RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF SOME MODIFIED NATURAL NANOCOMPOSITE POLYMERS AND STUDY THEIR THERMAL AND MECHANICAL PROPERTIES

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Manuscript Info

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Abstract

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Dextrin, tannic acid and different proportions of silver nanoparticles (AgNPs) are used to prepare novel materials. The functional and morphological characterization of the prepared nanocomposites was carried out by using Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM). The mechanical strength (Impact,compressing, hardness, and swelling behavior) of composite were evaluated. The thermal stability of composites was evaluated. The addition of AgNPs to the polymer blend matrix improves the physicochemical of the matrix. Due to the cross-linking motion of AgNPs, it is found that the swelling degree slightly decrease. The composite containing AgNPs becomes effective in increasing thermal stability.

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Introduction:-

Nanotechnology has been competing for the world's attention since its rapid development in the fields of science, technology, industry, and health. Nanotechnology allows for the modification and synthesis of materials at the nanometer (nm) scale. The synthesis of nanoparticles (1–100 nm) has shown various advantages, including: minimizing material requirements, increasing activity due to increased surface area, and having unique physicochemical properties. Past studies indicate the wide synthesis of metal nanoparticles because they have superior biological, optical, electrical, catalytic activity, and antimicrobial properties [1,2].

Silver nanoparticles have several unique features, including electronic properties, catalytic properties, optical properties [3], high surface energy, and less aggregation, in addition to several other physical and chemical properties which are not possessed by other metal nanoparticles [4]. Silver nanoparticles have also been widely used in various fields such as photocatalyst, lithography, microelectronic biosensor materials, and pharmaceuticals. It can be used as an alternative to the use of a natural product as a medicinal substance which requires raw materials from biodiversity which are starting to become less available [5,6]. Silver nanoparticle has shown good antibacterial, antifungal, and antiviral activity [7]. In this decade, the synthesis of silver nanoparticles using bio-synthetic or green synthesis methods has developed rapidly. For example, the use of materials or plant extracts as reducing agents in the synthesis of silver nanoparticles. This method has been chosen by many experts because of several advantages, including producing better antibacterial activity, as well as being inexpensive and eco-friendly [8]. There are two processes that occur in the synthesis of silver nanoparticles, namely the process of reducing Ag+ ions to Ag∘ , and the process of stabilizing the particle size. As stabilizing agent, micelles, ligands, and polymers have been widely used in past research [1,9]. The use of a polymer as a nanoparticle stabilizer is crucial to prevent the aggregation of nanoparticles, enabling the improvement of their biocompatibility properties [10]. Polymers can act as matrix

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1045

materials for the growth and stability of nanoparticles [11]. The immobilization of metal nanoparticles in a polymer matrix is an effective way in reducing metal nanoparticle aggregation and increasing the compatibility of the metal nanoparticles. This is caused by the ability of the matrix polymer to control and stabilize the metal nanoparticle. Some commonly used polymers for synthesizing silver nanoparticles spheres are chitosan, gelatin [12], liposomes, polylactic acid [13], polymethylmethacrylate [14], poly (L-lactide) [15] , poly lactide-dipentaerythritol [16] ,which are known to be used as a reducing agent or stabilizers of metal nanoparticles [5]. Several researchers have used polymers for the synthesis of silver nanoparticle spheres. For example, polysaccharides from microalgae [17], polystyrene [5], and chitosan [18] have successfully been used in the synthesis of silver nanoparticles.

In this work, we advanced the synthesis of silver nanoparticles using tannic acid and dextrin as a stabilizer and sodium citrate ($C_6H_5O_7Na_3$) as a reducing agent. The concentration of sodium citrate used in this study was lowest (0.01 mole). The tannic acid-dextrin-silver nanoparticles microsphere composite (TA-DE-AgNPs) was characterized using FT-IR spectroscopy, Field emission scanning electron microscopy (FESEM) and Thermogravimetric analysis (TGA). In this study, the Compressing force, Impact force,Hardness test and Swelling DegreeofTA-DE-AgNPs was also determined in comparison with epoxy resin.

Materials and Methods:-
Materials:-
Silver nitrate ($AgNO_3$) was purchased from POCL Chemicals, Ltd, India. Dextrin99.9% were purchased from CDH. Ltd. China. Tannic acidwas purchased from Alpha Aesar. Ltd., Germany. Deionized water was used to prepare all the aqueous solutions.

Methods:-
Synthesis of amine functionalized Dextrin (DE-NH$_2$)
Epichlorohydrin (1.46 ml) was added to ammonium hydroxide (3.78 ml) and heated to 65 °C for 2 h (This reaction is highly explosive in a closed container as the heating of ammonium hydroxide solution results in the evolution of gaseous ammonia in the reaction chamber, Therefore, in order to keep the gaseous ammonia below the explosion limit, a cooling water reflux system was used, which also increased the reaction yield). DE (1.00 g) was dispersed in water (70 ml) , PMDETA was added to the mixture in a round bottom. Contents from the first reaction were removed using a syringe and added to the second mixture in a drop-wise manner. The reaction mixture was stirred for (3 h) and heated at (50 °C) for studies on the optimal reaction conditions.

The above procedure was repeated using Tannic acid for the synthesis of amine functionalized Tannic acid (TA-NH$_2$).

Synthesis of Silver nanoparticles
A (2.5 g) of silver nitrate was dissolved in (800 ml) of distilled water in around flask, then the solution was heated to a temperature (95 ° C) and then (125 ml) of sodium citrate solution (0.01 mol) was added to it very slowly, Uniform with vigorous stirring by magnetic stirrer and maintaining high temperature to be constant,according to the following reaction equation:

$$4Ag^+ + C_6H_5O_7Na_3 + 2H_2O \longrightarrow 4Ag\downarrow + C_6H_5O_7H_3 + 3Na^+ + H^+ + O_2\uparrow$$
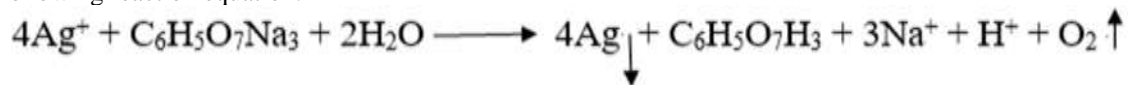
During the reaction, the silver mirror begins to appear on the walls of the beaker. After the addition is completed, the solution is left to stagnate, then the particles are collected by filtering using filter paper (no.44), then the particles are washed several times using ethanol, and then the particles are dried in the oven at a temperature (90 ° C) for a period of time 2hours. After that, silver nanoparticles were obtained, and tests were conducted on it to confirm its nanoscale size.

Synthesis of Nano polymeric composites
A (2 g) of DE-NH$_2$ was dissolved in (80 ml) of distilled water in a 100 ml beaker and the solution was shaken by ultrasonic device for two hours, then (2 g) of TA-NH$_2$ was mixed in (80 ml) of distilled water in the beaker, and the solution was shaken by an ultrasonic device for two hours. Then, 0.25 gm of silver nanoparticles was dissolved in 25ml of distilled water in a 50-ml beaker, and the solution was shaken by an ultrasonic device (for the purpose of dispersing silver nanoparticles). Then the previous three solutions were mixed together in 500-ml beaker and the

solution was shaken by an ultrasonic device for three hours, and at the end of the reaction period, the product was collected by filtration and dried in an electric oven. Then the product weighted, which is equal to 3.8 grams.

Measurements:-

The FTIR was measured by using the apparatus (Shimadzu), FE-SEM of AgNPs was measured by using the microscope type (TESCAN, BRNO-Mira 3 LUM).Composites thickness was measured by using a digital micrometer screw gauge (Brown & Sharpe Micrometer, USA) with a precision of 0.01 mm, the thickness of the composites samples was determined at five different random points, and the mean values were recorded as the average thickness. While the mechanical properties like compressive force were tested by mechanical testing machine (Humboldt, Norridge,1L, model H-4454, USA), Compressive test bar specimens were prepared by filling a Teflon mold with diameter 10 mm and height 20 mm.Impact force were tested by Izod impact machine (Ceast, model 6530, USA).

Thermogravimetric analysis (TGA) was carried out using a (Thermogravimetric Analyzer; product name: SDT-Q600 V20.9 Build 20; Universal V4.1D TA instrument. The heating rate was carried out at 10°C/min under nitrogen gas atmosphere from 20°C to 800°C. The reported results were averaged from a minimum of five specimens.

The discrepancy between the weight of the dry nanocomposites and the weight of the nanocomposites after immersion in distilled water for 24 h at 37 ◦C and subsequent elimination of surface water by blotting with tissue paper is used to calculate the swelling degree (%) of the nanocomposites. It was calculated as follows:

$$ EDS\ (\%) = \frac{W_s - W_d}{W_d} \times 100 $$

Wd:Weight of the dried sample(g)
Ws:Weight of the sample after immersion in water(g).

Results and Discussion:-

FTIR of TA and TA-NH$_2$

FTIR was used to characterize the TA compound, in the form of potassium bromide discs for solid models. Figure (1) indicates the infrared spectra of the TA compound, as this compound has an absorption band at (3387.11) cm^{-1} due to the presence of a group of phenolic hydroxyl (OH), and the presence of an absorption band at (1708.99) cm^{-1} that is due to the presence of the conjugated carbonyl group, as well as the presence of an absorption band at (1612.54) cm^{-1} which is due to the presence of the carbonyl group (C=O), As for the absorption band at (1450.52) cm^{-1}, which is due to the presence of the double bond (C = C), and the tannic acid contains a group (COC), which was noticed to be the absorption band belonging to it at (1207.48) cm^{-1}.

The prepared TA-NH$_2$ spectra shown in Figure (2) appeared the presence of an absorption band at (3414.12)cm^{-1} which attributed to the amine groups formed through the process of introducing amine group to the TA compound, which was not present in TA, and the presence of an absorption band at (1708.99) cm^{-1}, which is due to the presence of the successive carbonyl group, as well as the presence of an absorption band at (1612.54) cm^{-1}, which is due to the presence of the carbonyl group (C=O), while the absorption band at (1450.52) cm^{-1} is due to the presence of the double bond (C=C), and TA contains a group (COC), which is observed to have an absorption band at (1203.62) cm^{-1}. In addition to the presence of bands confined at (1030.02) cm^{-1}due to the frequency of C-N groups, which confirms the occurrence of the process of introducing amine groups to the TA compound.
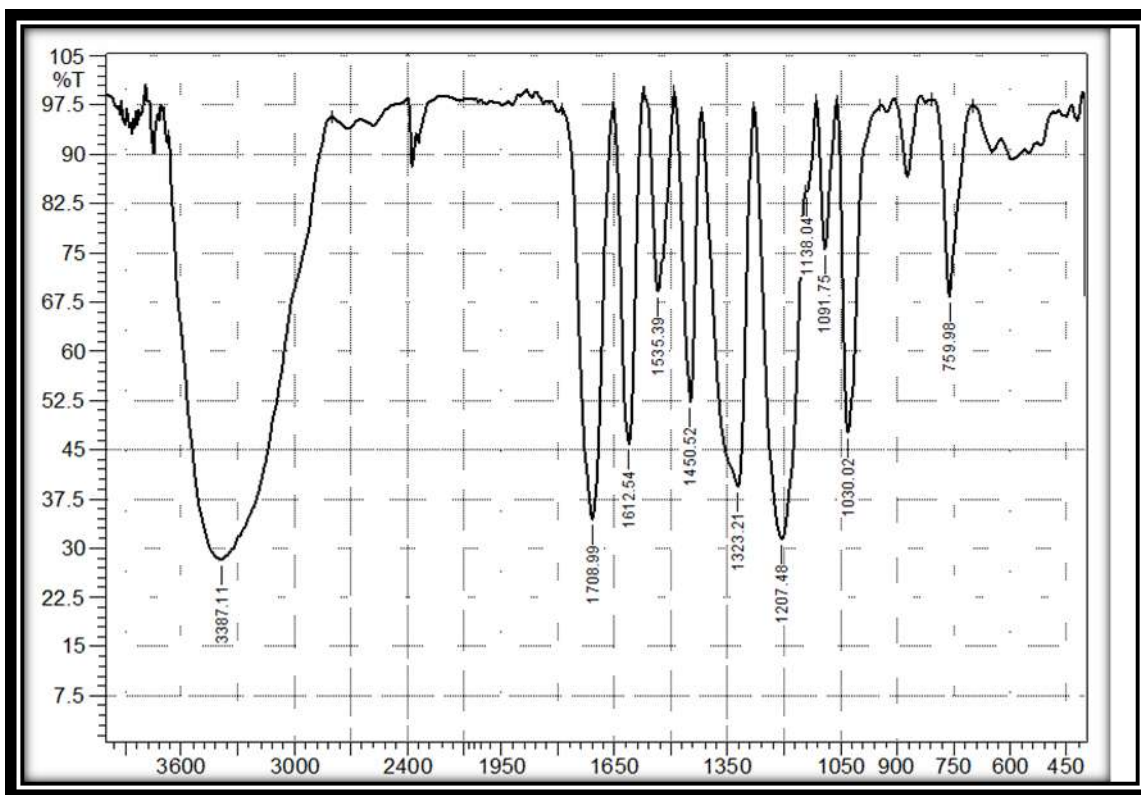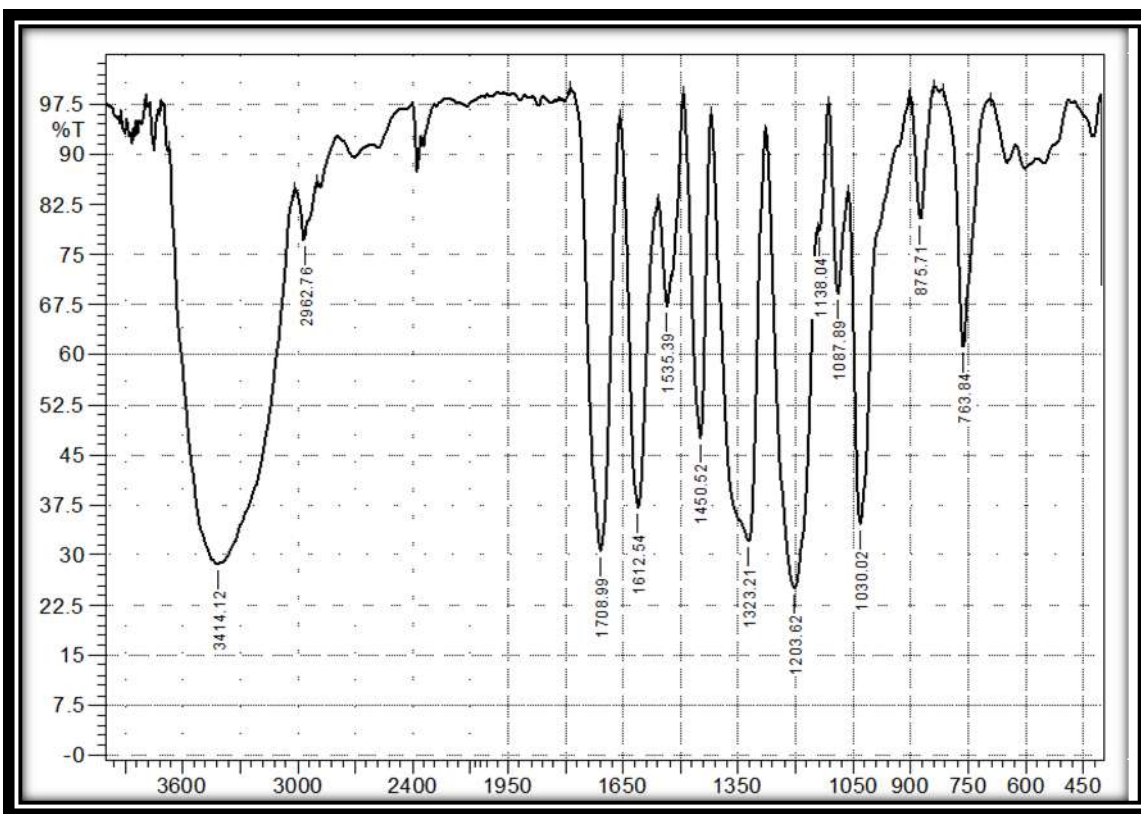
Fig.1:- FTIR of TA.

Fig.2:- FTIR of TA-NH$_2$

FTIR of DE and DE-NH₂

The infrared spectra of the DE compound shown in Figure (3) appeared the presence of absorption bands at (3383.26) cm^{-1} due to the presence of the hydroxyl group (OH), and the presence of absorption bands at (2928.04) cm^{-1} that indicate the presence of a CH group. As for the absorption bands at (1647.26) cm^{-1}, they are due to the presence of the (ROR) group in the DE compound.

The prepared DE-NH₂ spectra shown in Figure (4) appeared the presence of bands at (3448.84) cm^{-1} which was attributed to the amine groups formed through the process of introducing the amine to the DE compound, which were not present in it, in addition to the presence of a band at (1462.09) cm^{-1} refers to the frequency of CN groups which confirms the occurrence of the process of introducing amine groups to the DE compounds.
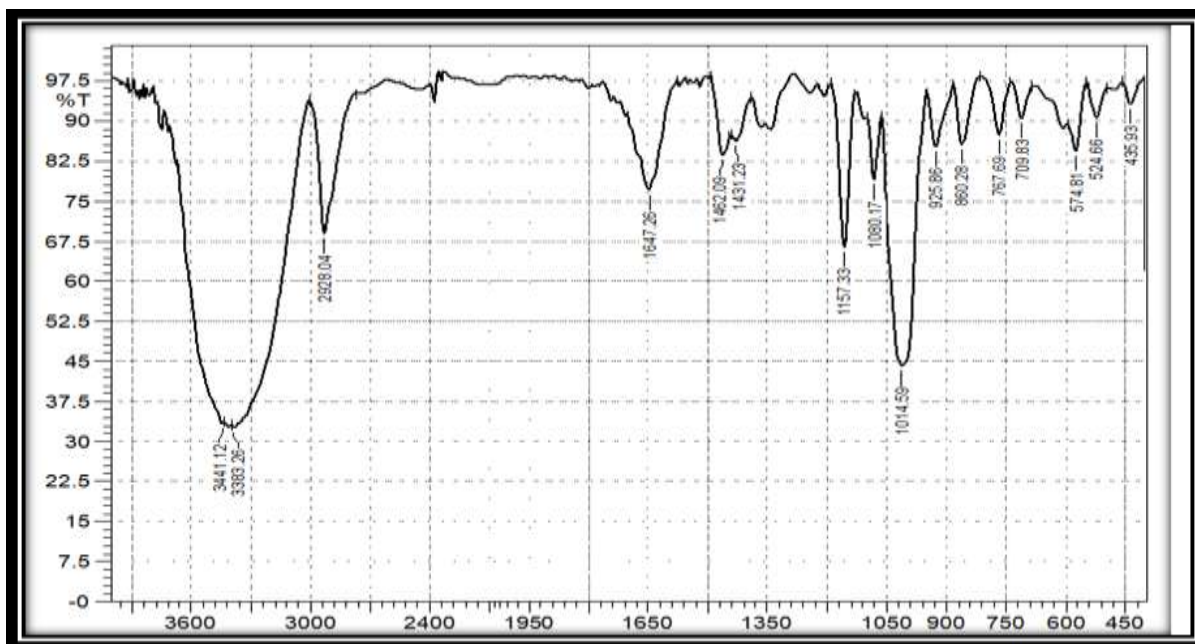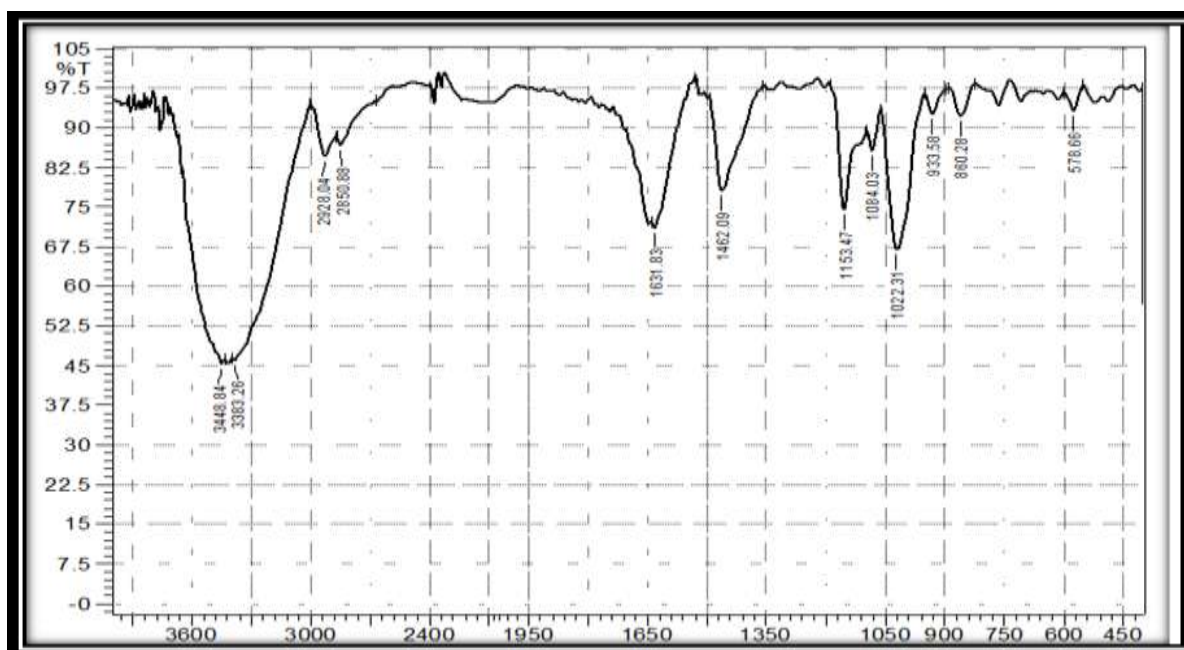

Fig.3:- FTIR of DE.

Fig.4:- FTIR of DE-NH₂

FTIR of TA-DE-AgNPs Composite
Figure (5) show the infrared spectra of TA-DE-AgNPs composites prepared from the reaction of the polymeric complex DE-TA with AgNPs, which showed the presence of a band at 3448.84 cm^{-1}, which was attributed to the vibrational frequency of the amine groups , and two bands at 2924.18 cm^{-1} and 2827.74 cm^{-1} which were attributed to the vibrational frequency of CH groups, and a band at 1454.38 cm^{-1} which was attributed to the vibrational frequency of CN groups, as well as the appearance of a decrease in the intensity of the band at 1080.17 cm^{-1} which is due to to the bending frequency of the CO groups, which is attributed to the stability of the bonding of AgNPs to CO group.
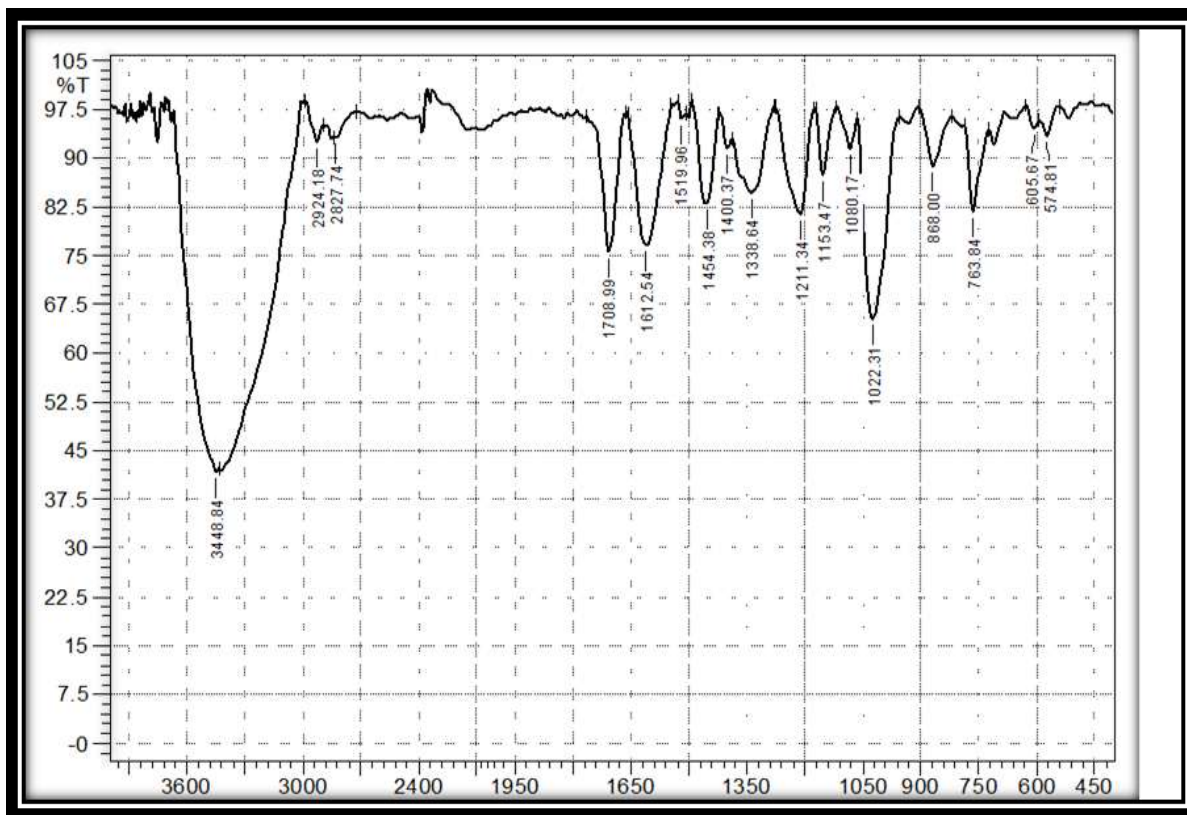

Fig.5:- FTIR of TA-DE-AgNPs.

FESEM of AgNPs
Figure (6) shows that AgNPs were fused into clusters and the reason is that when the reaction mixtures of the AgNPs preparation medium were heated at a temperature of 95 °C for 6 h, most of the nanoparticles tended to aggregate. When AgNPs aggregate, the metal particles become electronically bonded. Moreover, the drying agent of AgNPs could be one of the factors affecting the combination rate of the synthesized AgNPs. According to the FESEM images of the obtained AgNPs, was evident that the morphology of the AgNPs was within an average size of 59.33 nm with diameters ranging from 19.83 nm to 98.84 nm. In addition, AgNPs were mostly spherical and oval in shape. Similarly, the increase in temperature leads to the emergence of spherical and irregularly shaped nanoparticles with a size of 200 nm.
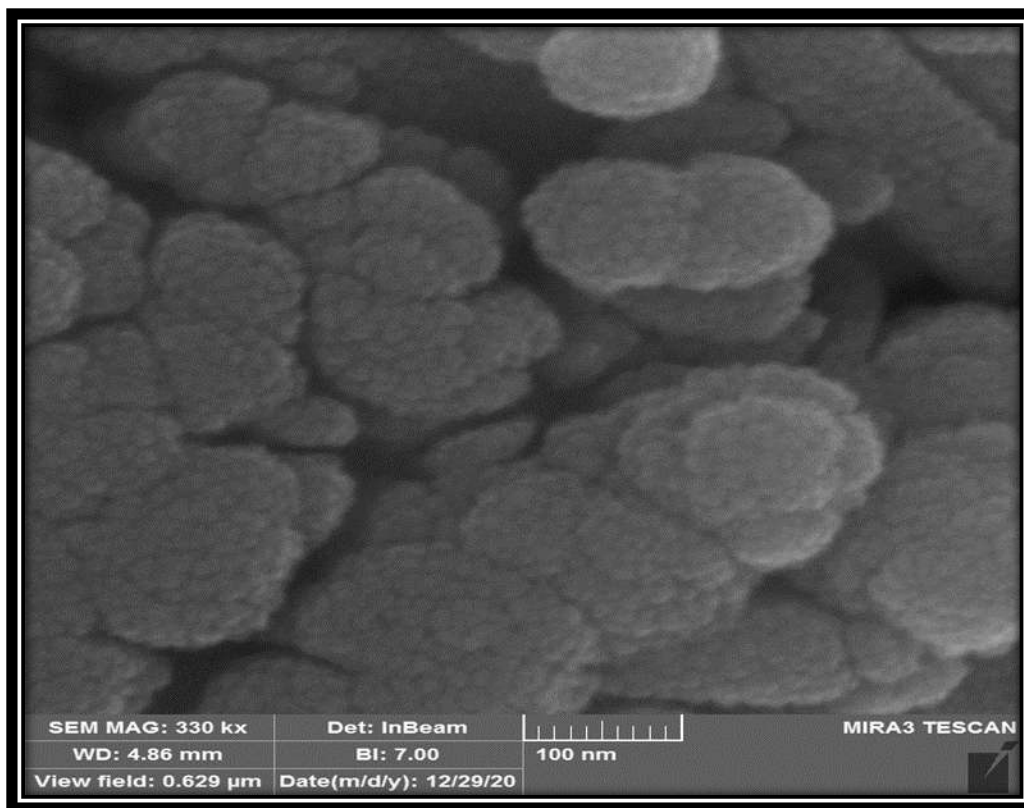
Fig. 6:- FESEM of TA-DE-AgNPs.

Thermogravimetric analysis (TGA)
When comparing the TA and DE compounds (after adding amine groups) (Figures 7-8) with the basic natural polymers [19,20], we notice an increase in the thermal stability of the TA and DE polymers after the modification processes, and this may be due to the presence of amine groups that lead to a kind of chain crosslinking polymer among themselves, which leads to an increase in the polymer's resistance to many factors such as acids, bases and solvents, in addition to its good resistance to high temperatures compared to the primary TA and DE polymers before reacting with epichlorohydrin.

By observing the results of the thermal analysis of the TA-DE-AgNPs composite(Fig.9) , we note an increase in the thermal stability of the prepared TA-DE-AgNPs compositecompared to the primary polymers, where the decomposition temperatures of the compounds ranged in the range of 175 - 640 ^{0} C, while the range of the decomposition temperatures of the primary polymers was in the range of 19-550 ^{0} C and this indicates that the prepared polymeric composites in the presence of AgNPs are more thermally stable than they were before.On the other hand, we note that the presence of AgNPs within the composition of polymeric TA-DE significantly increases their resistance to temperature increase.AgNPs can add many desirable properties for the prepared polymeric composites and can be used in many important applications.

The thermal decomposition processes of the prepared polymers are known in many previous literatures [21-22], where the temperature ranges between 50-150 ^{0} C can be attributed to the loss of moisture and water molecules that may be present within the composition of the TA an DE, especially as they contain many hydroxyl groups are easily able to hydrogen bond with water molecules. After this degree (150 ^{0} C), the dissociation curves can be attributed to the loss of many organic molecules from the prepared polymer structures in the form of gases such as carbon dioxide, carbon monoxide and some alcohols. To the loss of larger molecules of alcohols, phenols and organic acids until the process of dissociation is complete.Table (1) shows the functions that were calculated for of the prepared compounds.
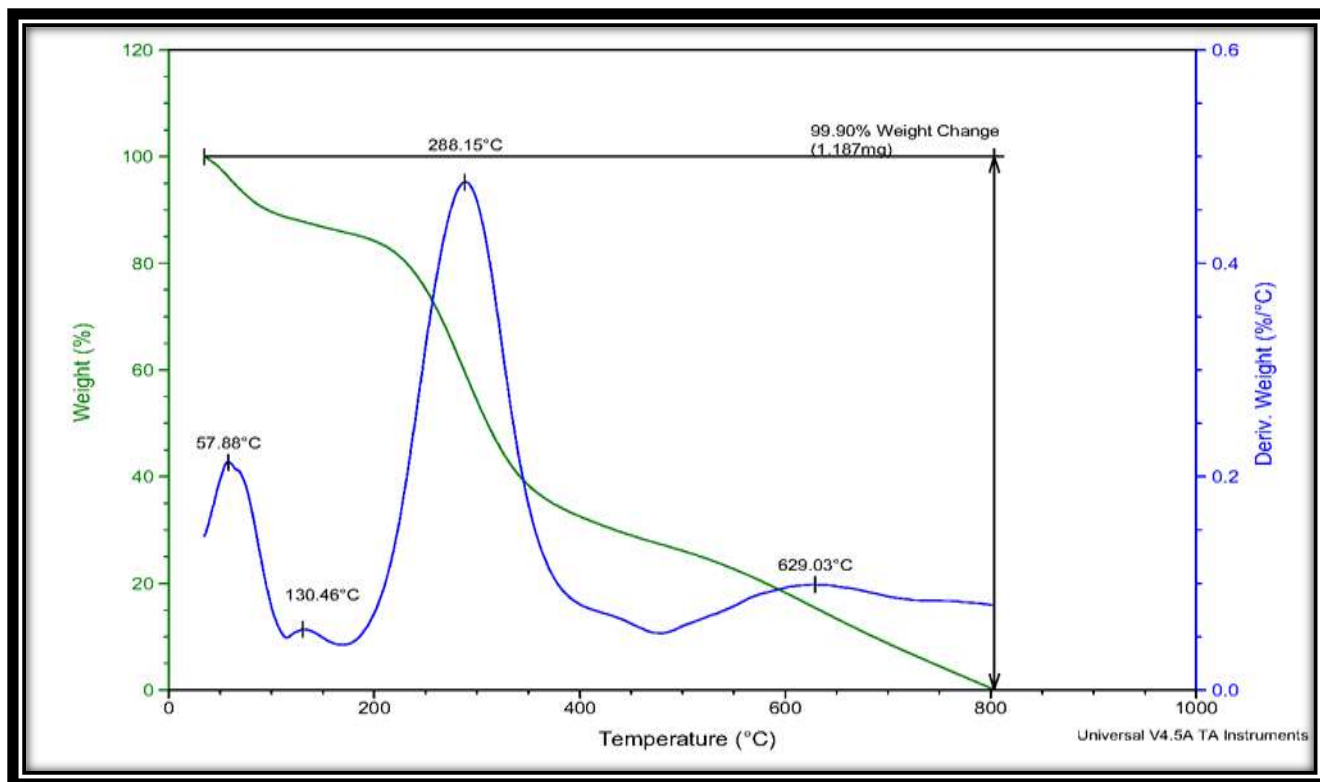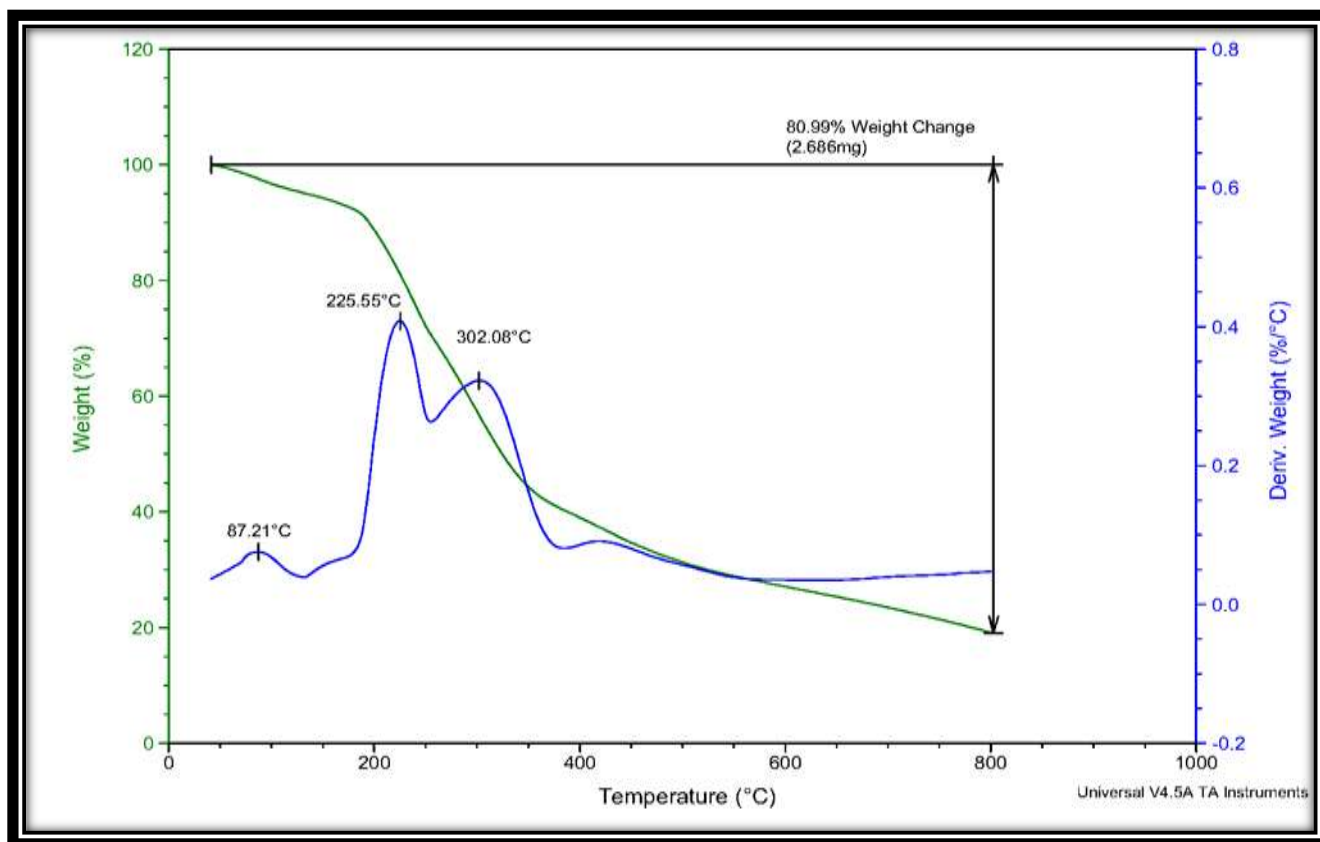
Fig. 7:- TGA of TA-NH$_2$.
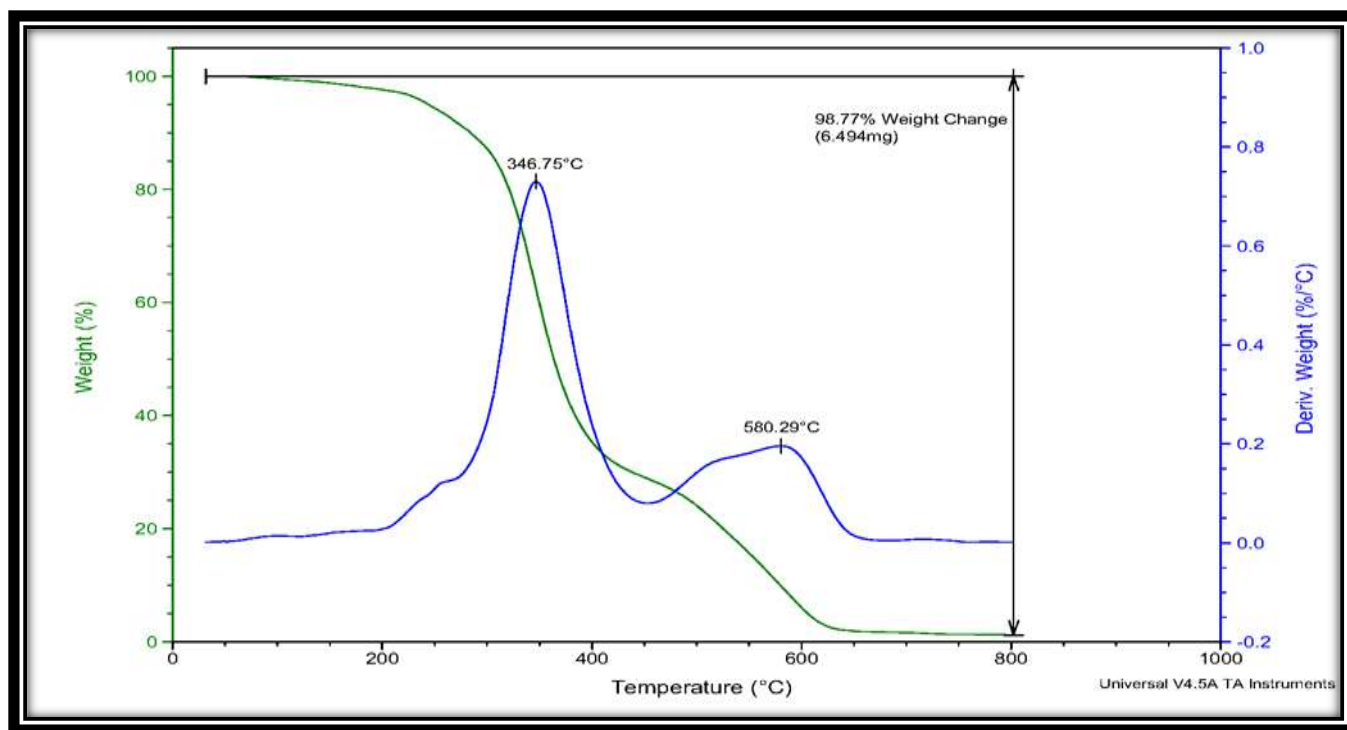

Fig. 8:- TGA of DE-NH$_2$

Fig. 9:-TGA of TA-DE-AgNPs.

Table 1:- Some of the values obtained from the gravimetric thermal analysis curves of prepared polymers.

Polymer Code	Decomp stage	T_i (ºC)	T_f (ºC)	Top (ºC)	Rate of Decomp. %/min	Ea Kcal.mol⁻¹	T. (ºC) Range for Ea	Weight Loss %	T 50% weight loss-ºC	% Char Residue 800º
DE-TA-AgNP	**1ST**	215	375	327	0.323	9.3	265-290	41	471	**20**
	2$^{end.}$	430	600	537	-	-	-	80		
TA-NH$_2$	**1ST**	19	165	57.8	-	-	-	15	340	**0.1**
	2$^{end.}$	190	390	288	0.313	2.7	215-245	99.99		
DE-NH$_2$	**1ST**	170	505	275	0.28	1.2	200-225	80.99	370	**19.1**

Mechanical properties
Compressive Strength
Compressive force is defined as the force applied to the unit area, and it is one of the important mechanical properties in the manufacture of polymeric needs. It differs from the tensile strength in terms of the type of model prepared for examination in shape and dimensions, as it differs in terms of the type of force applied to the model. The compressive strength of TA and DE compounds and TA-DE-AgNPs that were prepared from them was studied. It was noted through the results shown in Table (2) that the value of compressive strength of epoxy resin alone is 9.618 MPa, while these values decrease using the following polymers when added to epoxy resin where the sequence was as follows:

Epoxy resin >TA-DE-AgNPs> DE > TA

This can be attributed to the high crystallinity of epoxy resin, while DE, TA and TA-DE-AgNPscompounds in branching reduce the compressive strength.

Table 2:- Compressive Strength(MPa)of TA, DE and TA-DE-AgNPs.

Compounds	Compressive Strength (MPa)
Epoxy resin	9.618
DE	6.588
TA	5.754
DE-TA-AgNPs	8.165

Impact Strength

The impact resistance tests are a measure of the strength of the material and its resistance to breaking under the influence of stress at high speeds, and it is defined as the ability of materials to resist fracture under high shocks or the ability to resist crushing under stress at high speeds. The strength of the impact is directly related to the durability of polymeric materials, which means the ability of the polymer to absorb the energy spent on it. To measure the collision force, some of them are based on pendulum collisions such as (Charpy), (Izod) and (Chip) collisions, including those based on stress and elongation curves at high speed, and others based on the force caused by objects that are dropped on the models under examination.

The impact strength of the compounds prepared in this study was examined using the (Charpy) method, which is characterized by the use of models with a notch in the form of a letter (V), the sample is fixed on one side and the shock position is on the other free end, and therefore the most important factors affecting the impact strength . In this way, the notch radius is the lower radius of the stress focusing, the lower this impact force, in addition to being affected by other factors such as molecular weight, diffusion, crystallization, orientation of chains, and others [23]. The collision resistance was calculated from the following equation:

$$Impact\ Strength = \frac{Average\ load\ break}{Width\ of\ specimen}$$

In general, the impact strength depends on the degree of glass transition (Tg) of the polymers and that any factor that increases Tg decreases the impact strength, so crystallized polymers have a high impact strength when the degree of use is higher than the degree of glass transition to them.

Table (3) shows the impact strength of the TA-DE-AgNPs composite prepared in the present study, which were all done under the same conditions in terms of temperature and size of the models in addition to their curing conditions. The cured epoxy resin, as the value of the impact strength was 0.02 J/mm^2, while the values   of the impact strength of TA-DE-AgNPscomposite was the highest value (0.094 J/mm^2)of the impact strength of the epoxy resin alone, and this depends on the nature of TA-DE-AgNPs composite material in terms of the degree of crosslinking . This can be explained by the strength of the entanglement that occurs during the interaction within the mixture of the compound material and for all models.

Table 3:- Impact Strength(J/mm^2)of TA-DE-AgNPscomposite and epoxy resin.

Compounds	Impact Strength(J/mm^2)
DE-TA-AgNPs	0.094
Epoxy resin	0.020

Hardness Test

The hardness is one of the important mechanical properties for studying the surface of the material. It is defined as the resistance of the surface of the material to stitches or scratching, or it is the material's resistance to local plastic deformations. The hardness of materials depends on the type of bonding forces between molecules and on temperature. There is more than one method for measuring hardness, including Shore hardness, Meyer hardness, and Rockwell hardness. It is considered one of the easy tests because it does not require complicated and expensive equipment, in addition to that it is considered a non-destructive test.

The results shown in Table (4) using Shore method to examine the hardness indicate that the hardness values of TA-DE-AgNPs(115 Shore) are higher than the hardness value of epoxy resin alone, which was the hardness value of (92.6 Shore), and this means that the presence of natural polymeric materials within the polymeric network increases the strength of the chemical bonding between the aggregates and thus makes the surface more resistant. This can be explained depending on the structure of the polymer in addition to the possibility of not smoothing the surface of the

model during the preparation process, knowing that these results are the sum of five readings taken from different areas of the modelsurface .

Table 4:- Hardness (Shore)of TA-DE-AgNPs composite and epoxy resin.

Compounds	Hardness (Shore)
DE-TA-AgNPs	115
Epoxy resin	92.6

Swelling Degree (%W)

The process of water absorption for all types of polymers and compound materials when exposed to surrounding moisture or when immersed in water or solutions follows the first law of diffusion (the mass of water and the absorbed solution increases linearly with the square root of time gradually and slowly until reaching the saturation state). In the current study, the percentage of water absorption was calculated according to ASTM D570 standard specifications, using the equation:

$$EDS \ (\%) = \frac{W_s - W_d}{W_d} \times 100$$

Wd: Weight of the dried sample(g)

Ws: Weight of the sample after immersion in water(g)

Table (5) shows the results obtained for the swelling degree (%W) of the TA-DE-AgNPs composite which found to be (22%), which indicate that it is much higher than the swelling degree value of the epoxy resin (1.2%), and this is due to the presence of natural polymers in the TA-DE-AgNPs composite, most of which contain many hydroxyl groups, which qualify them to form hydrogen bonds with water, which leads to an increase in their absorbency.

Table 5:- Swelling Degree (%W) of TA-DE-AgNPs composite and epoxy resin.

Compounds	Swelling Degree (%W)
DE-TA-AgNPs	22
Epoxy resin	1.2

Conclusions:-

We successfully produced nanocomposite using naturally derived polymer materials TA and DE to reduce the environmental harm caused by synthetic polymers.The synthesis of silver nanoparticles using a sodium citrate as a reducing agent with concentrations of 0.01 mole, produces a complex form of AgNPs. Characterization using FESEM, showed that AgNPs added to a 0.01 mole $C_6H_5O_7Na_3$ produced the smallest average particle size of 59.33 nm, also showed that AgNPs produced particles with regular spheres, a smooth structure, and were relatively nonporous. FTIR studies of TA-DE-AgNPs composite revealed the possible interactions between the AgNPs and matrix.

It is worthy to notice that, TA-DE containing AgNPs led to simultaneous improvement in the mechanical properties and thermal stability of nanocomposite formed. This allows processing without degradation of polymer.

Acknowledgments:-

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