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Fourier Transform Infrared (FT-IR) Spectroscopy of Modified Heat Cured Acrylic Resin Denture Base Material

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ABSTRACT

Aims: Modifying heat cured denture base acrylic resin with new additives and the use of FT-IR spectroscopy to investigate and characterize the produced materials.

Methods: Thermally activated Zinc Oxide (ZnO) and Zinc Diacrylate (ZDA) powders were synthesized. Heat cured acrylic resin denture base material had modified by adding inactivated ZnO powder with and without acrylic acid (AA), thermally activated ZnO powder, AA liquid, or ZDA powder in 5%by weight. FT-IR Spectrophotometer was used to assess the chemical conversion of the cured samples.

Results: Both ordinary and thermally activated ZnO filler appear to have no chemical bonding with the cured resin structure. FT-IR analysis proved the successful synthesis of ZDA and its polymerization with MMA to form copolymer poly (methyl methacrylate-co-zinc acrylate) copolymer. The addition of AA resulted in a copolymer poly (methymathacrylate-co-acrylic acid) but failed to conjugate the ZnO to the resin matrix.

Conclusion: The addition of an inactivated ZnO or a thermally activated ZnO powders appear to be just incorporation of a filler without changing the PMMA structure, while the addition of AA or ZDA result in copolymers with PMMA. The method in which the ZDA was added to the heat cured acrylic resin could be considered as a new way of chemical bonding or engagement of Zn ions to acrylic structure to produce a new enhanced denture bases.

Keywords: Acrylic acid, Acrylic resin, Denture base, FT-IR spectroscopy, ZnO, Zinc diacrylate.

INTRODUCTION

The selection of materials for the construction of dentures is crucial because this directly relates to the performance and life span of the appliance during service in the oral cavity [1]. However, it was in 1937, “Dr. Walter Wright” introduced PMMA material as denture base material and it was found to be the most superior material over all other denture base materials [2,3]. It is a combination of advantages rather than one excellent aspect that accounts for its wide usage [4], including its popularity in satisfying aesthetic demands, its ease of processing, low cost, light weight, low water sorption and solubility; and ability to be repaired easily [1,5-7]. However, it has certain drawbacks like residual monomer allergy, inferior mechanical strength, brittleness, relatively low modulus of elasticity, low thermal conductivity, high coefficient of thermal expansion, thermal shrinkage, porosity, crazing, war page, poor adhesion to metal and porcelain and requirement of mechanical retention makes it more prone to failure during the clinical service [1,4,5,8].

Generally, there are three ways which have been investigated to improve the mechanical properties of denture bases; development of an alternative material to PMMA, reinforcement of PMMA with stronger materials and chemical modification of PMMA [9]. The reinforcement of polymers used in dentistry with metal-composite systems has been a prime interest [10]. The essential requirement for obtaining reinforced acrylic resin material with desiring mechanical properties is good adhesion between reinforcements and acrylic matrix [11]. In addition, the size of metal oxide particles should be small for better dispersion and proper processing [12].

Because of its diverse properties, both chemical and physical, zinc oxide is widely used as an additive in numerous materials and products including industrial, food and health products [13,14]. Zinc salts are formulated into oral health products as antibacterial agents to reduce malodor, and control plaque and calculus formation. In addition, it is used in dental restorative materials to reduce the demineralization of enamel [15,16].

Over the past decade much work has been done on developing organic inorganic composites produced by the action of modified inorganic carriers with polymer matrices. Such procedures make it possible to produce new classes of polymeric materials which combine properties of both inorganic particles and organic polymer matrices [17-19].

Acrylic acid (2-Propenoic acid: $C_3H_4O_2$) is an organic compound is the simplest unsaturated carboxylic acid which has double bond and carboxyl group in C3 one molecule with the structure [CH_2=$CHCO_2H$] (Figure 2) [20,21]. Acrylic acid polymerizes easily when exposed to heat, light or metals [22]. This simplest unsaturated carboxylic acid has two reaction points or functional groups required for polymerization process, consisting of a vinyl group (CH_2=CO-), that is, two carbon atoms double bonded to each other, connected directly to a carboxylic acid terminus (-COOH). Acrylic acids readily combine with other monomer molecules to form copolymers (Figure 2) [23].

Acrylic acid and polymers have wide uses in medical field. It was reported that they had been used in the production of pharmaceutical drugs [24], hard tissue adhesives [25,26], protective coating of orthopedic implants [27] bone cements and filling materials for the fixation of joints prosthesis between the artificial implant and the bone in orthopedic surgery and dental applications [28], cavity cements and filling composites in conservative dental treatment [29].

Acrylic acid coupled with ZnO (Figure 1) was used in bone adhesives in both dental and orthopedic therapies [30] and in dental cements [31-35].

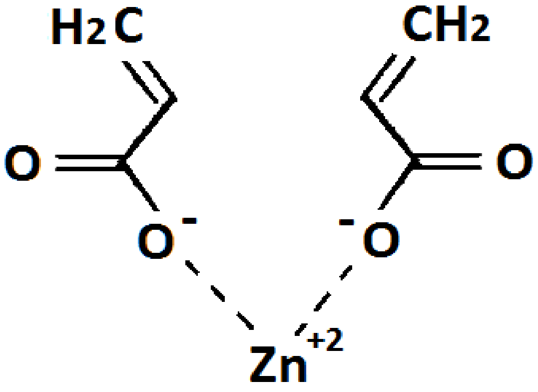

Figure (1): Zinc diacrylate

When AA is combined with MMA, poly (methyl methacrylate-co-acrylic acid) copolymer was result (Figure 2). This copolymer exhibits many characteristics of a successful carrier system for therapeutic molecules [36,37].

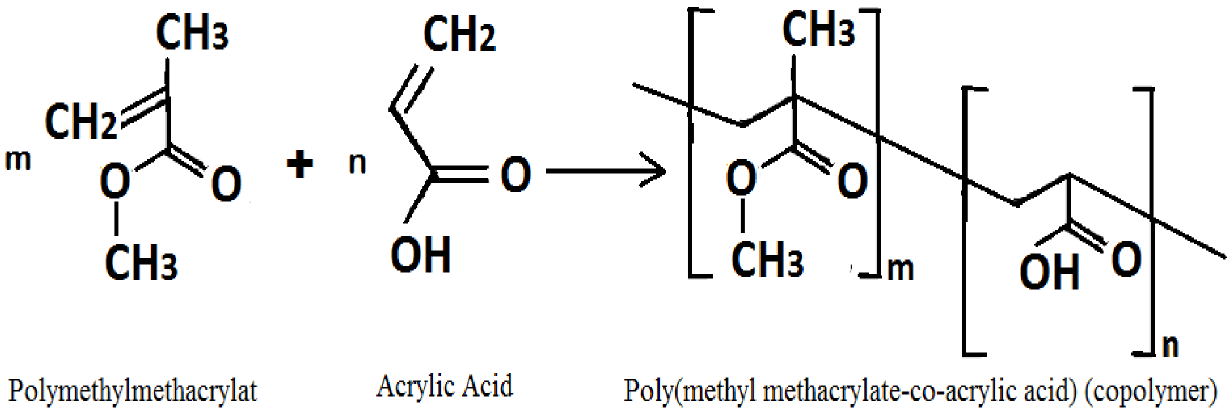

Figure (2): Reaction of Acrylic Acid with poly methylmethacrylat to form Poly(methyl methacrylate-co-acrylic acid) (copolymer)

The aim of our study was to investigate different ways of modifying heat cured acrylic resin denture base material in order to improve acrylic resin properties and durability.

MATERIAL AND METHOD

Six modified heat cure acrylic resin samples and a control sample were prepared and termed as follow: S1; Unmodified acrylic resin sample without any additive (control sample). S2; Modified acrylic resin sample contain 5% inactivated (ordinary) ZnO. The ZnO powder was added as received without any preparation. S3; Modified acrylic resin sample contain 5% inactivated (ordinary) ZnO and 5% Acrylic Acid. The ZnO and AA were added as received without any preparation. S4; Modified acrylic resin sample contain 5% thermally activated ZnO. The activated ZnO was prepared as described later. S5; Modified acrylic resin samples contain 5% Acrylic Acid (AA). The AA was added as received without any preparation. S6; Modified acrylic resin samples contain 5% Zinc diacrylate (ZDA). The ZDA was prepared as described later.

Preparation of thermally activated ZnO: It was treated by placing a particular weight of ordinary ZnO powder in a crucible in a furnace and heating it at 950°C for 3 hours. After cooling, the powder was weighed. This procedure was repeated until a constant weight was obtained. Then ZnO powder was milled using a Vibratory Disc Mill. The milled powder was sieved with a 25µm sieve to get a very fine powder. This ZnO powder was carefully collected and stored in a perfectly sealed container until use. Then the prepared ZnO powder was characterized by Laser Diffraction Technology to differentiate its particle size distribution.

Zinc Diacrylate (ZDA) was synthesized by the following procedure; ZnO (8.14 g, 0.1 mol) and 33 ml deionized water were introduced in a round bottom flask. After strong stirring, the mixture turned into suspension. Then (14.4 g, 0.2 mol) acrylic acid was added drop wise within 10 minutes at 5° C. The reaction was carried out at room temperature for 24 hours. Then the insoluble precipitate was filtered off using suppression Buchner and the filtrate was collected. Finally, the filtrate was dried under reduced pressure at room temperature to obtain zinc diacrylate, and further purification wash with methanol absolute was done. ZDA was dried on air at room temperature and milled using porcelain mortar and pestle.

Heat cured denture base acrylic resin prothyl press EVO 162 (Zhermack® technical Italy/ Complies with UNI EN ISO 20795-1) was used to prepare the tested sample. Flasking, mould separation, packing and clamping procedures followed the daily routine work for sample preparation in dental laboratory.

The manufacturer’s recommended powder to liquid mixing ratio for Zhermack heat-cured acrylic resin (10 g powder to 4.5 ml liquid) was followed. Composites with varying amounts of additives were prepared by replacing a weight fraction of the pre-mixed PMMA powder and MMA liquid with an equal weight of additive. The weight fractions of substituted acrylic resin by the additive fillers were (5%). In other words, in samples with additives, each of ZnO, AA, ZDA was added either in (5%) by weight of the mixture.

The heat curing process was carried out using a thermostatically controlled water bath. The curing cycle was achieved at 73°C for 90 min, then after; the water bath temperature was raised to 100°C and left boiled for 60 min. It was then switched off and let it to cool down slowly while the flasks still there. The cured specimens were examined by FT-IR Spectrophotometer after being crushed into very small pellets of 2-3 mg. All spectra were recorded in the range extending from 4000-400 cm^{-1} where the double beam optical null is the method of detecting the absorption bond and the IR spectrum scanning period of 20 seconds. Infrared spectra were recorded for the following materials; MMA liquid, AA liquid, and ZDA powder, and for the heat cured acrylic resin samples; S1-S6.

RESULTS

LASER Diffraction

Different sizes (micron to nanometer) of zinc oxide particles have been characterized using by LASER Diffraction Technology. Thermal activated ZnO was synthesized using heating, milling and sieving of ZnO powder. The LASER Diffraction reveals the particles’ size ranging from (0.1090 – 1.0550) µm with a median of (0.1457) µm. The mean value was (0.2597) µm and the geographic mean was (0.1861) µm.

FT-IR Spectrophotometer: Nine recorded infrared spectra are shown in figures (3-11).

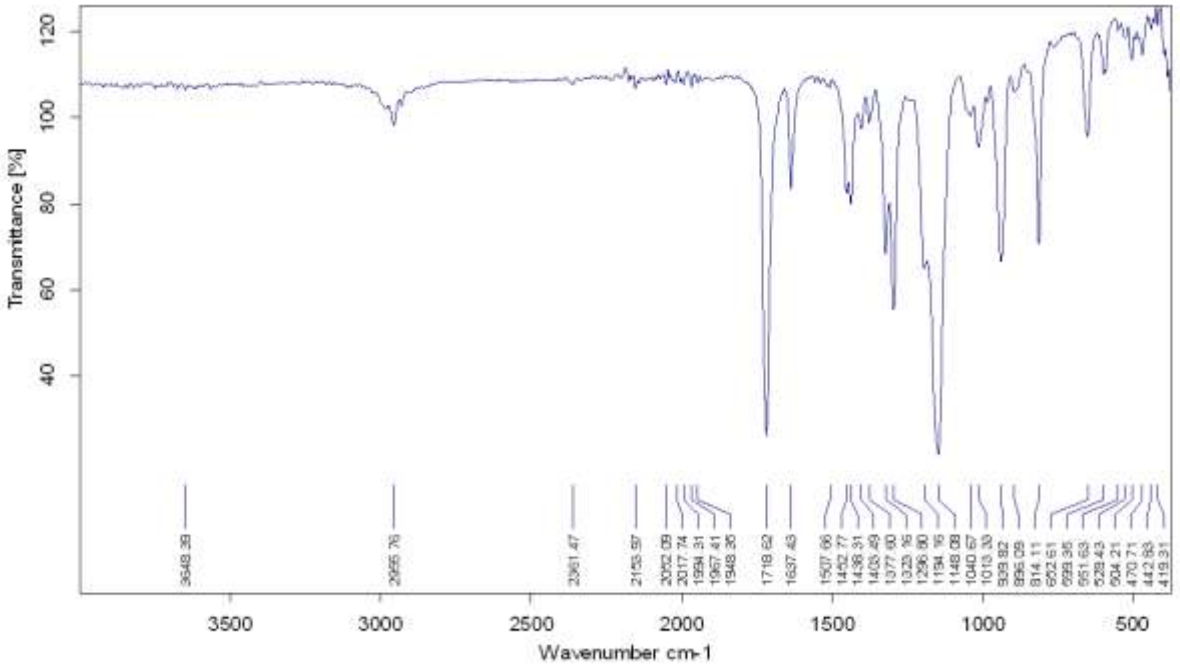

Figure (3): IR spectra of MMA liquid.

Figure 3shows IR spectra of MMA liquid. The spectra involves an aliphatic medium stretch (–C-H) bond absorption at 2955 cm^{-1} , strong stretching absorptions of (C=O) and (C-O) bonds at 1718 cm^{-1} and 1148 cm^{-1} respectively. The carbon-carbon single bond (C-C) has a medium absorption at 1434 cm^{-1} . The carbon-carbon double bond (C=C) has a medium absorption at a wavenumber of 1637cm^{-1}.

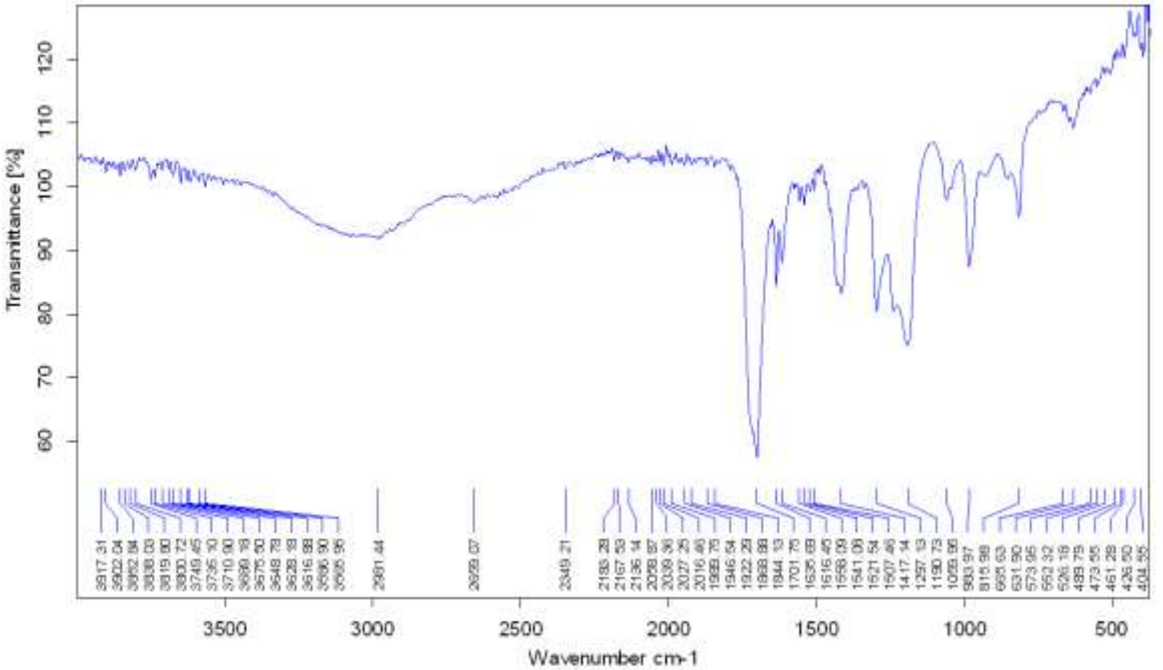

Figure (4): IR spectra of AA liquid

Figure 4, which represents IR spectra of AA liquid, shows the characteristic spectra of the carboxylic acid. This involves a strong finger shaped stretching (C=O) bond absorption at 1701 cm^{-1}, a strong (C-O) stretching absorption at 1190 cm^{-1}, and a strong, very broad trough absorption of (O-H) bond at 2981 cm^{-1} . A medium sharp stretch peak at 1635 cm^{-1} is of (C=C) bond.

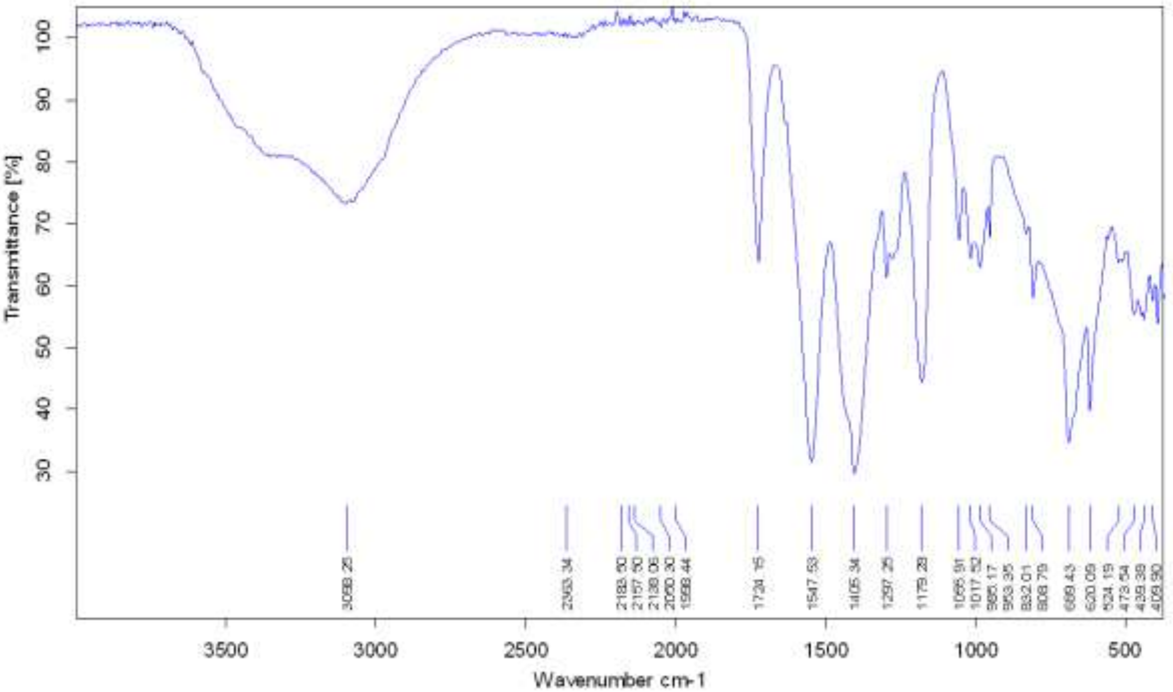

Figure (5): IR spectra of the prepared ZDA additive

Figure 5, which represents IR spectra of the prepared ZDA additive, shows a strong stretching (C=O) bond absorption at 1724 cm^{-1}, a strong (C-O) stretching absorption at 1179 cm^{-1} , and a medium stretching(=C-H) bond absorption at 3098 cm^{-1} . The wavenumber 1547 cm^{-1} and 1405 cm^{-1} are the (–COOZn) spectrum.

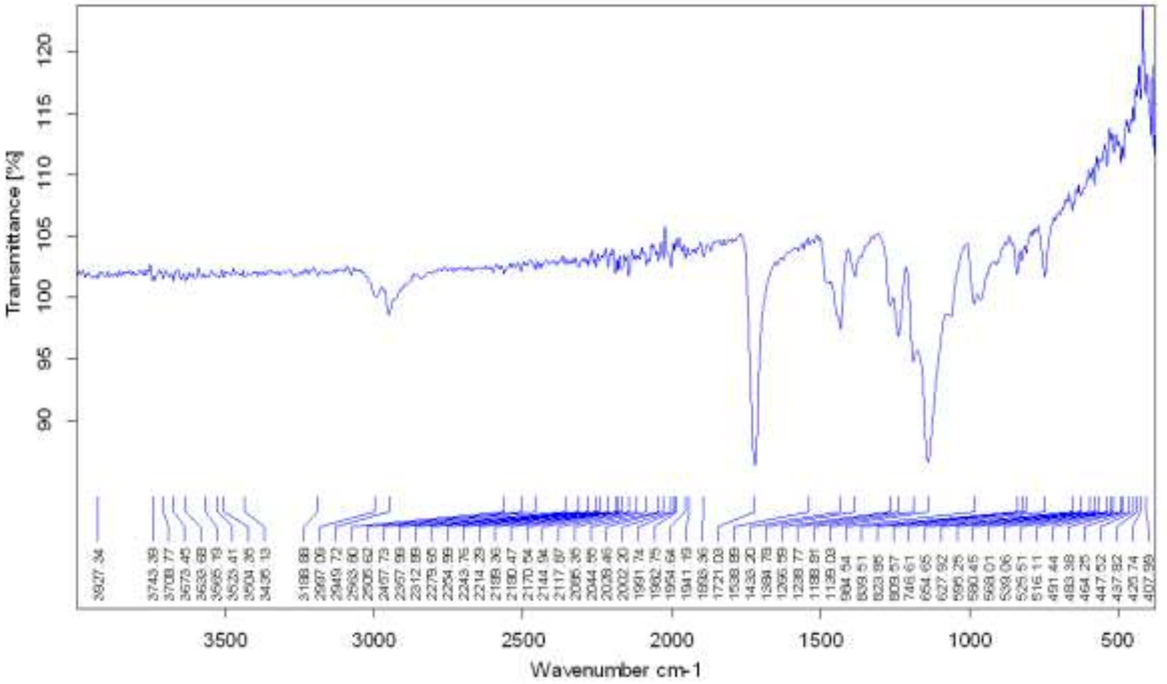

Figure (6): IR spectra of S1; Unmodified acrylic resin sample without any additive (control sample).

Figure 6 shows IR spectra of PMMA control group. The medium stretch (–C-H) bond absorption presents at 2950 cm^{-1} , strong stretching absorptions of (C=O) and (C-O) bonds at 1722 cm^{-1} and 1142 cm^{-1} respectively. The carbon-carbon single bond (C-C) has a medium absorption at 1434 cm^{-1}. While the carbon-carbon double bond (C=C) absorption around the wavenumber of 1637 cm^{-1} was absent.

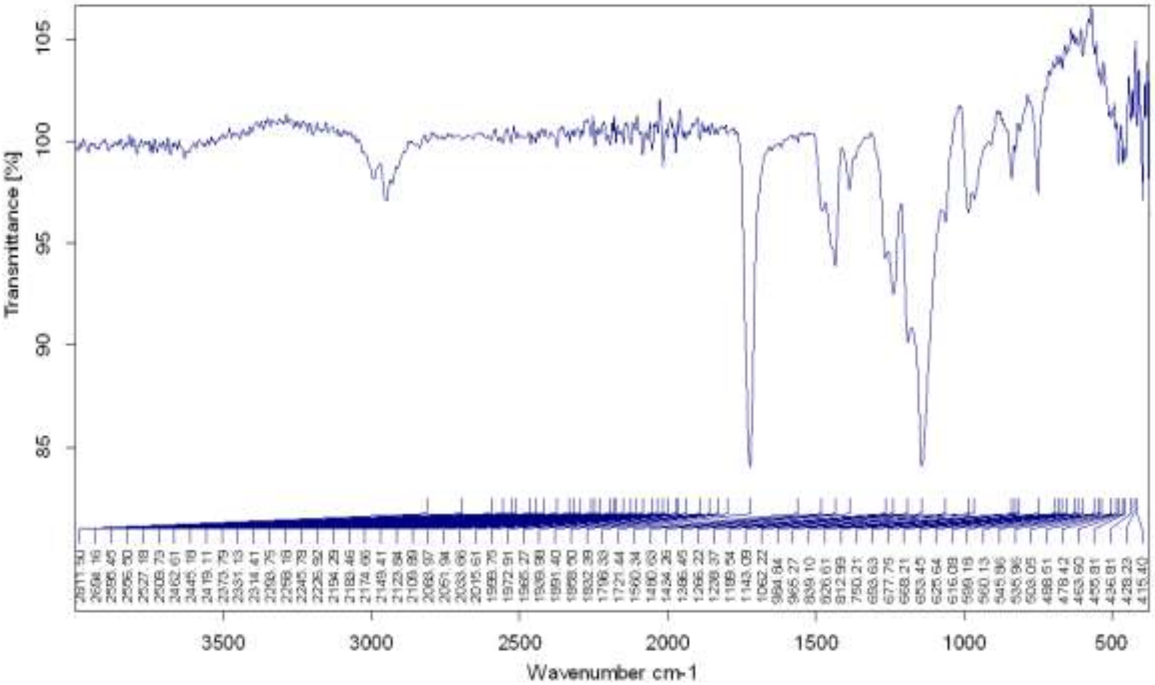

Figure (7) : IR spectra of S2; Modified acrylic resin sample contain 5% inactivated (ordinary) ZnO

In Figure 7, The strong finger shaped spectrum absorption of (C=O) and (C-O) bond at 1721 cm^{-1} and 1143 cm^{-1} respectively are clear. A wavenumber of 1434 cm^{-1} represents the (C-C) bond spectrum.

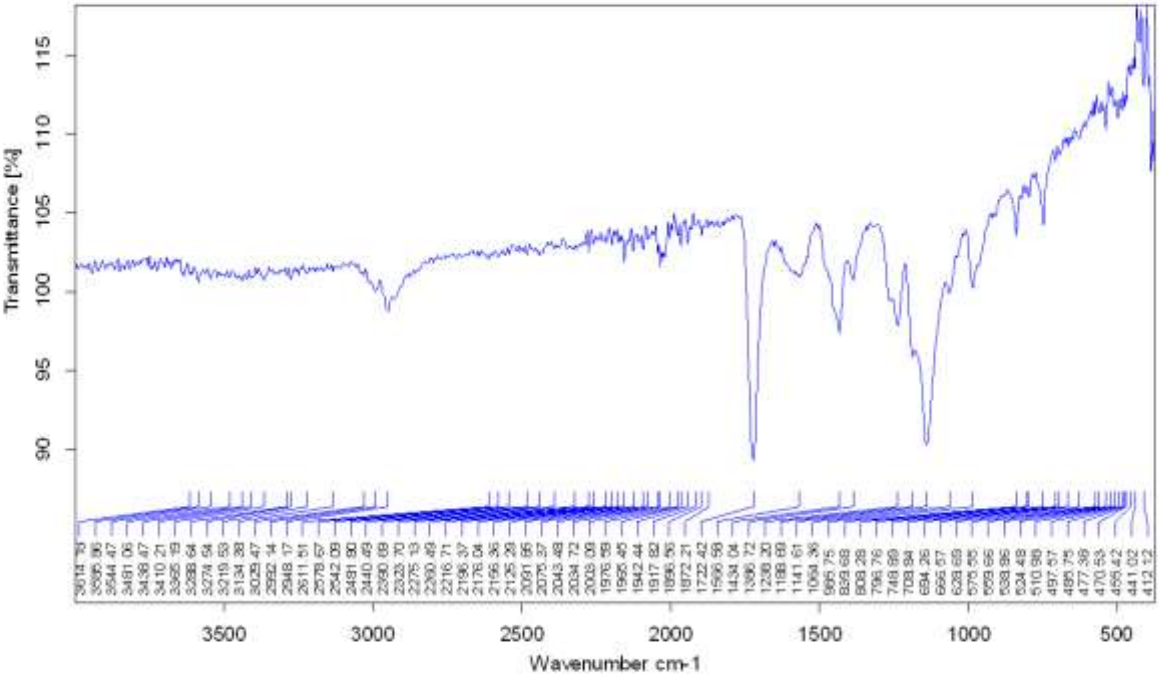

Figure (8): IR spectra of S3; Modified acrylic resin sample contain 5% inactivated (ordinary) ZnO and 5% Acrylic Acid.

Figure 8 represents IR spectra of an inactivated (ordinary) ZnO with AA additive. The characteristic IR spectra of the strong finger shaped stretching (C=O) bond absorption at 1722 cm^{-1}, a strong (C-O) stretching absorption at 1141 cm^{-1} are clear. The (C-C) bond has a medium absorption at 1434 cm^{-1} . While the (C=C) bond spectrum (1600-1680) cm^{-1} was absent. Both of a medium stretch (–C-H) bond spectrum at 2948 cm^{-1} and (O-H) bond spectrum at 3029 cm^{-1} are present.

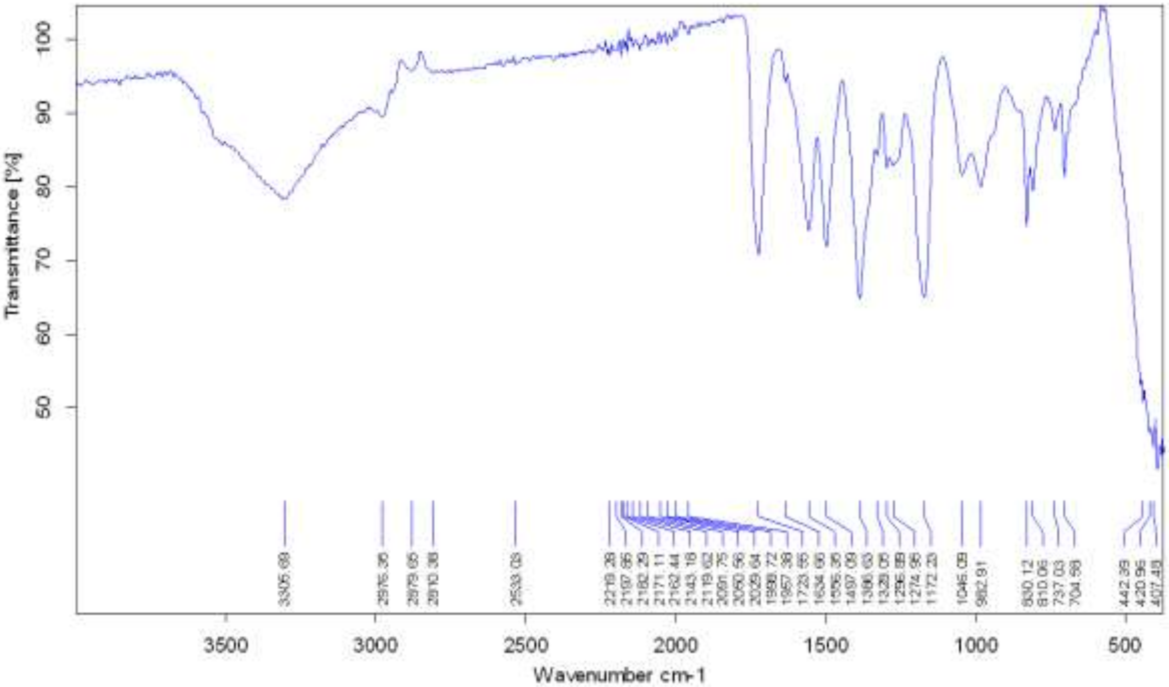

Figure (9): IR spectra of S4; Modified acrylic resin sample contain 5% thermally activated ZnO.

Figure 9 represents IR spectra of an activated ZnO group. The characteristic IR spectra of the strong finger shaped stretching (C=O) bond absorption at 1723 cm^{-1}, a strong (C-O) stretching absorption at 1172 cm^{-1} are clear. The (C-C) bond has a medium absorption at 1497 cm^{-1} . The (C=C) bond spectrum at 1634 cm^{-1} was also present. Both of a medium stretch (–C-H) bond spectrum at 2976 cm^{-1} and a strong broad (O-H) bond spectrum at 3305 cm^{-1} are present.

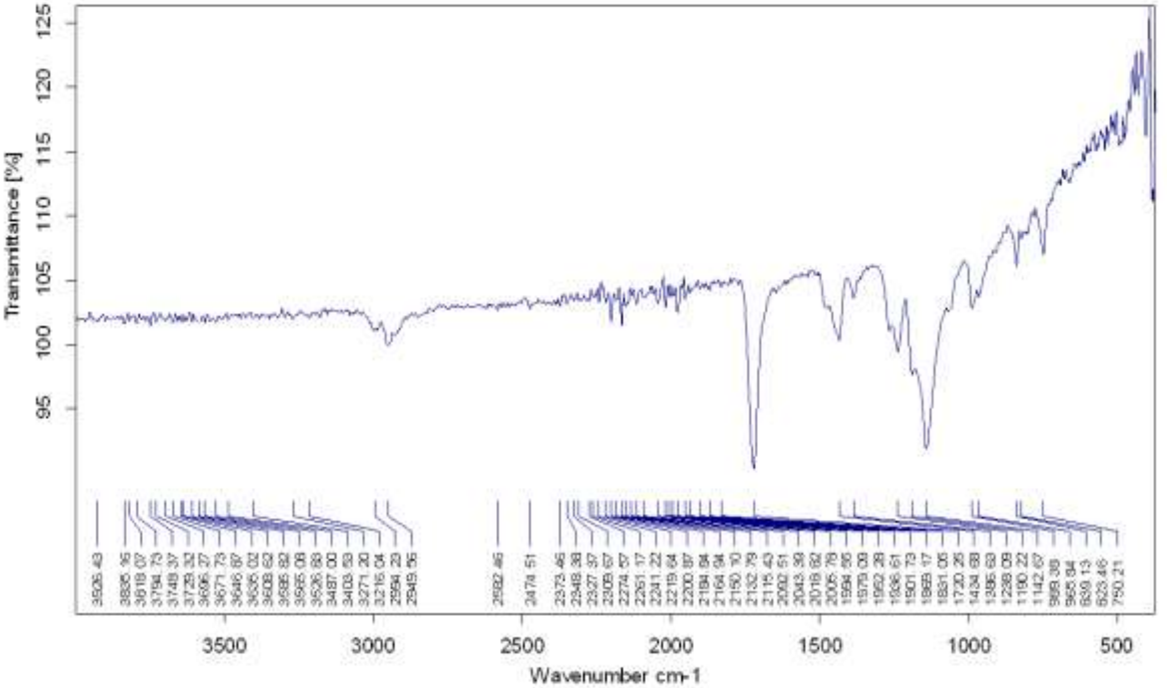

Figure (10): IR spectra of S5; Modified acrylic resin samples contain 5% Acrylic Acid (AA).

Figure 10, which represents IR spectra of AA 5% group, shows the characteristic IR spectrum of a carboxylic acid that involves both (C=O) bond with its strong finger like absorption at 1720 cm^{-1} and (C-O) bond absorption at 1142 cm^{-1} . The strong and broad spectrum absorption of (O-H) bond of AA ranged between (2300-3000) is absent. A wavenumber of 2949 cm^{-1} represents the (C-H) bond spectrum.

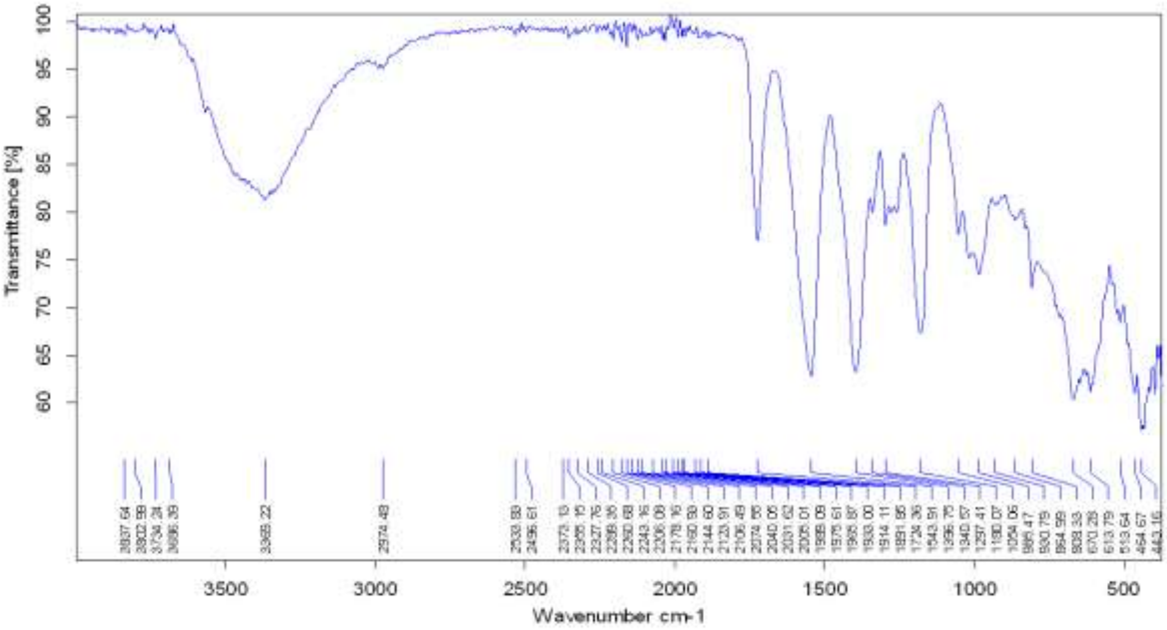

Figure (11): IR spectra S6; Modified acrylic resin samples contain 5% Zinc diacrylate (ZDA).

Figure 11 represents IR spectra of ZDA 5% group. This figure shows a strong stretching (C=O) bond absorption at 1724 cm^{-1}, a strong (C-O) stretching absorption at 1180 cm^{-1} , and a medium stretching (-C-H) bond absorption at 2974 cm^{-1}. The wave numbers 1543 cm^{-1} and 1396 cm^{-1} are the (–COOZn) spectra. The strong and broad spectrum at 3369 cm^{-1} is of (O-H) bond absorption.

DISCUSSION

Infrared spectroscopy is the study of interaction of infrared light with matter, which can be used to identify unknown materials, examine the quality of a sample or determine the amount of components in a mixture. Infrared spectrum is molecular vibration spectrum [38]. Fourier Transform Infrared Spectrometer (FTIR) are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. In addition, the mechanism of chemical reactions and the detection of unstable substances can be investigated with such instruments [39].

In our study, it is very important to investigate the chemical structures of the prepared materials before and after curing and their conversion after curing. We chose FT-IR spectrometer for such investigation because of its several prominent advantages. Among these advantages are significantly high signal-to-noise ratio of spectrum, high accuracy of wave number, sensitive technique, extremely fast scan with high resolution (0.1 ~ 0.005 cm-1) and the peak positions, intensities, widths, and shapes all provide useful information [40].

Infrared spectra were recorded for each precursor (i.e. MMA and AA), prepared additive (i.e. activated ZnO and ZDA) before curing and for each resulted group of polymerized acrylic resin after curing. In addition, as IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups, it can also be a quick and convenient way to check if a reaction has proceeded as planned. Therefore, IR spectra were recorded for each starting compound. All the IR absorption bands were compared to typical reference spectra [41-45].

The spectra of MMA and PMMA control group were used as standards to compare the other polymerized acrylic groups. MMA has strong finger shaped stretching (C=O) and (C-O) bonds present at 1718 cm^{-1} and 1148 cm^{-1} respectively (Figure 3). The characteristic peaks of aliphatic carbon-carbon bonds (C=C and C-C) are also observed at 1637 cm^{-1} and 1438 cm^{-1} respectively. Comparing IR spectrum of the cured PMMA (Figure 6), the (C=C) peak is absent which indicates the conversion of MMA to polymer.

AA spectrum (Figure 4) was used to check if the preparation of the ZDA has proceeded as planned beside its use as a stander to check its copolymerization with MMA. AA is a carboxylic acid. Its carboxylic terminal bonds are clear in its IR spectrum; a very strong stretching (C=O) bond absorption at 1701 cm^{-1} and (C-O) bond peak at 1417 cm^{-1}and a very broad and strong trough at around 2981 cm−1 corresponds to (O-H) stretching. This (O-H) absorption looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap the (C-H) region. This is the characteristic carboxylic acid (O-H) single bond stretching absorbance. The (O-H) stretching absorption for such acid is very strong and broad, extending from 2981 cm^{-1} to 3565 cm^{-1}. This absorption overlaps the sharper (C-H) stretching peaks, which may be seen extending beyond the (O-H) envelope around 2948 cm^{-1}.

The broad peaks at 1190 cm^{-1} could be assigned to (C–O) bond and also to (C–C) bonds. The peaks observed at wave numbers 1653 cm^{-1} and 1616 cm^{-1} can be assigned to the aliphatic carbon-carbon double bond (C=C). An IR spectrum of the prepared zinc diacrylate (ZDA) additive before its addition to the MMA and curing is shown in Figure (5). The characteristic spectra of a carboxyl ate; strong stretching (C=O) and (C-O) bonds' absorption at 1924 cm^{-1} and 1179 cm^{-1} respectively were observed. In AA the carbonyl stretching frequency of (C=O) bond is found near 1701 cm^{-1}, but is increased by 23 cm^{-1} in the monomeric state as in ZDA (1724 cm^{-1}).

Comparing Figure (5) with Figure (4) of AA spectrum, three new bonds were visible. Two of them have very strong absorption at 1547 cm^{-1} and 1405 cm^{-1} can be assigned to the (Zn-O) bonds. In general, the greater the polarity of the bond, the stronger is its IR absorption. The (Zn-O) bond is very polar -ionic bond- and absorbs very strongly. The (O-H) bond, in contrast, is much less polar -covalent bond- and thus a stretching vibration do not result in a large change in the overall dipole moment of the molecule. Thus (O-H) bonds in the AA absorb rather weakly compared to (Zn-O) bonds in the ZDA acrylic groups. The third new bond is the (=C-H) bond absorption of alkene at a wave number 3098 cm^{-1}. From the former, we ensured that the chemical reactions for the production of zinc diacrylate were achieved successfully.

Below 1500 cm^{-1} the spectra have very high sensitivity and this region is known as the fingerprint region where (C-C) bond stretching and bending motions overlap, making it difficult to predict functional groups [44-46].

In S2 sample, ordinary (ZnO) powder was added to the acrylic resin as received without any pre treatment phase. Although this addition was made in the same way as other additives, groups but its IR spectrum (Figure 7) ensures that there is no change in the term of chemical structure of the resultant cured product when comparing it with the IR spectrum of the control group (Figure 6). In other word, the cured product after addition of inactivated (ZnO) is still a poly methyl methacrylate and the (ZnO) particles fill the intermolecular spaces of the organic matrix chains.

In S3 sample, we added the AA to the MMA and ZnO mixture. This technique was done to make sure if the AA can enhance the ZnO molecules to bond with the functional terminals of the MMA and to be a part of the polymer matrix. The IR spectrum of this addition (Figure 8) proved the copolymerization of the AA with the MMA while the proposed bonding of the added ZnO cannot be achieved. The spectrum in this figure is similar to those in figures 10.

Another technique used to achieve bonding of ZnO particles to acrylic resin structure was the thermal and mechanical activation of ZnO. This activation resulted in the spectrum of Figure 9 which explained the success of ZnO to make bonding (–COOZn) at 1556 cm^{-1} and 1386 cm^{-1}. In the same figure we can see a stretching of vinyl group (C=C) at 1634 cm^{-1} which indicates the presence of the nonreacted MMA monomer. The (C=C) stretching absorption bond was taken as representative of the nonreacted monomers [47].

The striking in this figure is a very strong stretching at 407– 442 cm^{-1}. This is the spectrum of ZnO nanoparticles which characterized by a wave number ranged between 400 - 500 cm^{-1} [48]. A very broad, strong and short peak of aqueous (O-H) bond is present at 3305 cm^{-1}.

Figure 10 represents the IR spectra of AA5% They show the characteristic strong finger shaped peaks of (C=O) and (C-O) bonds and the medium stretching (–C-H) absorption around 2948 cm^{-1}. The evidence of the copolymerization is the absence of the carbon-carbon double bond (C=C) which appears at 1637 cm^{-1} in MMA and at 1635 cm^{-1} AA monomers (Figure 3 and Figure 4 respectively).

Figure 10 gives us a lot of readings. The absence of the aliphatic carbon-carbon double bond is an indicative feature of polymerization. In the MIR region, the degree of conversion is determined by measuring the intensity decrease of the (C=C) stretch absorption bond as the monomer is converted to polymer [49]. In addition, a comparison of this figure with Fig. 6, (IR spectra of unmodified PMMA control group), new bands were visible at 1543 cm^{-1} and 1390 cm^{-1} . These bands are due to the presence of zinc acrylate. A shifting of the (C-H) bond spectrum absorption from the wave number 3098 cm^{-1} in the prepared ZDA additive to a new wave number of 2974 cm^{-1}. Finally, the rising of strong and broad polymeric hydroxyl bond (O-H) at 3396 cm^{-1} (Figure 11) is clear. All these are indicative signs confirm the copolymerization of both MMA and ZDA in the final product to form poly (methyl methacrylate-co-zinc acrylate) copolymer. Also the IR spectrum of ZnO particles was clear at wave number ranged between 427 cm^{-1}–467cm^{-1}.

A new sharp band at 1447 cm^{-1} becomes visible in the IR spectrum of composite. This indicates the presence of alkane group, which clearly can be attribute to participation of (–CH=CH) group in curing process and conversion of this group to alkane during cross linking process. The smaller peaks protruding at 2533 cm^{-1} in Fig. 11 are characteristic of the dimer [50].

More researches will be done to assess the benefits of such modification of heat cured denture base acrylic resins.

CONCLUSION

A heat cured acrylic resin denture base material had been modified in different ways. The addition of ordinary ZnO or a thermally activated ZnO powders appear to be just incorporating filler without chemical bonding with the resin matrix. AA as an additive reacted with MMA to form a copolymer but failed to conjugate the ZnO to the resin matrix. A successful synthesis and copolymerization of ZDA with MMA was achieved and aimed to chemically conjugate Zn ions with the resin matrix. The method in which the ZDA was added to the heat cured acrylic resin could be considered as a new way of chemical bonding or engagement of Zn ions to acrylic structure with the hope of improving its properties.

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