

Syntheses and Characterization of Chitosan-Expired Amoxicillin/Natural Rubber Copolymers for Slow-Release Fertilizer

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As the global population rises, so does the urgency with which the agricultural sector must increase crop output to keep up with demand. The spread of nutrient deficiencies in the soil led to economic losses and a significant decrease in nutritional quality and total quantity of grains for humans and livestock. Fertilizers can increase nutrient use efficiency through the slow release mechanism and targeted or controlled delivery. Coating fertilizers with polymers is one of the most important and effective aspects of slow-release fertilizers in the soil. In this study, urea fertilizer was coated with a grafted polymer prepared from chitosan and expired amoxicillin using condensation reaction and vulcanized with natural rubber using tetramethyl thiuram disulfide (TMTD) as catalyst. The expired amoxicillin. The swelling, water retention, slow release of urea, biodegradation and remoter tests of the chitosan/NR/expired amoxicillin compounds were characterized. The slow release rate of urea was decreased with the increase in the concentration of amoxicillin. The highest release percentage in soil media was 2.69 g/L for the B2 blend. The highest swelling ratio was 189.482 % for the C4 blend while the highest water retention was 75.69% for the B2 blend. It was also shown a good biodegradability, where the highest concentration of amoxicillin with chitosan gave the highest rate of biodegradation to be 14.63% for C4. The homogeneity of the mixtures was studied by FE-SEM technique. It was concluded that the C1-4 blends were the best for slow-release fertilizer application.

Keywords: Chitosan, Natural rubber, Slow release fertilizer, Expired amoxicillin, Urea.

INTRODUCTION

With a growing global population [1], increased crop output is crucial; however, reducing wasteful fertilizer applications has proved to be a challenging task. The scientists worked to improve fertilizer performance by delaying the release of nutrients [2-4]. The loss of nitrogen from uncoated fertilizers in the soil requires the use of large amounts of fertilizers to meet the requirements of the plant, which causes serious environmental problems such as leaching volatilization and mineralization [5]. Controlled, slow-release fertilizers are the main strategy for delaying the release of nutrients dissolve according to the needs of the plant [6,7].

Several studies have been conducted in regard to approach of coating granular fertilizers *via* polymers synthetic greatly prevents the loss of nutrients and delays their release [8,9]. However, the main drawback this coating approach is associated with is the coating material itself. In addition, after the composting process, plastic residues accumulate in the soil. It was reported that the reason for the serious degradation of arable land is that about 50 kg of plastic per hectare each year accumulates in the soil [10]. Biodegradable natural polymers have been tested as alternatives like this applications. Several studies have successfully explored biodegradable polymers to improve the availability of nutrients in the roots [11-15].

Copolymerization was added as an enticement to natural rubber (NR) in the new uses by chemically modifying it with halogens [16], chlorohydrination [17], epoxidation [18] and hydrates [19]. Graft polymerization of hydrophilic monomers such as acrylonitrile [20], maleic anhydride [21], methacrylic acid [22] and dimethylaminoethyl methacrylate [23] in solution or natural rubber latex was carried out. Products modified for

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compatibility [21], drug storage [24], modified NR applied in environmental friendly fertilizers. Vudjung & Saengsuwan [25] biodegradable interpenetrating polymer network (IPN) hydrogels based on pre-vulcanized natural rubber (NR) and cassava starch using sulphur and glutaraldehyde as crosslinkers were developed in a solution form as a coating membrane for slowrelease urea. Riyajan *et al.* [26] prepared a NR-modified with starch using polymer grafting processes and use it as a polymer membrane for urea controllability.

Chitosan has been widely used as a potential matrix for controlled fertilizers such as fibers and hydrogels due to its non-toxicity, biocompatibility, biodegradability and low sensitivity [27,28]. Chitosan is usually derived from *N*-deacetylation of chitin under alkaline conditions [29]. Some reactive chemical modifications can be made to the amino groups inherent in chitosan, which gives many important applications [30]. The structure of chitosan can be modified through a condensation reaction (Schiff base reaction) and the products of this reaction have several applications in different fields such as water treatment, sensing, catalysis and biology [31,32].

The well-known Schiff base is one of the chemical modifications of the chitosan imine product that has garnered a lot of interest. Amoxicillin is one of the most important heterocyclic compounds. It has two nitrogen atoms (N), presence heterogeneous rings with specific pharmaceutical chemistry characteristics and the ability to participate in a wide variety of reactions (including Schiff reactions) thanks to its primary amine group (NH₂) and carbonyl group ketone (C=O) [33]. In this research, chitosan grafted with amoxicillin was prepared by condensation reaction and the product was reacted with natural product to produce a new compound to enhance agricultural efficiency.

EXPERIMENTAL

Chitosan with *m.w.* of 400,000 g/mol, 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 amoxicillin drug was supplied by Co-Amoxiclav, India. Tetramethyl 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.

Preparation of chitosan/amoxicillin grafting using condensation reaction: The reaction of amoxicillin and chitosan was performed by the condensation reaction [34,35]. The graft polymer of chitosan/amoxicillin was synthesized by the reaction in different ratio of weight (1:1), (1:0.5), (1:0.1), 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 min and 350 W, then cooled to room temperature (**Scheme-I**).

TABLE-1 THE WEIGHT RATIO DATA OF AMOXICILLIN/CHITOSAN FOR POLYMER USING CONDENSATION REACTION									
Materials	CH1	CH2	CH3						
Chitosan (CH)	100	100	100						
Amoxicillin (AO)	10	50	100						

Preparation of graft chitosan/NR blends: The graft chitosan/NR blends were prepared by interaction graft chitosan (CH1, CH2 and CH3) with natural rubber, at various concentrations of 25, 50, 100 and 150 phr of the gross weight of NR as shown in Table-2. A specific amount of NR was mastication through two roll mills for softening of NR. Then, the graft chitosan, zinc oxide and stearic acid were added to NR. After getting good mixing, the accelerator (TMTD) was added to the mixture. 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 170 °C and the pressure of 3.5 MP for 15 min [36].

Preparation of encapsulated urea fertilizer with A, B and C blends: The urea fertilizer granules were coated with different coating materials such as A0, A1-4, B1-4 and C1-4 blends. It was dissolved 4.5 g from each blend in 30 mL CH₂Cl₂ for one day to ensure for complete dissolution. 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 h and then cured at 140 °C for 30 min [37].



Graft chitosan

Scheme-I: Linking the compounds of the chitosan and recycled amoxicillin using condensation reaction

TABLE-2													
FORMULATION OF CH1, CH2, CH3/NR BLENDS IN wt.%													
Materials	A0	A1	A2	A3	A4	B1	B2	B3	B4	C1	C2	C3	C4
CH1	0	25	50	100	150	0	0	0	0	0	0	0	0
CH2	0	0	0	0	0	25	50	100	150	0	0	0	0
CH3	0	0	0	0	0	0	0	0	0	25	50	100	150
NR	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO ^a	3	3	3	3	3	3	3	3	3	3	3	3	3
Stearic acid ^a	2	2	2	2	2	2	2	2	2	2	2	2	2
TMTD ^a	3	3	3	3	3	3	3	3	3	3	3	3	3
^a phr (parts per hundred rubber) from total of CH1, CH2, CH3/NR blend; TMTD = tetramethyl thiuram disulfide													

FE-SEM studies: FE-SEM (model: TESCAN-mira3) was used to check the tensile fracture surfaces of samples to analyze morphology of the vulcanize mixtures, distribution and treatment. Before morphological analysis, the cross-section samples were covered with a thin layer of gold to avoid electrostatic charges [38].

Rheological properties: Some characteristics of a grafted polymer/NR, such as curing time and maximal torque, were determined at the varying temperatures. It was conducted according to ASTM D2084 for vulcanization at 20 Pa and 185 °C for 6 min by placing 6 g sample of vulcanized mixture in a rheology machine (oscillating disc rheometer, ODR No. 131, India) at the specified preheated temperature. The curing rate indicators (CRI) for the samples were measured according to the following equation [39]:

CRI (min-1)(%)
$$\frac{100}{t90}$$
 - ts2 (1)

ts2 = scorch time (min); tc90 = cure time (min).

Swelling test: The samples were cut from vulcanized rubber sheets with dimensions of 1.5 cm × 1.5 cm and dried at 50 °C for 1 h and then weight was measured. The samples were immersed in distilled water for different periods. The sample was taken from the water and pressed the samples between the filter paper gently and then the weight was measured again.

Swelling ratio =
$$\frac{W_2 - W_1}{W_1} \times 100$$
 (2)

where W_1 and W_2 are the weight of before and after immersing the sample in water, respectively [40].

Biodegradation test: To measure the biodegradability of the grafted polymer/NR samples, the pieces of vulcanized rubber samples with dimensions of 1 cm \times 1 cm, were dried at a 80 °C for 30 min and were weighed. Then the sample was buried under the soil using a quantity of 100 g of soil at the delpth of 7 cm below the surface of the soil [41]. Water was weekly added for 3 months, the sample was taken every week, washed with distilled water, dried at 80 °C for 1 h and then weighed. The biodegradation was measured by the weight loss of the sample according to eqn. 3 [42]:

Weight losses (%) =
$$\frac{W_2 - W_1}{W_1} \times 100$$
 (3)

Measurement of water retention in soil: The water retention test was measured by taking 2 g of grafted polymer/ NR blend was mixed with 200 g of dry soil, stored in a plastic container and then added 200 mL of water into a container and weighed. The controlled sample was performed (sample without grafted polymer/NR blend). Containers were stored at room temperature and daily weighed for 30 days. The estimation of the remaining percentage of water (WR%) according to eqn. 4 [43]:

Water retention (%) =
$$\frac{W_i}{W_i} \times 100$$
 (4)

Measurement of urea release in soil: To understand the method of releasing urea fertilizer, it was done by using an ultraviolet spectrometer to measure the amount of urea emitted from the coating blend. Dried sample (1 g) mixed with 200 g of soil was added to 700 mL of distilled water to form a homogeneous solution, stored in a fully covered beaker and kept for various periods at room temperature. After 20 days, the concentration of urea release was estimated using ultraviolet spectroscopy (UV Biochem Ltd., Cambridge) [44].

RESULTS AND DISCUSSION

Characterization of A, B and C blends

FTIR studies: In chitosan, the presence of a peak of the primary amine group at approximately 3352 cm⁻¹ and the aromatic CH at 2977-2886 cm⁻¹ while OH groups appeared at 3777-3652 cm⁻¹ [45], as shown in Fig. 1a. The chemical structure of amoxicillin has several important peaks, for example, the primary amine group approximately appeared at 3443 cm⁻¹. The aromatic CH group was shown at 2974-2917 cm⁻¹ and the ketone group is appeared at 1769 cm⁻¹. The amide carbonyl appears at 1577 cm⁻¹, while the peak of 1682 cm⁻¹ is attributed due to the group C=C. The OH group appeared at 3778-3653 cm⁻¹ was due to the acid and alcohol groups [46] (Fig. 1a).

In blend A, the appearance of the azomethine group at $1582-1561 \text{ cm}^{-1}$ broad, formation with the amide carbonyl and the slight displacement of amide group to 1516 cm^{-1} [47] confirmed the formation of blend A (Fig. 1a).

In blend B, a shift in the amide carbonyl group band and the appearance of azomethine group at 1581 cm⁻¹ broad and the displacement of the amide group to 1517 cm⁻¹ with slight shift. Few functional group such as primary amine group was appeared at 3161 cm⁻¹ as well as the –OH group of the acid and the alcohol at 3652 cm⁻¹ [48] as in blends C, a wide presence of the azomethine group at 1561-1516 cm⁻¹ in conjunction with carbonyl amide. The primary amine group was displaced at 3150 cm⁻¹ [49] as shown in Fig. 1c. It is observed that the higher concentration of recycled amoxicillin in chitosan by



Fig. 1a. FTIR of amoxicillin (- AO), chitosan (- CH), material (- A)



Fig. 1b. FTIR of amoxicillin (- AO), chitosan (- CH), material (- B)



Fig. 1c. FTIR of amoxicillin (- AO), chitosan (- CH), material (- C)

the interaction of Schiff bases gives a broad band overlapping with the amide carbonyl group with a slight shift due to the effect of the active groups in amoxicillin compound.

Proposed mechanical reaction between chitosan and recycled amoxicillin: The Schiff reaction mechanism is another type of nucleophile as well as a carbonyl group. In this case, the amine is acted as nucleophile and in the first step, the reaction of amine with carbonyl group give an unstable compound called as carbinolamine. The carbinoiamine contains an alcohol, which loses a water molecule (dehydration) when an acid or base is used as catalyst, as shown in the following mechanism [50]:



The loss of carbinolamine to water is the defining step of the limit reaction. In the proposed mechanism of the reaction of chitosan with amoxicillin, the carbonyl ketone group of amoxicillin with the primary amine group of chitosan react to form azomethine (-CH=N-) and eliminate a water molecule from the reaction by using the acid as catalyst.

Surface morphology: Figs. 2-5 show the FE-SEM images of the fractured surface for A0, A1-4, B1-4 and C1-4, respectively, at the magnification of 5.00 KX. A uniform dispersion of the CH1 (A1-4), CH2 (B1-4) and CH3 (C1-4) component on the surface of NR indicates the homogeneous morphology of the samples. Increasing the loading of CH1, CH2 and CH3, gives the possibility of adhesion between the rubber and the grafted polymer, as confirmed from the images of the FE-SEM.

FESEM of chitosan and A0 blends: The FE-SEM images clearly shows two distinct identical structures of NR and CH grafted as observed in Fig. 2a-b. Due to the elasticity of NR, the blends are incompatible. Due to a small amount of graft chitosan in blends A1 and A2, a non-uniform distribution of graft chitosan was observed (Fig. 3a-b). In blends A3 and A4, mixing is better due to an increase in the amount of chitosan and a well-uniform distribution as shown in Fig. 3c-d [51].

FE-SEM of B1-4 blends: Among the chitosan grafted with amoxicillin/NR, the AO:CH at the concentration of 0.5:1 (blends of B1 and B2) (Fig. 4a-b) showed inadequate distribution and adhesion. Larger detachments and holes were also observed in these blends, while blends B3 and B4 (chitosan grafted with amoxicillin/NR) had better distribution and overlap as shown in Fig. 4c-d, with increasing loading of chitosan grafted with amoxicillin.

FE-SEM of C1-4 blends: According to the FE-SEM images in Fig. 5, homogeneous mixing was achieved when compared to the microscopy images of the reactants compounds in Fig. 2. Chitosan and rubber compounds were not examined for internal voids before blending, but the morphological properties of the blends changed after grafted chitosan was added at a concentration of 100:100 AO:CH, and voids were identified between the grafted chitosan flour and the matrix blends of C [52]. Through Figs. 3-5, the FE-SEM images of the blends in CH1, CH2 and CH3, it was observed that the higher concentration and the greater the amount of chitosan grafted with amoxicillin gave the greater biodegradation, as well as the increase in the rate of swelling, water retention and urea release rate

Swelling test: The swelling ratio of A0, A1-4, B1-4 and C1-4 blends for 7 days are illustrated in Fig. 6a-c, respectively.



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



Fig. 3. FE-SEM of fracture tensile strength for (a) A1 blend, (b) A2 blend, (c) A3 blend, (d) A4 blend of (CH1)/NR

Fig. 6a illustrates that the swelling ratio of A1-4 blends increased with increased amoxicillin contents. This behaviour is due to the main polar adsorption sites including amino, hydroxyl and carboxylic groups in amoxicillin and the water molecules are attracted to these groups. Besides the hydroxyl groups, the amide side chains and the COC peptide bonds to the main polypeptide chains in chitosan are also possible water absorption sites. Therefore, it gave the highest bloating rate at 150 phr of CH1 in the A4 blend (Fig. 6a). On the other hand, an increase of

amoxicillin in CH2/NR blends (B blends) leads to an increase in the swelling ratio more than in A blend and it became higher than 100 % in B3 and B4 blends. The maximum value of swelling ratio was observed in the B4 blend to be 122% (Fig. 6b). The reason may be to an increase in the percentage of amoxicillin in the graft polymer/NR blend and this leads to an increase in the number of hydrophilic groups, as mentioned above, which the energy of the water attracted with the polar groups and therefore, it gives the highest swelling ratio, as Vol. 35, No. 4 (2023)

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Fig. 4. FE-SEM of fracture tensile strength for (a) B1 blend, (b) B2 blend, (c) B3 blend, (d) B4 blend of (CH2)/NR



Fig. 5. SEM of fracture tensile strength for (a) C1 blend, (b) C2 blend, (c) C3 blend, (d) C4 blend of CH3/NR



shown in Fig. 6b. Moreover, the CH3/NR (C blends) exhibited the highest swelling ratio as compared with blends A and B, where it reached 190% (Fig. 6c). The reason may be that the addition of amoxicillin molecular to the blend with amino, carboxyl and hydroxyl groups at a high concentration as compared to the A and B blends led to the C blend having a higher swelling ratio [53]. The results showed that super-absorbent hydrogels could be made by blending chitin and molecular amoxicillin.

Rheological properties: Table-3 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, two catalysts (graft polymer and TMTD) were involved in the processing of graft polymer/ NR, which leads to an increase in the cross-correlation compared to the control sample (A0). This proves that the graft polymer participates in the treatment process. The CRI was increased compared to the control sample (A0) based on the increase in the concentration of graft polymer and its weight in the blend as an activator in vulcanization in the presence of stearic citric acid and zinc oxide [54].

TABLE-3 CURING PARAMETER OF GRAFT POLYMER/NR BLENDS							
Sample MH code (Ib.in)		ML (Ib.in)	T90 (min)	TS2 (min)	CRI (min)		
A0	16.28	3.94	2.33	0.87	68.49		
A1	13.52	1.28	1.69	0.94	133.33		
A2	18.30	1.53	1.40	0.83	175.43		
A3	26.55	1.67	1.05	0.65	250.00		
A4	22.31	1.81	0.66	0.41	400.00		
B1	9.61	1.04	1.36	0.83	188.67		
B2	10.20	1.37	1.13	0.74	256.41		
B3	8.12	1.63	0.79	0.53	384.60		
B4	5.28	2.27	0.56	0.49	1428.5		
C1	7.51	1.07	1.26	0.84	238.00		
C2	5.74	1.36	0.98	0.71	370.37		
C3	10.71	1.59	0.74	0.48	384.60		
C4	4.10	1.09	1.95	1.94	10000		

Water retention: One of the best properties of slow-release fertilizers, is good water retention capacity, especially in dry and desert areas, to accelerate plant growth. Fig. 7 shows the water retention behaviours in soil using blends of A1-4, B1-4 and C1-4, respectively, as compared with a control sample (A0) to 30 days. It was observed that the addition of amoxicillin to three prepared samples in soil reduced the water evaporation and increased water retention as compared to the control sample. Water retention of the control sample (A0) was 77.58 and 60.1% by weight on 15th and 30th days, respectively, while the water retention of blends A (A2 blend) gave the highest percentage of water retention as it reached 81.89 and 63.18 wt% at the 15th and 30 days (Fig. 7a), while blends of B (Fig. 7b), the water retention percentage of mixture B3 was the highest among blend B where water retention reached 86.1 and 74.9 wt.% at the 15th and 30th days, respectively. Fig. 7c shows the highest water retention value was in the C3 blend as compared to other C blends.

Urea release: The dissolution rate of urea fertilizers (UR) in soil, which were coated with the A1-4, B1-4 and C1-4 blends is illustrated in Fig. 8a-c, respectively. The results show that an initial release was slowed behaviour 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 A0, A1, A2, A3 and A4, respectively.

In Fig. 8b-c, the urea release of B1-4 and C1-4 blends had similar behaviour of A blend where they were decreased to be 2.35, 2.69, 2.48, 2.43 and 2.30, 1.950, 1.681, 1.546 g/L, respectively, at 20 days. The reason may be that its proportion to the results of the swelling study as observed in Fig. 6b-c, nutrients are released from the (CURF) hydrogel into the soil. In all the preparation of CURF hydrogels, the swelling ratio in soil solution low than in water. Thus, the diffusion of soluble fertilizers into the soil from CURF hydrogels is slow [55].

The urea fertilizer values of A blends are less than those of B blends, but the urea fertilizer values of C blends are less than those of A and B blends combined. Since there are more





Fig. 9. Biodegradation of (a) A0, A1-4 blends in soil, (b) A0, B1-4 blends and (c) A0, C1-4 blends

-OH groups available due to the higher amoxicillin content in the chitosan (1:1), blend C has superior urea release compared to blends A and B.

Biodegradation studies: The biodegradation of A0 and A1-4 blends increases significantly with the increase of CH1 contents and it is clearly observed that A4 blend has the highest weight loss among the other A blends (Fig. 9a). This behaviour is due to the large decomposition of fungi and bacteria in the soil activated by heat and moisture.

From Fig. 9b, it is clear that weight loss of B1, B2, B3 and B4 blends increased significantly with the increase of CH2 content. Among blends, B4 blend exhibit the highest weight loss as compared to other B blends. This is because B4 blend contains the highest amount of amoxicillin leads to more neutral decomposition by fungi and bacteria in the soil activated by heat and moisture. The higher concentration of CH3/NR in the A0, C1, C2, C3 and C4 blends observed that C4 blend had more decomposition as shown in Fig. 9c [56].

Conclusion

This study showed the slow-release fertilizers that were prepared by coating urea fertilizers with different blends. Natural rubber was mixed with the grafted polymer in the presence of a tetramethylthiuram disulfide (TMTD) as catalyst. The FT-IR studies revealed that the formation of the grafted polymer from the interaction of amoxicillin drug with the chitosan polymer in three weight ratios of 1:1,1:0.5, 1:0.1 was done by using condensation reaction between the C=O active group in chitosan and the NH₂ active group in amoxicillin. The FE-SEM images showed the overlap between the grafted polymer and natural rubber. The images showed the extent of adhesion between (amoxicillin and CH). This proves the interaction between the reactants in the presence of accelerators and catalysts and the C1-4 blends are considered the best mixtures to cover the urea. The rheology showed the extent of crosslinking between the grafted polymer and natural rubber. Increasing the curing ratio in a very large way from 68.49 in control sample (A0) to 400 in A blend at the loading of 150 phr of CH1 and 1428.5 in B blend at the loading of 150 phr CH2, while the highest ratio (10000) of the curing was in C blend at the loading of 150 phr CH3. The swelling ratio for A blends was less than 100%, while for B, C blends, it was higher than 100% and can be called the super hydrogel. The retention ratio was increased with increasing the weight of grafted polymer in natural rubber blends. The biodegradation in blends of A, B and C blends were also increased with the increasing ratio of the grafted polymer. In addition, the decomposition of blends was activated by microorganisms (fungi and bacteria) in soil present in the moisture. The urea release rate in soil revealed that it decreased by increasing the proportion of CH1, CH2 and CH3 in natural rubber and the CH3 blends was the better and had the lowest slow release. Thus, it can be said that amoxicillin 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.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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