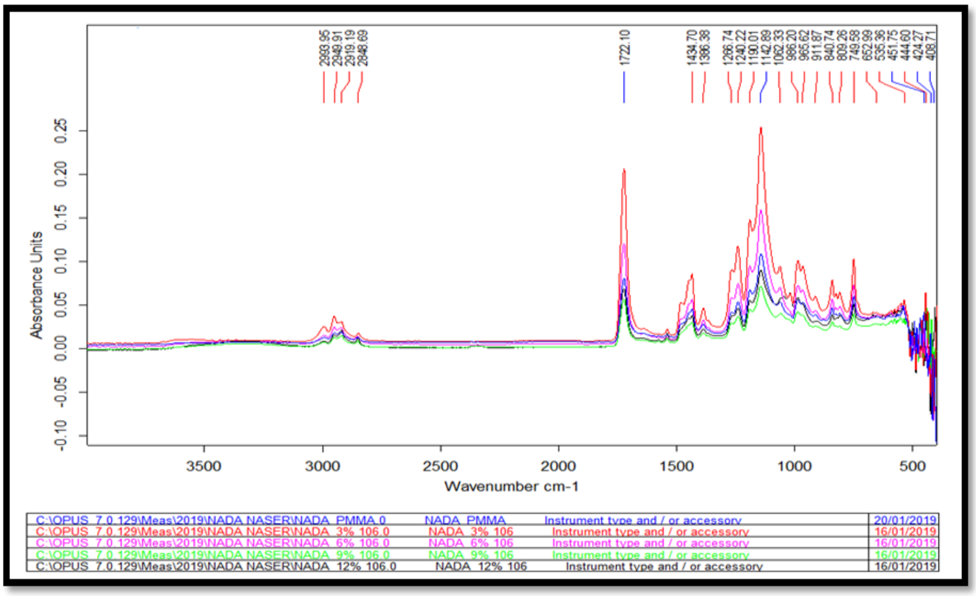

Fig. 3 : FTIR Spectrum of PMMA Composite Reinforced with Pistachio Shell Powder (wt.%) at Average Particle Size of (106µm.).

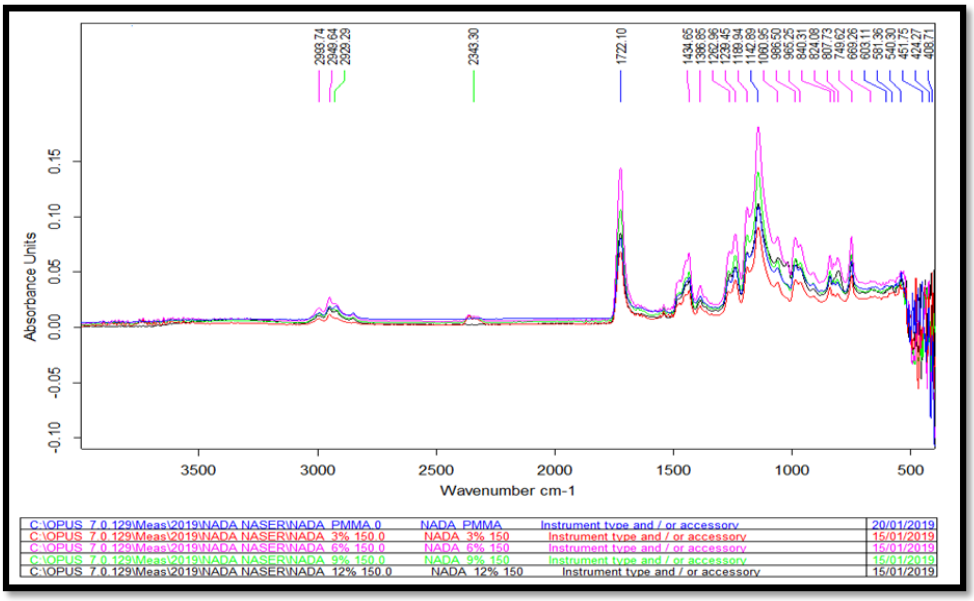

Fig. 4 : FTIR Spectrum of PMMA Composite Reinforced with Pistachio Shell Powder (wt.%) at Average Particle Size of (150µm.).

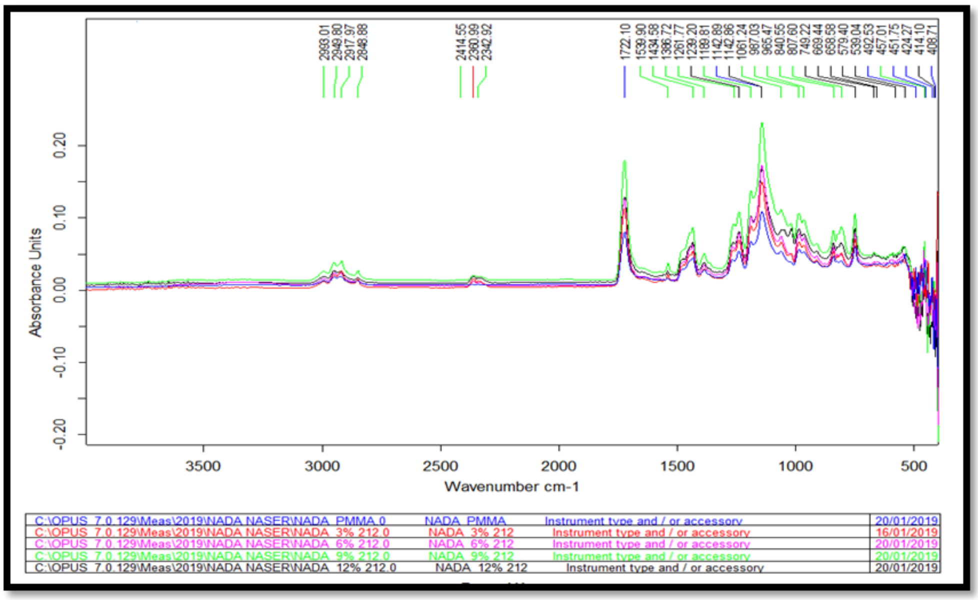

Fig. 5: FTIR Spectrum of PMMA Composite Reinforced with Pistachio Shell Powder (wt.%) at Average Particle Size of (212µm.).

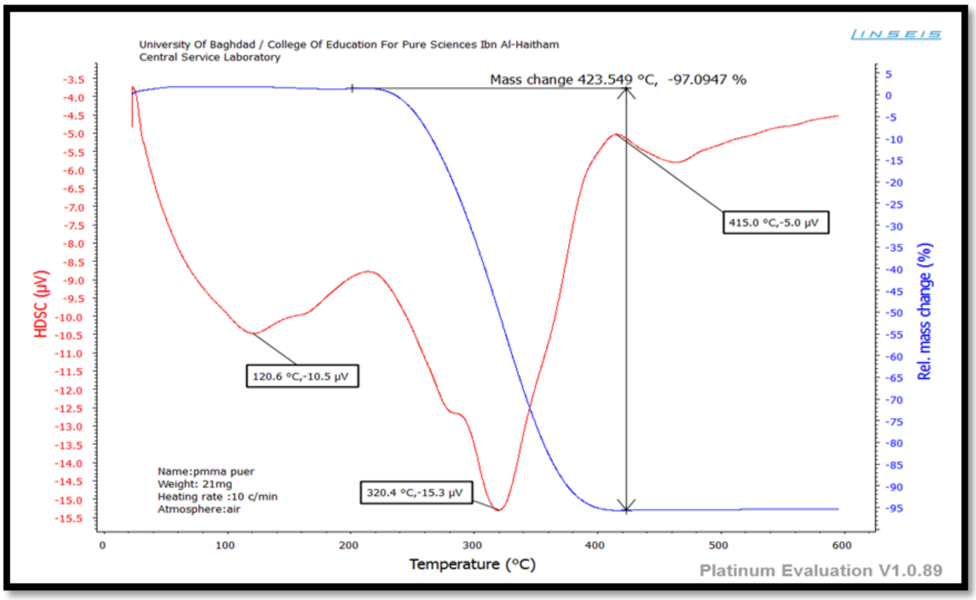

Fig. 6: Differential Scanning Clorimetery of Neat PMMA

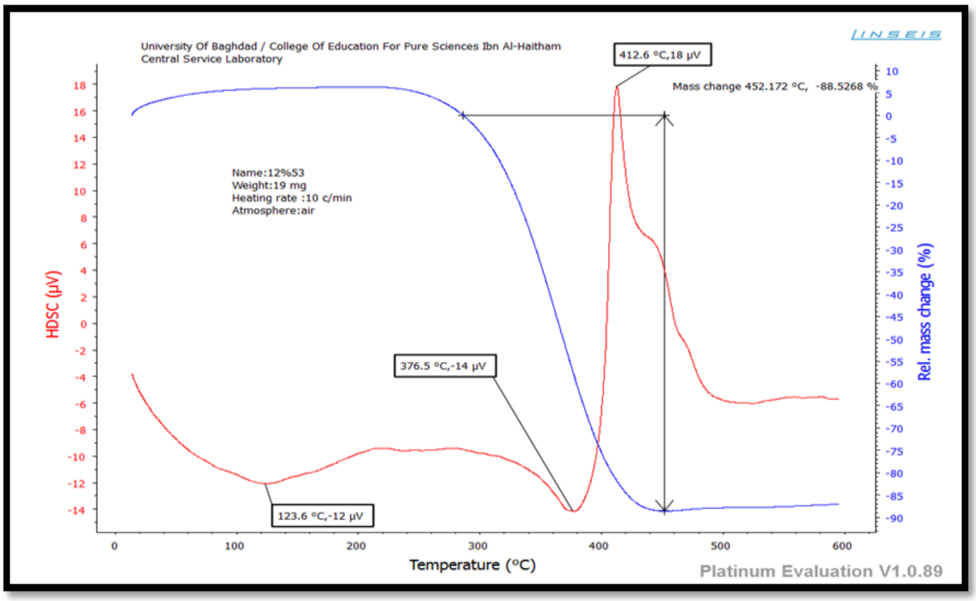

Fig. 7: Differential Scanning Clorimetery of PMMA Composite Reinforced with Pistachio Shell Powder (12%wt.) at Average Particle Size (53µm.).

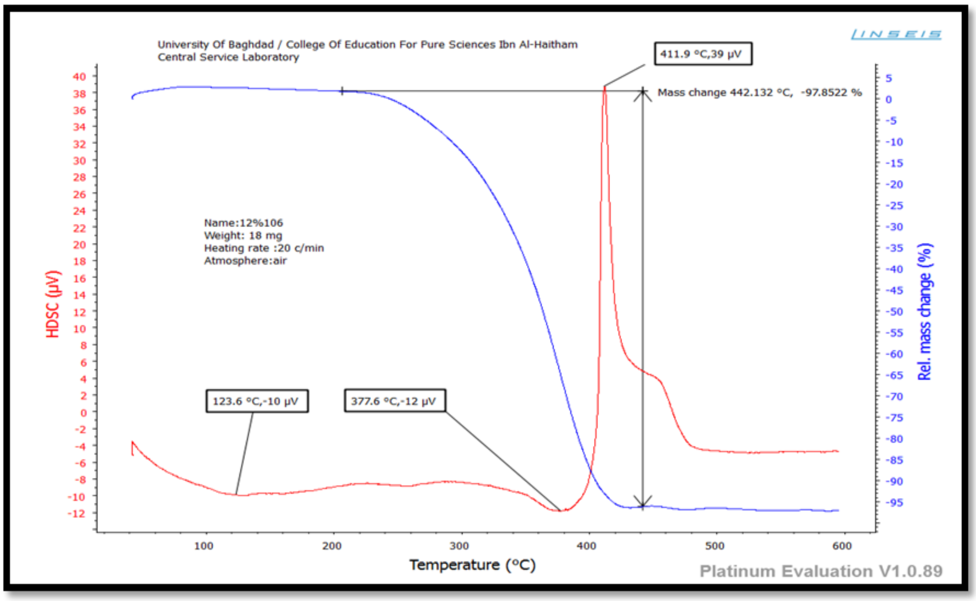

Fig. 8: Differential Scanning Clorimetery of PMMA Composite Reinforced with Pistachio Shell Powder (12%wt.) at Average Particle Size (106µm.).

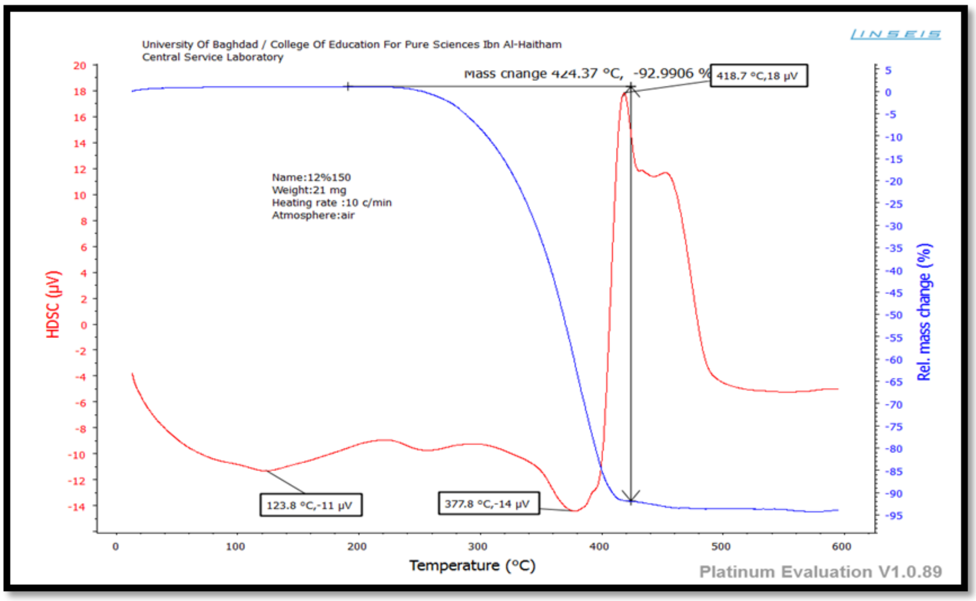

Fig. 9: Differential Scanning Clorimetery of PMMA Composite Reinforced with Pistachio Shell Powder (12%wt.) at Average Particle Size (150µm.).

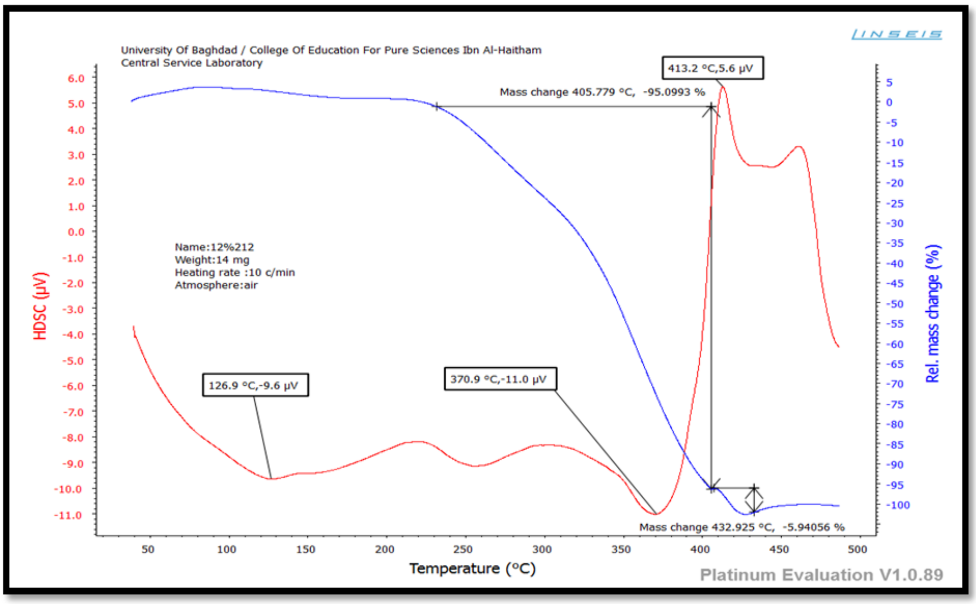

Fig. 10: Differential Scanning Clorimetery of PMMA Composite Reinforced with Pistachio Shell Powder (12%wt.) at Average Particle Size (212µm).

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