Syntheses and Characterization of Cephalexin-Chitosan/Natural Rubber network polymer for Slow-Release Fertilizer.

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ABSTRACT:

The increase in the world's population has forced the agricultural sector to increase the production of crops to meet food needs. The spread of nutrient deficiencies in the soil led to economic losses, a reduction in nutritional quality, and total grain quantity for humans and livestock. Coating fertilizers with polymers is one of the most important and effective aspects of slow-release fertilizers in the soil. aim this study, the reaction between chitosan and expired cephalexin as a grafted polymer was done and vulcanized with natural rubber in the presence of tetra methyl thiuram disulfide as catalyst to cover the urea fertilizer. The grafted polymer (chitosan/expired cephalexin compound) was prepared by the Schiff base method. The expired medicinal compound of cephalexin is rich in carbon, nitrogen, sulfur, and hydrogen atoms which improved the diffusion of the fertilizer .So the reaction of the validity of the reaction between chitosan and expired Cephalexin was confirmed by infrared (IR) and it was confirmed the presence of new absorption band due to the Azomethine group. The swelling, water retention, slow release of urea, and biodegradation of the NR/chitosan/expired cephalexin compounds were characterized. The rheometer test was carried out under the pressure of 250 bar and temperature of 170°C, The results showed that the Slow release of urea was increased with the increase in the concentration of cephalexin. The highest release percentage in soil media was 2.67 g/l for the C2 blend. The highest swelling ratio was 189.49 % for the C4 blend while the highest water retention was 75.67% for the C2 blend. It was also shown a good biodegradability, where the highest concentration of cephalexin with chitosan gave the highest rate of biodegradation to be 14.61% for C4. The homogeneity of the blends was studied by FE-SEM. It was concluded that the C1-C4 blends were the best for slow-release fertilizer application.

Keywords: Chitosan; Natural Rubber; Slow Release Fertilizer; cephalexin; Urea.

Introduction:- The global production of crops is under threat due to climate changes, and for this we face their challenge in providing the global population with sufficient food, which is constantly increasing, that the accumulation of gases in the environment at an increasing rate will increase the Earth’s temperature by about (2.5-4.3)C$_{\circ}$ approximately by the year 2080 in regions Agriculture in the world, the increase in temperature and the lack of water resources, in addition to desertification and harsh weather conditions, have a significant impact on crop production and lead to food shortages[1]. The continued use of these chemicals causes many losses as it consumes about 2.5 million tons of pesticides annually [2,3]. These chemicals increase pest resistance when used, and thus increase environmental pollution, reduce food quality and affect non-target organisms in the long run [4]. It is estimated that more than 90% of these chemicals are lost to water and air during their application, thus severely detrimental to the sustainability of agriculture and increase the cost to farmers [5], hence the need for an increased focus on environmentally friendly technologies and evaluation of alternatives used to get rid of waste Pollution and reduce dependence on harmful chemicals .

The tremendous progress in technological research in Nano science has led to interest in agricultural and food sciences through engineering and converging sciences. Nanomaterials have advanced these applications to solve the problems of controlled and controlled release of coated fertilizers, pesticides and micronutrients, and knowledge and detection of plant diseases and their causes [6].

The application of Nano materials helps in plant growth and protection, thus developing effective approaches to increase crop growth and ensure the control of pathogens. The application of Nano materials is related to changing plant gene expression and biological pathways affecting plant growth and development [7].

Nano materials contain many compositions, such as silicates, metal oxides, ceramics, polymers and magnetic materials, liposomes, emulsions, the use of each type depends on the formation of nanoparticles, for example, polymers of encapsulated nanoparticles are used for agricultural Chemicals as a carrier because of their control and ability to slow control, Metal-based nanoparticles exhibit size-dependent properties [6].

popular in the Recently, smart Nano-based delivery systems are becoming more and more agricultural field. Biodegradable nanoparticles have gained interest in delivering site-specific compounds to a number of biologically active compounds, such as plant growth regulators, micronutrients and vitamins.[8]There are many biomaterials that are environmentally friendly, such as lipids, proteins and polysaccharides, as transport for the controlled delivery of chitosan-based Nano materials, for example, Nano composites, nanoparticles, and Nano materials, which have received great interest in agriculture as antimicrobials, enhancing immunity, enhancing plant growth and controlling properties in agriculture. [9], so the choice of coating materials depends on several factors such as type of coating materials, size, biocompatibility, and surface properties.

2. Materials and methods:-

2.1. Materials

Chitosan with M.WT. of 400,000 g/mole, Viscosity of 200 mPa, was supplied by MACIAN company, China. Acetic acid, ethanol, and dichloromethane were supplied by Sigma-Aldrich. Natural Rubber (NR) was supplied by Standard Malaysian Rubber, Malaysia, while the cephalexin drug was supplied by Co-Amoxiclav, India. Tetra methyl thiuram disulfide (TMTD) and zinc oxide (ZnO) and Stearic acid were supplied by Al-Kiiubar Company, Saudi Arabia, ChemTAL SDN-BHD, Malaysia, and Acidchem-International CO Malaysia, respectively. Urea was supplied by Shiraz Chemicals Company, Iran.

2.2. Methods:- preparation of cephalexin /Chitosan grafting Using Schiff Base Method The reaction of cephalexin and chitosan was performed by the Schiff base method [10, 11]. The blends was prepared by the reaction of cephalexin /chitosan with NR was They were synthesized by the reaction in ratios of weight (1:1), as shown in Table 1. Separately, each ratio was dissolved in 15 ml of absolute ethanol. The mixture was infused in a microwave oven for 6 minutes and 350 W, then cooled to room temperature. Absolute ethanol is used to recrystallize the products.

Table 1: Cephalexin /chitosan for the reaction of Schiff bases as the weight ratio

Chitosan (CH)	**100**
Cephalexin (CE)	100

2.2.2- Preparation of the graft chitosan / natural rubber blends. At various concentrations of 25, 50, 100, and 150 phr of the 103 gross weight of NR, as shown in Table 2. A specific amount of (NR) was mastication through two roll mills (Comerio Ercole Busto Arsizo mill, Italy) for softening of NR. Then, the graft chitosan, zinc oxide (ZnO), and stearic acid were added to NR. After getting good mixing, the accelerator (TMTD) was added to the blends. when a homogeneous mixture was obtained, the sample was ready to be used in the vulcanization process. Where the mixture was entered into the mold preheated to a vulcanization temperature of 170 ° C. The homogeneous mixture was introduced in mold cavities for 15 min., then the mold was quickly closed to avoid mold cooling. The sample was compressed by the hydraulic heat press under the temperature of 170oC and the pressure of 3.5 MP for 15 min. [12].

Table 2: Formulation of blends in wt %.

Materials	C_0	C1	C2	C3	C4
NR	100	100	100	100	100
NCH-Ce	0	25	50	100	150
ZnO [a]	3	3	3	3	3
Stearic Acid [a]	2	2	2	2	2
TMTD [a]	3	3	3	3	3

a in phr (parts per hundred rubber) from total of graft Nano Chitosan / NR blend

2.2.3-Preparation of encapsulated urea fertilizer with blends. The urea fertilizer granules are coated with different coating materials such as C0, C1-C4 blends. It was dissolved 4.5 g from each blend in 30ml dichloromethane for one day to ensure that the blend is completely dissolved. A 15 g of urea fertilizer was well mixed for each type of the previous blend. Then, the coating capsules were left to dry at room temperature for 24 hours. After, drying samples were cured at 140 C for 30 minutes [13]

Results and Discussion:

3-characterization of blends:-

3.1- Fourier transform infrared (FTIR) spectroscopy :- In Chitosan, we note the presence of Used band instead of peak in the FTIR study of the primary amine group at approximately 3352 cm^{-1} , and the aromatic CH at 2886-2977 cm-1 while OH groups appeared at 2500-3652 cm^{-1} [14], as shown in Figure1. The chemical structure of Cephalexin has several important peaks, for example, the primary amine group approximately appeared at 3443 cm^{-1} . Aromatic C-H stretching appear over 3000 cm^{-1} and the Carbonyl group was shown at 1769 cm^{-1}. The amide carbonyl appears at 1577 cm^{-1} , while the peak of 1682 cm^{-1} returns to the group C = C. The OH group appeared at (3653- 3778) cm^{-1} belongs to the acid and alcohol groups [15] as shown in Figure 1. In blends . It was noted a shift in the tops of some groups and the appearance of the Azomethine group at 1561-1582 cm^{-1} broad and combined with the amide carbonyl and the displacement of the amide group to 1516 cm^{-1} with slight changes in the tops of other groups, for example, the primary amine group appeared at (3150) cm^{-1} [16]. as shown below: -

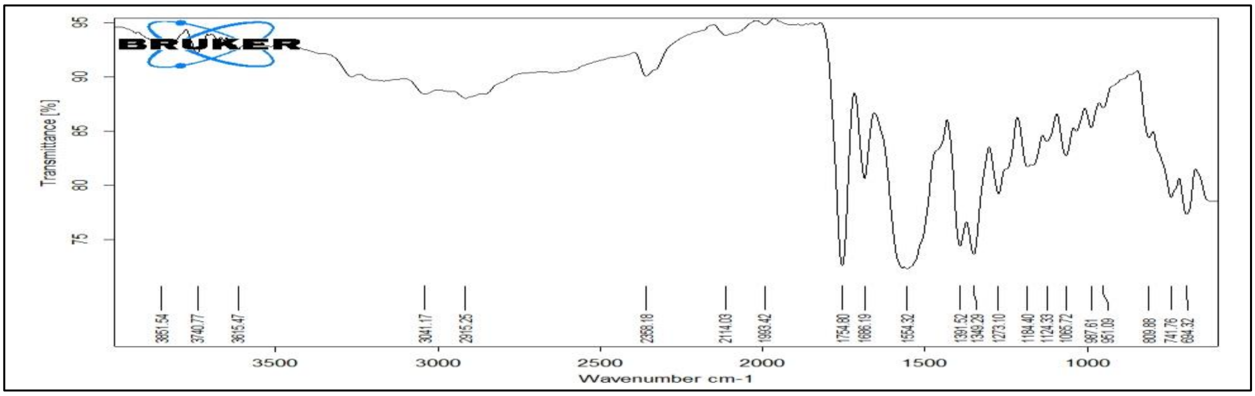


Figure 1. a. FTIR of Cephalexin 0.1(CE)

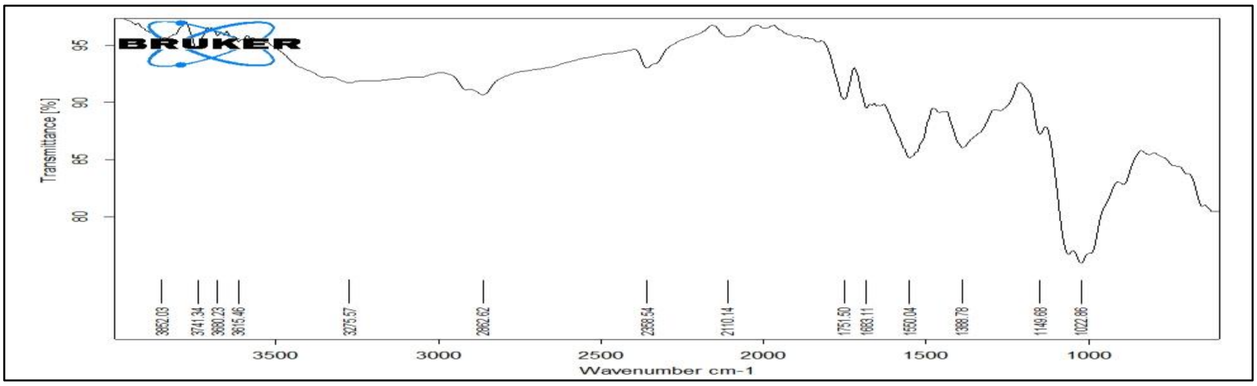


Figure 1. b. FTIR of Cephalexin 0.5 (CE)

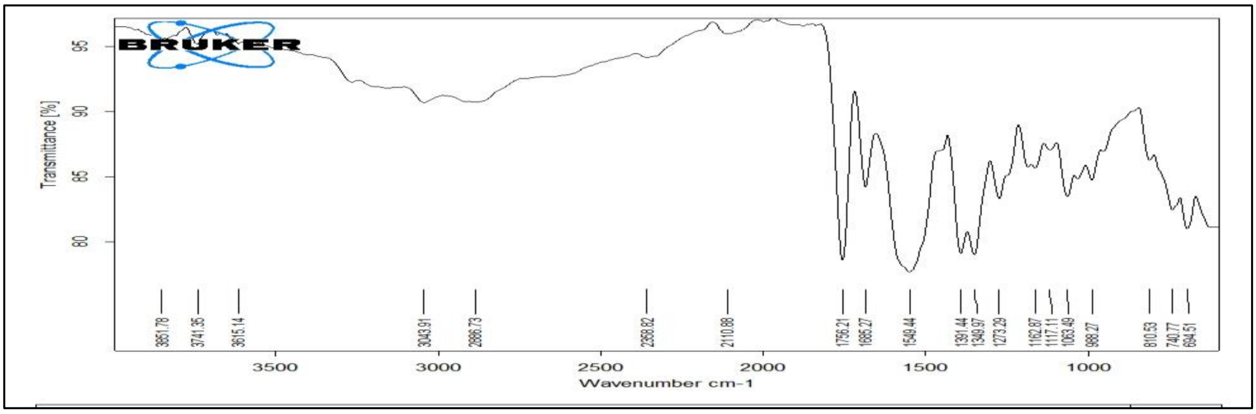
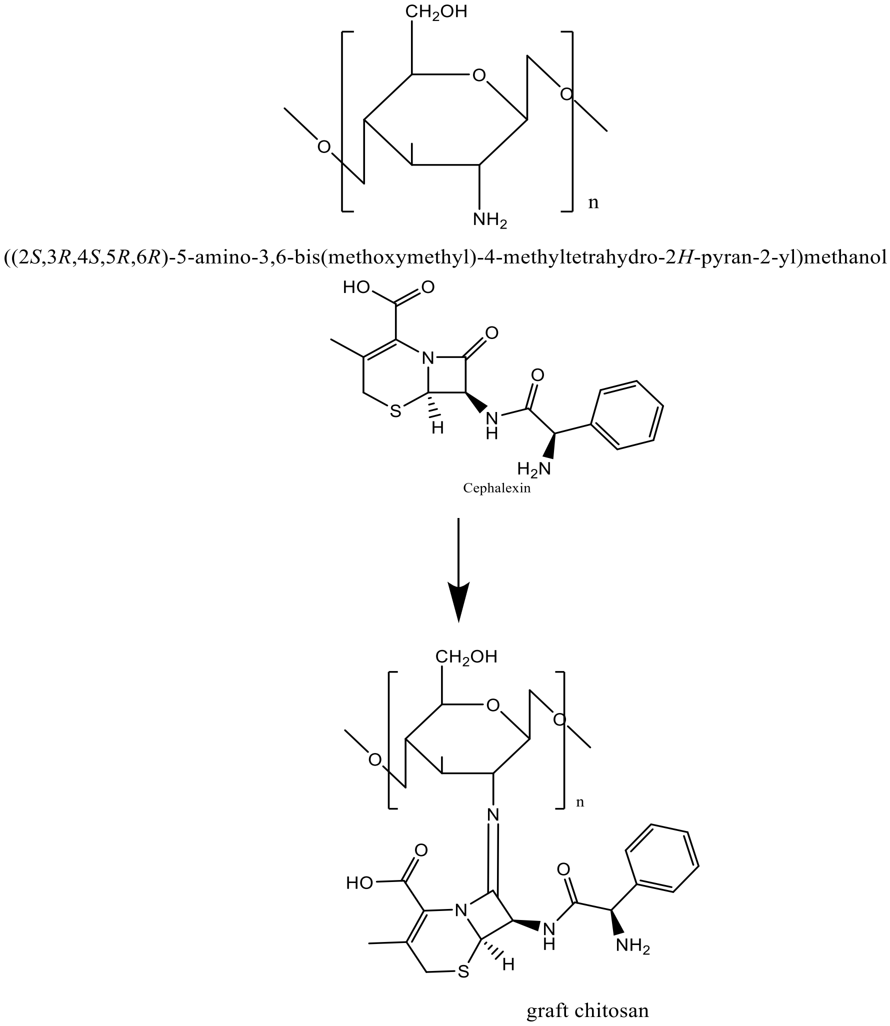


Figure 1. c. FTIR of Cephalexin 1 (CE)

Scheme 1: Linking the compounds of the chitosan and recycled amoxicillin using Schiff bases:-



3.2. ^{13}C-NMR of compounds:-

The C^{13}-NMR spectra showed the appearance of the signals between δ 157.29-162.56 of (-CH=N-) and signals between δ 14-29 of (CH2) group from ring of chitosan compound . These signals are another good evidence to the formation of Schiff bases.

Table 3. C^{13}-NMR Chemicals shift of Compounds(Ce, Ce-CH)

Comp. Symbols	Name of compound	C^{13}-NMR
Ce	Cephalexin	128.31-139.39(C)$_{\text{Phenyl ring}}$,58.86(C)-NH2, 166.9 -165.65 C,C=O $_{\text{amide}}$ and C,C=O $_{\text{acid}}$, 166.52 C,C=O $_{\text{amide}}$, 20.74-29.51 C,CH3.
Ce-CH	Cephalexin -Chitosan	128.31-139.39(C)$_{\text{Phenyl ring}}$,58.86(C)-NH2, 168.5 -166.92 C,C=O $_{\text{amide}}$ and C,C=O $_{\text{acid}}$, 167.75 C,C=O $_{\text{amide}}$, 18.05-33.45 C,CH3, 165.66 C, $_{\text{azomethine}}$.

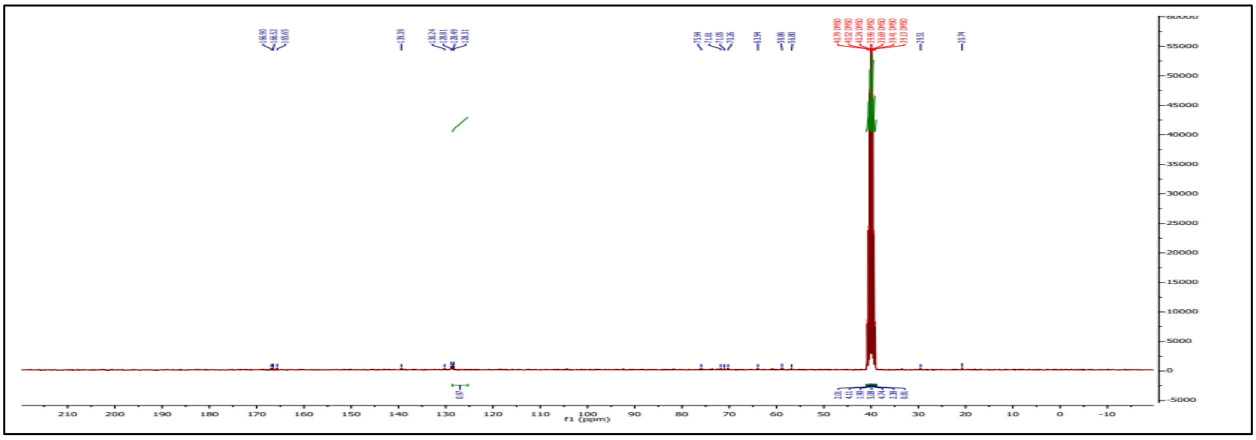


Fig. 1.d . ^{13}C-NMR of Ce

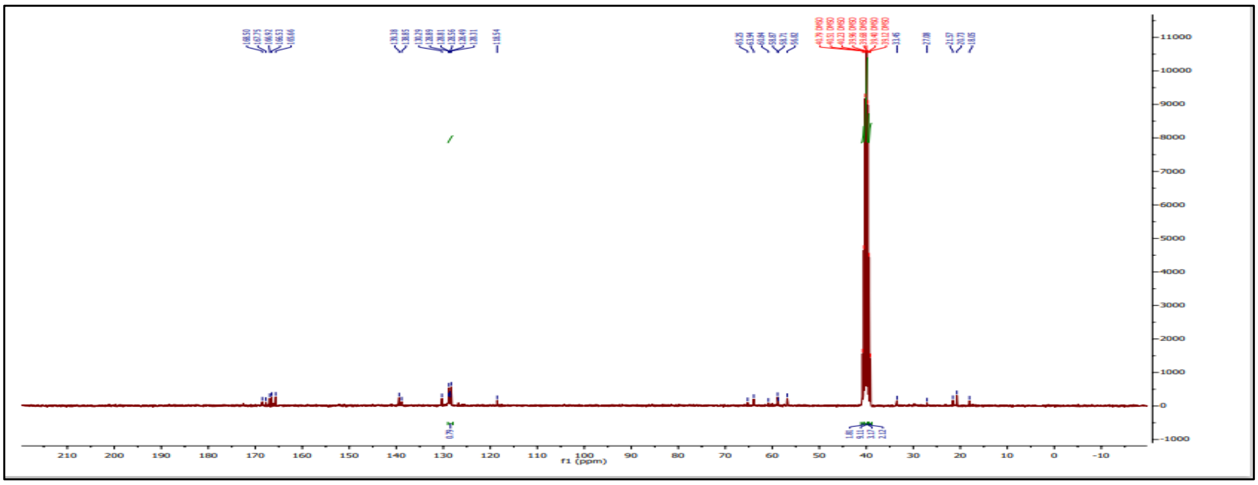


fig. 1.e. ^{13}C-NMR of Ce-CH(1:1)

3.3-Surface Morphology Studies :- To study the morphology of the synthesis, FE-SEM was used. Fig. 2.a, Fig.2.b, show FE-SEM images of the fractured surface for C0, C1- C4, respectively, at a magnification of 5.00 KX. FE-SEM show that there is a uniform dispersion of the C1-C4 component on the surface of the NR and indicates the homogeneous morphology of the blends. Increasing the loading of Cephalexin gave the possibility of adhesion between the rubber and the grafted polymer, as shown by the images of the FE- SEM,

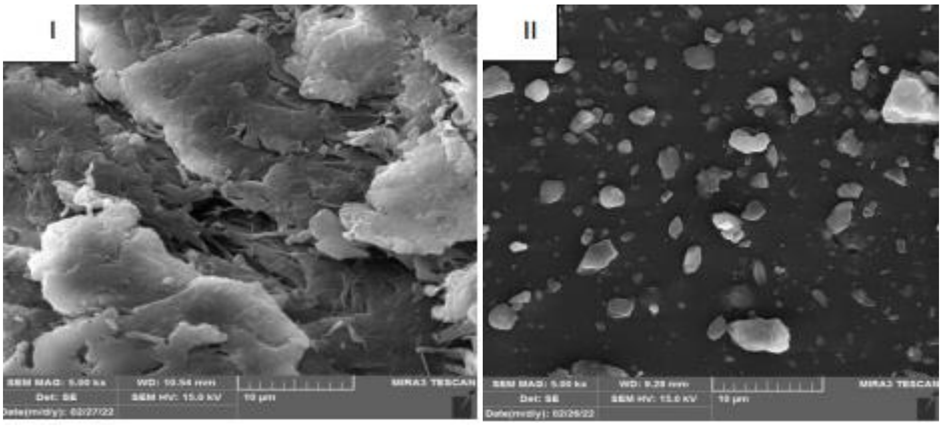


Fig. 2.a FE-SEM of fracture tensile strength for I) chitosan, II) A0 blend.

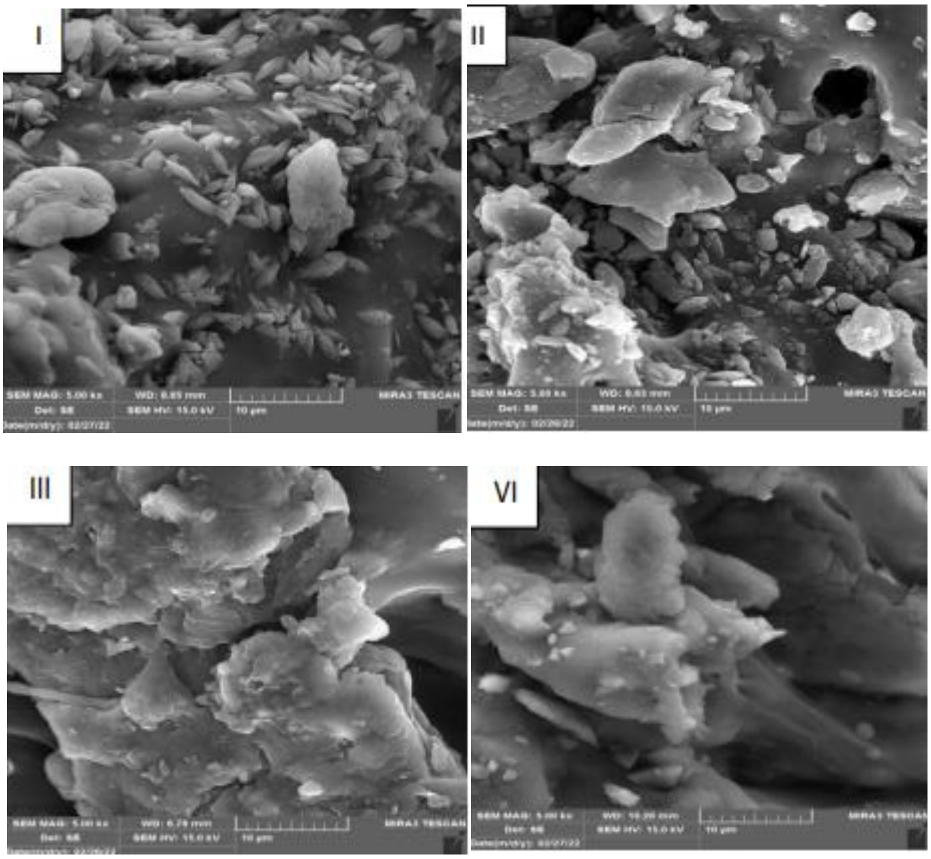


Fig. 2.b. FE-SEM of fracture tensile strength for I) C1 blend, II) C2 blend, III) C3 blend VI) C4 blends.

3.4: Swelling Test

the C1-C4 blends exhibited the highest swelling ratio it reached 190%, as shown in Figure 3.The reason may be I II III VI that the addition of Cephalexin molecular to the blends with amino, carboxyl and hydroxyl groups at a high concentration of blends having a higher swelling ratio, due to the increase in the number of hydrophilic aggregates, the higher the amount of the drug added [17]. It was concluded that the addition of Cephalexin molecular to Chitosan improves the swelling ratio and creates superabsorbent hydrogels.

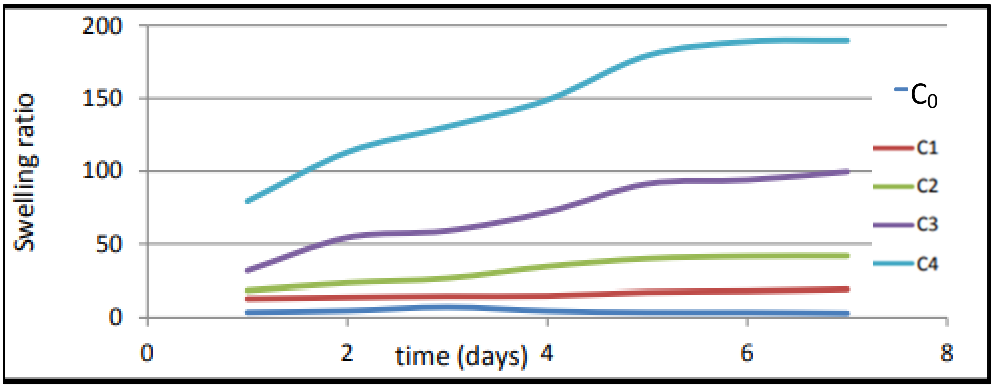


Figure 3. Swelling ratio of blends.

3.5. Rheological Properties of graft polymer/NR blends:-

Table 3 shows the curing rate index (CRI), maximum torque (MH), Minimum torque (ML), cure time, in minutes (t90), and scorch time, in minutes (ts2) of C0, C1-C4 blends.

Table 4 shows that the decrease in the cure time could be due to the increase in the weight of the graft polymers, which acted as an additional accelerator to interact with the existing accelerator (TMTD) and thus was responsible for shortening the curing time. The maximum torque (MH) and curing rate index increased significantly with the increase of grafted polymer content, the two catalysts (graft polymer and TMTD) are involved in the processing of graft polymer/NR. Which leads to an increase in the cross-correlation compared to the control sample (C_0). This proves that the graft polymer participates in the treatment process. The CRI was increased compared to the control sample (C_0) based on the increase in the concentration of the graft polymer and its weight in the mixer as an activator in vulcanization in the presence of stearic citric acid and zinc oxide [18].

Tablet 4 curing parameter of graft polymer /NR blends

Sample code	MH(Ib.in)	ML(Ib.in)	T90 (min)	TS2 (min)	CRI(min)
C1	7.51	1.07	1.26	0.84	238
C2	5.74	1.36	0.98	0.71	370.37
C3	10.71	1.59	0.74	0.48	384.6
C4	4.10	1.09	1.95	1.94	10000

3.6: Water retention test:- One of the best properties of slow-release fertilizers, is good water retention capacity, especially in dry and desert areas, to accelerate plant growth. Figure 4 shows water retention behaviors in soil using blends of C1-C4, as compared with a control sample (C_0) to 30 days. was clear that the addition of Cephalexin to the concentrations of samples in the soil was reduced water evaporation and was increased water retention as compared to the control sample. Water retention of the control sample (C_0) was 77.58 and 60.1% by weight on the fifteenth and thirty days, respectively, while the water retention of blends, A2 blend gave the highest percentage of water retention as it reached 81.89 and 63.18 wt% at the fifteenth and thirty days, as shown in Fig. 4, [19,20]. Thus, all hydrogels show a high water-retention capacity in the soil, and thus, water can be saved and managed. It can be concluded that all the hydrogels synthesized in this study can be used for agricultural applications.

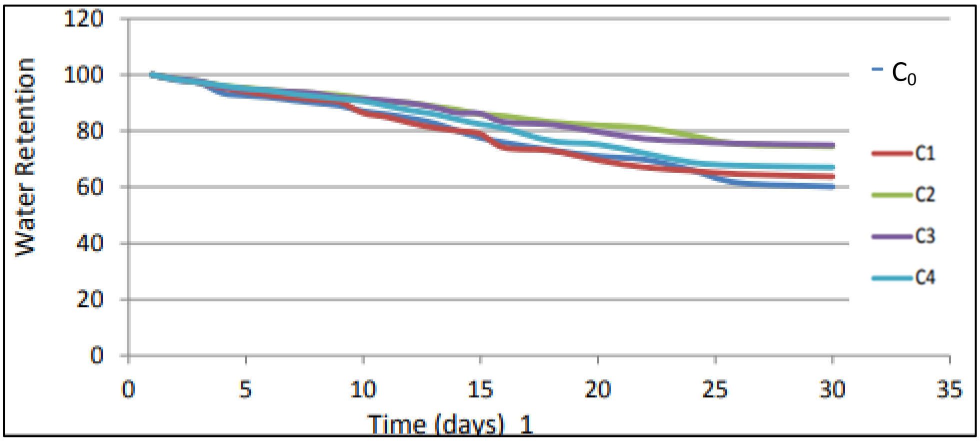
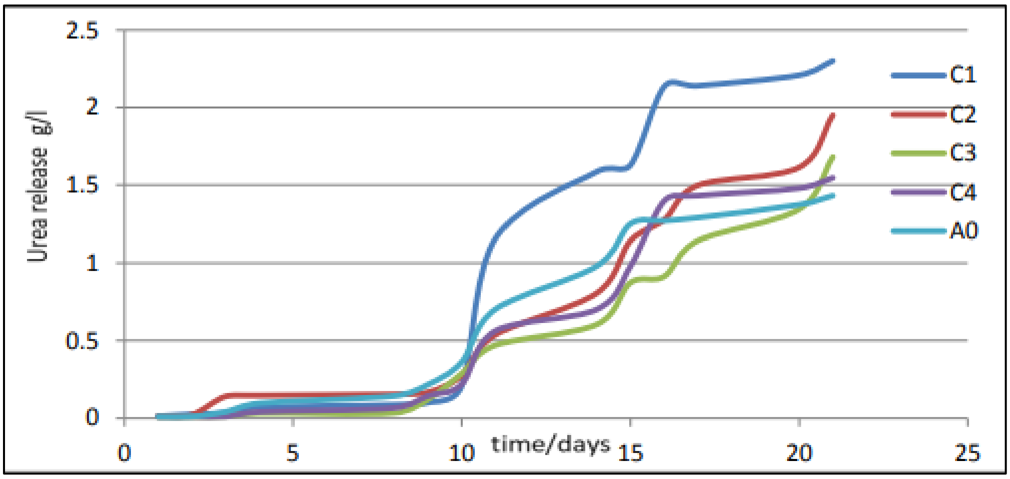


Figure 4. Water retention of blends in soil.

3.6: Urea Release Test:-

The dissolution rate of urea fertilizers (UR) in soil which were coated with the C1-C4 blends was illustrated in Fig. 5. The results show that an initial release was slowed behavior and the release was increased after 9 days. The reason was the control urea releases fertilizer(CURF) hydrogels swell with the soil solution as the soluble part of compost dissolves, and nutrients slowly diffuse through the CURF hydrogel structure and release into the soil. With increasing time, urea release was decreased at 20 days to 1.43, 2.47, 2.40, 2.33, and 2.28 g/l for C0, C1, C2, C3, and C4, respectively.



Figures 5. Urea release of blends in soil.

3.7: Biodegradation Test :- The biodegradation of A0, A1-4, B1-4 and C1-4 blends in the soil as in Fig.6. shows that biodegradation of the C0 and C1-C4 blends increases significantly with the increase of the Cephalexin contents, and it is clearly observed that the C4 blend has the highest weight loss among the other blends. This behavior is due to the large decomposition of fungi and bacteria in the soil activated by heat and moisture.

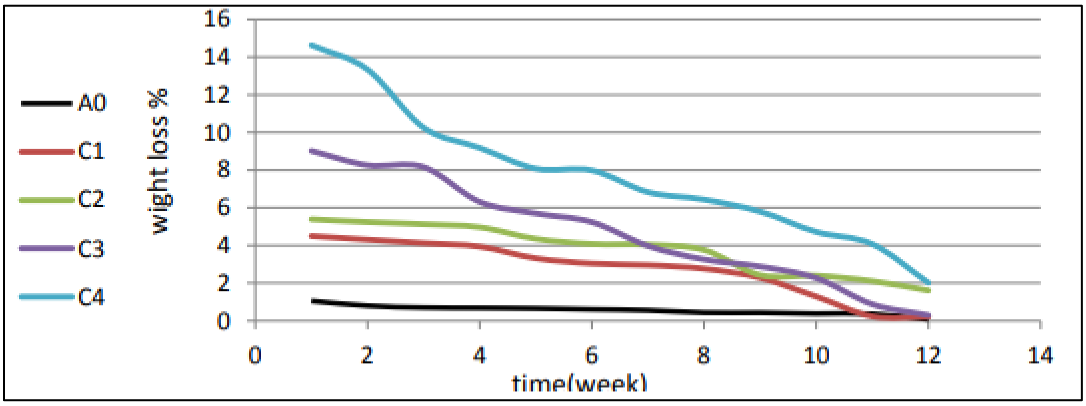


Fig. 6. Biodegradation of blends.

4. Conclusion:-

First one to synthesis of this blends

1-The results of FT-IR revealed that the formation of the grafted polymer from the reaction of the Cephalexin drug compound with the chitosan polymer in C_0, C1, C2, C3, and C4 Wight loss % time(week) weight ratios of 1:1, was done by using Schiff base reactions between the C=O active group in chitosan and the NH2 active group in Cephalexin.

2-FE-SEM images showed the overlap between the grafted polymer and natural rubber. The images showed the extent of adhesion between (CE and CH). This proves the reaction between the reactants in the presence of accelerators and catalysts and the C1-C4 blends were considered the best mixtures to cover the urea.

3-The swelling ratio for blends was higher than 100%, and they can be called the super hydrogel.

4-All blends have good ability of water retention in soil. The retention ratio was increased with increasing the weight of grafted polymer in NR blends. Therefore, the water can be stored and reused for the plant grows.

5-The biodegradation in blends were increased clearly through increasing the ratio of grafted polymer. In addition, the decomposition of blends was activated by microorganisms (fungi and bacteria) in the soil with present the moisture.

6- The urea release rate in soil revealed that it decreased by increasing the proportion of Ce-CH, in natural rubber .

From results, it can be said that Cephalexin drugs can be used in soil treatment by introducing them in natural reactions with polymers and rubber or both, and the results showed that the ratios of 100-150 phr was the best.

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