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Preparation of Silver Cyclohexane di Carboxylate: B-cyclodextrin Inclusion Complexes and Their Use in the Production of Poly(vinyl alcohol) Nanowebs

Gümüş Siklohekzan Di Karboksilat: B-Siklodekstrin Inklüzyon Komplekslerinin Hazirlanmasi Ve Polivinil Alkol Nanoağ Üretiminde Kullanimlari

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PREPARATION OF SILVER CYCLOHEXANE DI CARBOXYLATE: β-CYCLODEXTRIN INCLUSION COMPLEXES AND THEIR USE IN THE PRODUCTION OF POLY(VINYL ALCOHOL) NANOWEBS

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ABSTRACT: In this study, guest:host inclusion complexes of silver cyclohexane di carboxylate (Ag-CdC) with β-cyclodextrin were prepared by kneading and physical mixing techniques, and analyzed via Fourier transformed infrared spectroscopy (FTIR) and thermogravimetric analyser (TGA). The 1:1 and 1:2 stoichiometry of the guest:host were prepared. Obtained FTIR and TGA results showed that formation of silver cyclohexane di carboxylate (Ag-CdC): β-cyclodextrin (β-CD) inclusion complexes occurred at a mass ratio of both 1:1 and 1:2. Furthermore, these prepared inclusion complexes were doped in poly(vinyl alcohol) nanofibers during electrospinning process for obtaining nanowebs. The formation of nanowebs were investigated with scanning electron microscopy (SEM). Besides, FTIR and TGA analysis were also carried out. Results showed that both inclusion complex preparation and inclusion complex added PVA nanowebs production were successful.

Keywords: β-cyclodextrin, silver cyclohexane di carboxylate, inclusion complex, electrospinning, PVA.

GÜMÜŞ SİKLOHEKZAN Dİ KARBOKSİLAT: β-SİKLODEKSTRİN İNKLÜZYON KOMPLEKSLERİNİN HAZIRLANMASI VE POLİVİNİL ALKOL NANOAĞ ÜRETİMİNDE KULLANIMLARI

ÖZET: Bu çalışmada, gümüş sikloheksan di karboksilat (Ag-CdC) ile β-siklodekstrin içeren konuk:konak inklüzyon kompleksleri yoğurma ve fiziksel karıştırma teknikleriyle hazırlanmış ve Fourier dönüştürülmüş kızılötesi spektroskopi (FTIR) ve termogravimetrik analizör (TGA) ile analiz edilmiştir. Konuk:konak, 1:1 ve 1:2 stokiyometri ile hazırlandı. Elde edilen FTIR ve TGA sonuçları, gümüş sikloheksan di karboksilat (Ag-CdC): β-siklodekstrin (β-CD) inklüzyon komplekslerinin oluşumunun hem 1:1 hem de 1:2'lik kütle oranında gerçekleştiğini gösterdi. Ayrıca, hazırlanan bu inklüzyon kompleksleri, nanoweb elde etmek için elektrospinning işlemi sırasında poli(vinil alkol) nanofiberlere katılmıştır. Nanoweblerin oluşumu taramalı elektron mikroskobu (SEM) ile araştırıldı. FTIR ve TGA analizleri de ayrıca yapıldı. Sonuçlar, hem inklüzyon kompleksi hazırlama hem de inklüzyon kompleksi eklenmiş PVA nanoweb üretiminin başarılı olduğunu gösterdi.

Anahtar Kelimeler: β-siklodekstrin, gümüş siklohekzan di karboksilat, inklüzyon kompleks, elektroçekim, PVA.

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1. INTRODUCTION

In recent years functional textiles with wash-resistance antibacterial effect gained importance especially for the use in medical textiles field. Silver itself is an antibacterial material and its antibacterial properties has been well studied in the literature [1-6]. With the aim of producing complex form of silver and by the way eliminating the risk of getting into human skin, Yildiz et al. synthesized and characterized silver cyclohexane mono carboxylate and silver cyclohexane di carboxylate complex compounds and impregnated onto cotton fabric for investigation of their antibacterial properties. Prepared cotton fabrics were tested for their antibacterial activity against selected gram-negative bacteria (*Escherichia coli, Klebsiella pneumonia, Pseudomonas aeruginosa*), and selected gram-positive bacteria (*Staphylococcus aureus, Bacillus subtilis, Enterococcus faecalis*). Antibacterial properties of silver naphthenates impregnated cotton fabrics were also investigated after several washings, and it was reported that inhibition to bacterial growth was observed on treated cotton fabrics even after 20 washings [7].

Inclusion complexes (ICs) consist of a guest and a host material. The guest compound accommodates in the cavities of the host compound to form inclusion complexes. A number of different compounds can be used as the guest material while compound that can be used as the host material is limited [8-12]. One of the most commonly used host material is "cyclodextrin" (CD), which are cyclic oligosaccharides consisting of glucopyranosyl units. The number of the glucopyranosyl units in the structure expresses the prefix α-, β- and γ- cyclodextrin [9]. Detailed information on cyclodextrins and their uses can be found elsewhere [13-15].

Atav et al. studied the inclusion complex formation characteristic of silver cyclohexane mono carboxylate with β-cyclodextrin (β-CD). Prepared complexes were analyzed by using FTIR, TGA and SEM analysis. They reported that formation of ICs occurred both in 1:1 and 1:2 mass ratio. In addition to preparation and characterization of inclusion complexes, ICs were applied on cotton fabrics via pad-dry method. In order to investigate the wash resistance of antibacterial effect, inclusion complex containing cotton fabrics were repeatedly washed and tested up to 50 washes. It was determined that cotton fabrics loaded with Ag-CC:β-CD 1:2 inclusion complexes showed antimicrobial efficiency against *S. aureus, B. subtilis and P. aeruginosa* even after 50 washings [16].

Jose and Kuriakose synthesized and characterized inclusion complexes consisted of silver nanoparticles and functionally modified β-cyclodextrin [17], while Pande et al. prepared inclusion complexes by synthesizing normal and inverted gold:silver (core:shell) structures, and using them as the guest material for β-cyclodextrin [18]. Jaiswal et al. studied the effect of the amount of β-cyclodextrin (β-CD) in the inclusion complex on antibacterial properties of silver nanoparticles (the guest material). Their observation was that the increasing amount of β-CD in the complex caused the delay of bacterial growth, due to being able to host more of silver ion [19].

Silver cyclohexane di carboxylate and silver cyclohexane mono carboxylate have already been synthesized, characterized and applicated onto cotton fabric through padding for obtaining antibacterial functionality [7]. In another study, silver cyclohexane mono carboxylate: β-cyclodextrine inclusion complexes were prepared and applicated on cotton fabric for achieving wash-resistant antibacterial functionality [16]. However the inclusion complex of silver cyclohexane di carboxylate:β-CD has not been studied previously. On the other hand, in the literature there is no study on the use of these compounds for obtaining nanowebs via electrospinning. For this reason, it is believed that current study is original. In this study, inclusion complexes of silver cyclohexane di carboxylate and β-cyclodextrin were prepared. Two types of complexes were prepared by varying the mass ratios of guest:host (1:1 and 1:2). Kneading and physical mixing techniques were used, and the effect of preparation technique and the mass ratio of guest:host were studied and evaluated via FTIR and TGA. Furthermore, these prepared inclusion complexes were doped in polyvinylalcohol nanofibers during electrospinning process for obtaining nanowebs. The formation of nanowebs was investigated with scanning electron microscopy (SEM). Besides, FTIR and TGA analysis were also carried out.

2. EXPERIMENTAL DETAILS

2.1. Silver Cyclohexane Di Carboxylate Synthesis

The synthesis of silver cyclohexane di carboxylate (Ag-CdC) compounds were occurred as a result of naphthenic acid and silver salt reaction. The cyclohexane di carboxylic acid solution was put into a flask and stirred at 40-45°C for 60 minutes. During the stirring process, %10 (v) NaOH solution was dropped from the dropping funnel to adjust the medium pH. Then appropriate amount of AgNO3 was added to the mixture and stirred for an hour. After 24 hours, liquid phase and the organic phase were seperated via an extraction flask. Detailed information on Silver cyclohexane di carboxylate synthesis can be found in the literature [7, 16].

2.2. Preparation of Ag-CdC:β-CD Inclusion Complexes

Synthesized Ag-CdC nanoparticles (NPs) and β-CD were then used to form inclusion complexes. For the formation of inclusion complexes, the kneading technique was followed, with a mass ratio of 1:1 and 1:2 for the guest:host compounds. Ag-CdC:β-CD NPs were also physically mixed at a mass ratio of 1:1 and 1:2 as reference. Mass ratios and weights of the compounds used in the inclusion complexes are given in Table 1.

Table 1. Inclusion complex stoichiometries of Ag-CdC:β-CD

Mass Ratio, gram	Ag-CdC:β-CD, gram:gram
1:1	1.135:1.135
1:2	1.135:2.260

Inclusion complexes of Ag-CdC and β-CD were prepared by kneading technique which is suitable, especially when the guest

material's water solubility is poor [20]. Briefly, β-CD (host) was stirred in 1 mL of water, and formed a slurry. Then Ag-CdC (guest) was added in the slurry and kneaded together in the mortar for 20 minutes. After kneading, a paste-like material obtained. The obtained paste dried and prepared for analyzing.

For preparation of reference materials, β-CD and Ag-CdC were physically mixed by being stirred in a flask with the help of a baguette. Stirring process was carried out for 5 minutes at room temperature. Prepared samples were then analyzed under a Thermo brand Fourier alternating infrared spectrophotometer (FTIR) and a Perkin Elmer TGA4000 thermogravimetric analyzer (TGA) to investigate whether the formation of inclusion complexes occurred or not.

2.3. Electrospinning of Ag-CdC : β-CD Inclusion Complexes Doped PVA Nanowebs

Inovenso Technology Inc. Nanospinnner1 model electrospinning device was used in nanofiber production. 1%, 2% and 4% Ag-CdC:β-CD inclusion complexes were added to PVA (10% by weight) solution in water and mixed for 8 hours and then ultrasonic homogenization was processed for 30 minutes. The solution drawn into the 10 mL syringe and it was converted to nanofibrous material at room temperature. Electrospinning production parameters are given in Table 2.

Table 2. Electrospinning parameters

Polymer/Complex	Distance, cm	Flow Rate, mL/h	Voltage, kV
PVA	15	0.5	9
PVA/ β-CD:Ag-CdC	15	0.5	17.5

FTIR and TGA analyses of obtained nanowebs were performed. Thermo brand FTIR and Perkin Elmer brand TGA were used for this purpose. To investigate the formation of nanowebs, samples were also analyzed under FEİ brand QUANTA FEG 250 model SEM.

3. RESULTS AND DISCUSSION

3.1. Results Related to The Preparation of Ag-CdC:β-CD Inclusion Complexes

Aiming the formation of inclusion complexes, we expect to see peaks similar to β-CD in the FTIR spectra of Ag-CdC:β-CD inclusion complexes. In Figure 1, transmittance spectra of pure β-CD, pure Ag-CdC, their mixtures prepared by stirring, and inclusion complexes prepared by kneading technique are given.

The peaks seen on FTIR spectra of β-CD exhibited significant peaks at wavelengths of 940 (skeletal vibrations involving α-1,4 bonds), 1090 and 1160 (ν (CO), ν (CC), ν (COH) peaks), 1340 ((H-CH) peaks), 1420 (δ (CH) peak from CH_2 and CH_3), 2930 (ν CH peak) and 3300 ν (-OH peak) cm^{-1} as previously reported by Norasiha et al. [20].

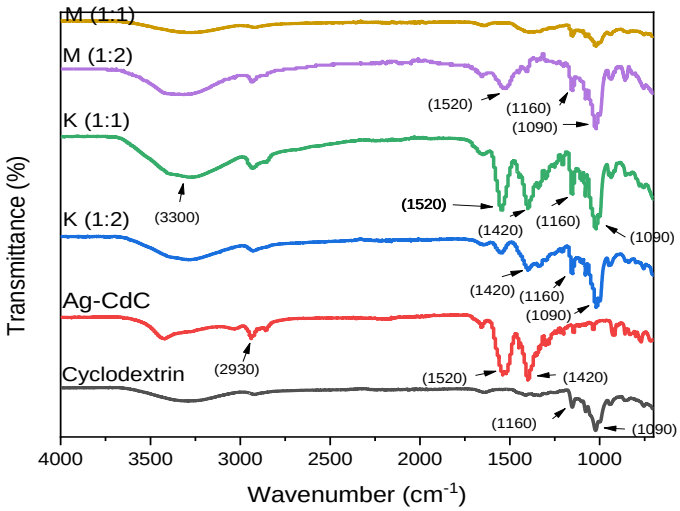

Figure 1. FT-IR results of mixtures of Ag-CdC prepared with β-CD according to kneading (K) and mixing (M) techniques

In FTIR spectra of Ag-CdC, the peaks at wavelengths of around 1000 and 1250 cm^{-1} present C-O stretching, peaks at 1400 and 1450 cm^{-1} are attributed to methylene groups while the peaks around 1680 and 1730 cm^{-1} are representative for -COO groups in the structure as previously reported by Yildiz et al. [16]. According to the spectra given in Fig. 1, the inclusion complexes were formed at both mass ratios of 1:1 and 1:2. The transmittance peaks of Ag-CdC:β-CD inclusion complexes, prepared via kneading, comprise FTIR peaks of both pure Ag-CdC and pure β-CD. The reason why the characteristic peaks of Ag-CdC did not disappear after inclusion complex formation could be well understood when the molecular structure of Ag-CdC is investigated.

Comparing the spectrums of inclusion complexes K (1:1) and K (1:2), it can be said that spectrum of K (1:1) has the similar peaks to Ag-CdC which means there are still Ag-CdC in the medium ready to be hosted by β-CD. When the amount of β-CD is doubled, since more Ag-CdC can be hosted by β-CD, the spectrum of K (1:2) exhibits similar peaks to β-CD. Therefore, it can be said that the number of complexes formed in K (1:2) is higher than that of complexes formed in K (1:1). For this reason, the inclusion complexes of Ag-CdC: β-CD (1:2) prepared via kneading method was chosen for the nanofiber production.

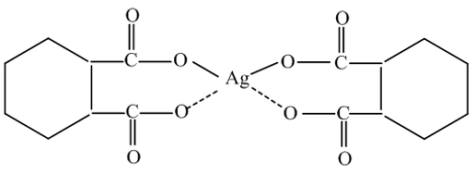

Figure 2. Molecular structure of silver cyclohexane di carboxylate

As can be seen from Figure 2, silver cyclohexane di carboxylate is a complex molecule and probably it is not completely included in β-CD cavity during inclusion complex formation. Possible inclusion complex formation mechanism of Ag-CdC with β-CD is given in Fig. 3.

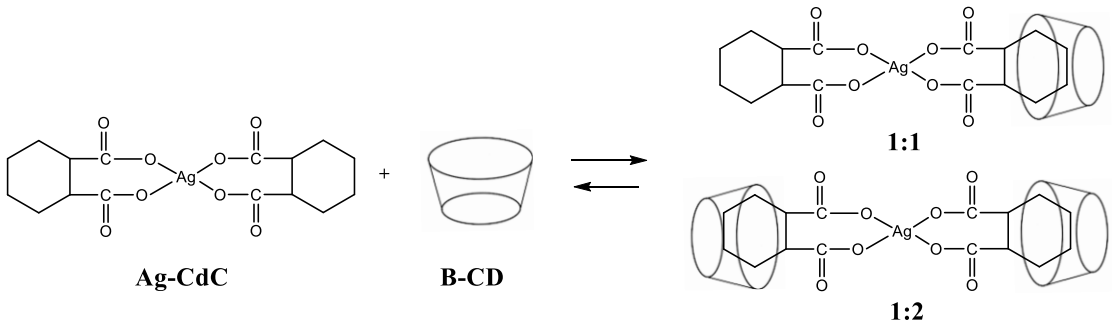

Figure 3. Inclusion complex formation mechanism of Ag-CdC with β-CD

As can be seen from Figure 3, after inclusion complex formation both at a mass ratio of 1:1 and 1:2, cyclohexane rings of Ag-CdC are included in β-CD while carboxylic acid groups stayed free. For this reason, peaks related to the carboxylic acid at a wavelength number of about 1400 cm^{-1} also exists in inclusion complexes.

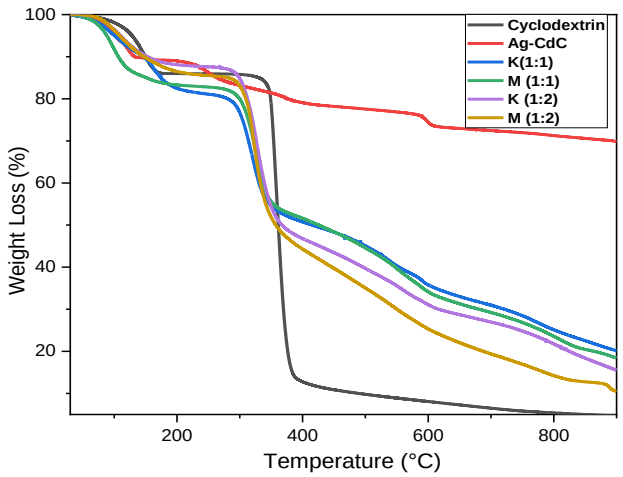

Figure 4. TGA results of mixtures of Ag-CdC prepared with β-CD according to kneading and mixing techniques

Thermograms of pure β-CD, pure Ag-CdC, their mixtures prepared by stirring, and inclusion complexes prepared by kneading technique are given in Figure 4. It can be seen in the thermograms that a sharp mass loss of pure β-CD occurred at about 400°C due to the thermal degradation. The mass loss of pure Ag-CdC happened gradually. When the thermograms of Ag-CdC:β-CD inclusion complexes discussed, it can be said that both 1:1 and 1:2 Ag-CdC:β-CD inclusion complexes differ significantly from pure Ag-CdC but more similar to the pure β-CD. Therefore, it is possible to say that the inclusion complexes were formed and due to the encapsulation of pure Ag-CdC, the characteristics of their heat distortion curves changed. It is noteworthy that complex preparation stoichiometry (1:1 and 1:2) had a very small effect on the results obtained.

3.2. Results Related to The Electrospinning of Ag-CdC:β-CD Inclusion Complexes Doped PVA Nanowebs

In Figure 5, transmittance spectra of pure PVA nanowebs and PVA nanowebs containing 1-2-4% β-CD:Ag-CdC inclusion complexes prepared according to kneading technique at 1:2 mass ratio are given. FTIR spectrum of pure β-CD:Ag-CdC inclusion complex is also given in Figure 5.

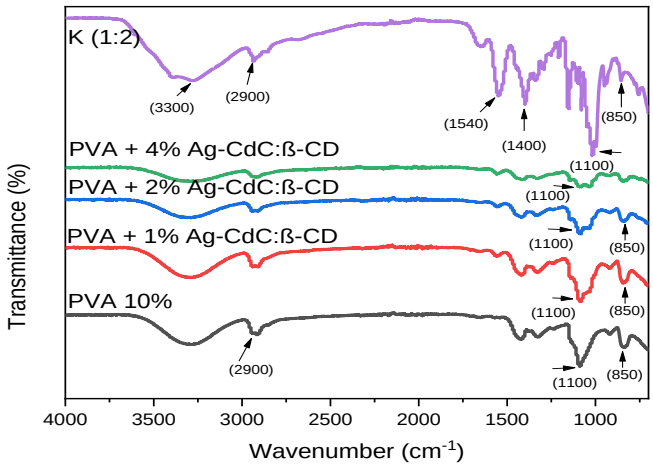

Figure 5. FT-IR results of pure PVA nanowebs and PVA nanowebs containing 1-2-4% Ag-CdC:β-CD inclusion complexes

As can be seen from Figure 5, PVA nanowebs have the absorption peaks at around 3300, 2900, 1400, 1100 and 850 cm^{-1} attributed to ν (OH), νs (CH_2), δ (H-O-H), ν (C-O) and ν (C-C) respectively [21]. Since the peaks at wavelengths of 940, 1090, 1160, 1340, 1420, 2930 and 3300 cm^{-1} are attributed to the existence of β-CD in the structure, the same peaks can be considered as indirect respresentatives for the presence of the inclusion complex in the nanofiber structure. PVA nanowebs containing β-CD:Ag-CdC in different ratios (1-2-4%) also gave the nearly same spectra with pure PVA nanowebs. In other words, the characteristic peaks of inclusion complexes disappeared. This means that β-CD:Ag-CdC inclusion complexes were successfully doped into PVA nanowebs.

Thermograms of pure PVA nanowebs and PVA nanowebs containing 1-2-4% β-CD:Ag-CdC inclusion complexes prepared according to kneading technique at 1:2 mass ratio are given in Figure 6.

It can be seen in the thermograms that a sharp mass loss of PVA nanowebs occurred at about 300°C due to the thermal degradation. When the thermograms of PVA nanowebs in which Ag-CdC:β-CD inclusion complexes were doped is discussed, it

can be said that their thermograms are very similar with pure PVA nanowebs which again means β-CD:Ag-CdC inclusion complexes were successfully doped into PVA nanowebs. On the other hand, with the increase in inclusion complex concentration doped in PVA nanoweb, final weight loss is decreased due the presence of Ag, which does not decompose with heat, in the structure.

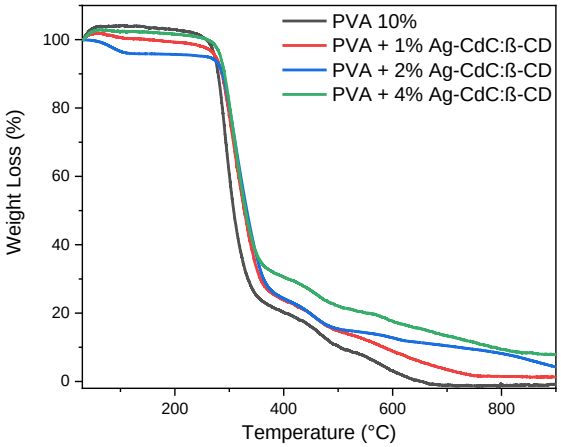

Figure 6. Thermograms of pure PVA nanowebs and PVA nanowebs containing 1-2-4% Ag-CdC:β-CD inclusion complexes

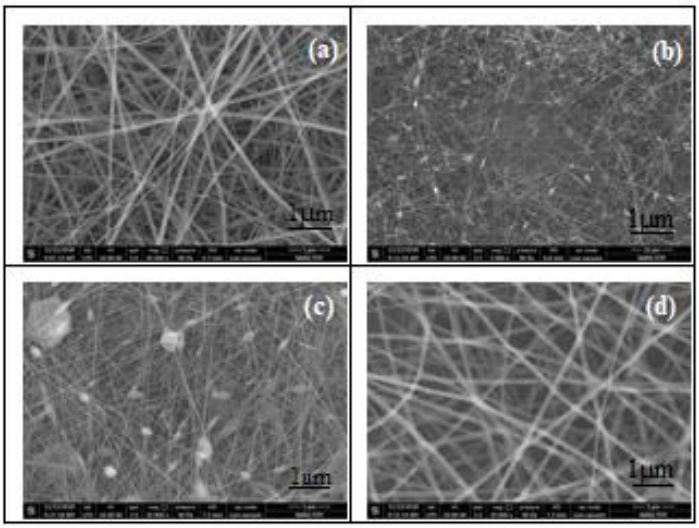

Figure 7. SEM photos of pure PVA nanowebs (a) and PVA nanowebs containing 1% (b), 2% (c), 4% (d) Ag-CdC:β-CD inclusion complex

SEM images of pure PVA nanowebs and PVA nanowebs containing 1-2-4% Ag-CdC:β-CD inclusion complexes are given in Figure 7. It is seen in the images that fiber formation occurs in all nanofibers produced by adding Ag-CdC: β-CD inclusion complex in different ratios into 10% PVA. The SEM image of the pure PVA sample shows that the fiber diameter is lower and the fiber diameter increases in direct proportion to the amount of inclusion complex dopped into it. When drawing fiber from pure PVA, the elongated polymer in the drafting area formed by electrostatic forces increases the charge density on the surface of the jet and the elongation of the jet, which leads to thinning of the fibers. On the other hand, as the amount of inclusion complex increased, the amount of beat and the thickness of the fiber increased. Thickness of nanofiber containing 1% inclusion complex is 56-270 nm. Thickness of the nanofibers containing 2% and 4% inclusion complexes were 82-296 nm and 230-1210 nm, respectively.

4. CONCLUSIONS

In this study, silver cyclohexane di carboxylate (Ag-CdC) and β-cyclodextrin (β-CD) inclusion complexes were prepared via kneading and physical mixing techniques. Two mass ratios (1:1 and 1:2) were used for guest:host (Ag-CdC:β-CD). Prepared materials were characterized by Fourier transformed infrared spectroscopy and thermogravimetric analysis to investigate the formation of inclusion complexes.

Obtained results indicated that formation of Ag-CdC:β-CD inclusion complex occurred at a mass ratio of both 1:1 and 1:2. Furthermore, PVA nanowebs containing Ag-CdC:β-CD inclusion complexes in different amounts (1-2-4%) were produced. Both FTIR, TGA and SEM analysis confirmed the formation of nanowebs. The obtained nanowebs have the potential to be used in medical applications as the Ag-CdC:β-CD inclusion complexes have antibacterial potential. In future studies antibacterial tests could be realized for the produced nanowebs.

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