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Synthesis, Characterization and Antimicrobial Study of Polyacetal-Co complex/Nano Chitosan polymer blend

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Abstract

Polycyclicacetal was prepared by the reaction of PEG with 4-nitrobenzaldehyde. Cobalt was used for producing a polymer metal complex and solution casting was used to produce a polymer blend including nano chitosan. All produced compounds have been characterized by FT-IR, DSC/ TGA, and SEM techniques as well as biological activity. The production of polyacetal is illustrated by the FT-IR analysis. The DSC/TGA results indicate the prepared polymer blends' thermal stability. Staphylococcus aureas, Klebsiella pneumoniae, Bacillus subtilis, and Escherichia coli were the four types of bacteria selected to study and evaluate the antibacterial activity of produced polyacetal, its metal complex, and polymer blend. Results indicates that there is a greater potential to kill bacteria by increasing the amount of polyacetal-Co complex.

Keywords: PEG, Polyacetal, Polymer blend, antimicrobial polymer.

1. Introduction

Antibacterial compounds are now required in biomedicine and other related sectors of science and technology. Many people pass away each year because of diseases brought on by microorganisms [1]. The pharmaceutical industry is paying particular attention to bacteria among the various pathogens (bacteria, viruses, fungi, algae, and others), primarily because of the emergence of so-called multidrug resistant microorganisms (MDR). Antibiotic resistance, which can harm anyone of any age and anywhere in the world, is one of the largest threats to global health and food security, according to the World Health Organization (WHO) [2]. Most polymeric materials with antibacterial capabilities are composed of one or two polymers that have been combined and typically modified by the

addition of inorganic particles or active molecules that can impede the growth of bacteria. These energetic molecules can be combined with the polymer or added afterwards as a finishing or post-treatment. For this reason, antibacterial polymeric materials can be created using most polymer processing techniques [2]. Blends of polymers are mixtures of two or more polymers, with or without chemical bonds between the components [3]. Most naturally occurring polymers are hydrophilic because they contain polar groups like hydroxyl and amine groups in their structure [4]. The advantage of this mixture is the possibility of obtaining a new material without synthesis of a new polymer or copolymer, saving research time and expenses as well as the high cost of chemical synthesis and the development of these products [5]. As a result, the invention of these materials allows for the manufacturing of a variety of products using multiple polymer percentages, offering many benefits according to the physicochemical characteristics of each Polymer [6].

Chitosan-based nanoparticles have attracted the interest of researchers in the biomedical area due to their versatility, non-toxicity, biocompatibility, and biodegradability [7]. Chemical modification of nano chitosan has drawn a considerable amount of attention. Due to its ability to maintain its fundamental skeleton, which maintains its physicochemical and biological properties, chitosan chemical modification is of enormous interest [8]. PVA polycyclicacetals are significant industrial materials with a wide range of applications in the auto and aviation sectors and in biomedical applications [9]. The degree of acetalyzation, the amount of aliphatic to aromatic acetal moieties, the stereochemistry, and the random or block character of the acetal polymer are all important factors that affect the physical and chemical properties of poly (vinyl acetal) [10]. In the current research polymer metal complex with cobalt and polymer blend with nano chitosan were prepared to develop a new polymer blend material that comprises desirable properties in the biomedical field.

2. Experimental

2.1. Synthesis of Polyethylene glycol acetal

Polyethylene glycol (PEG) (1.5 gm) was first dissolved in (25 ml) H_2O at a temperature of (50 °C), and then the solution was added while mixing. *p*-nitrobenzaldehyde (1.2 g/1 mmole) was added to the solution, which was then stirred magnetically at a temperature of (50 °C) for

24 hours before being neutralized by adding a few drops of (5 N) NaOH solution. Crude products have been washed with acetone and distilled water many times. The products were dried for 12 hours at a temperature of (40 °C) [11]. Moreover, figure 1 illustrates the preparation reaction process of polyacetal.

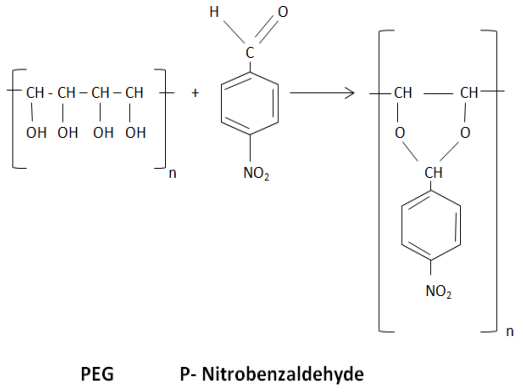

Figure1: The preparation reaction of polyacetal.

2.2. Polymer metal complex preparation

Polyacetal (0.6 g/1 mmole) was mixed with $CoCl_2.H_2O$ (0.2 g/1 mmole) then dissolved in 20 ml of DMSO, heated at 60 °C for 12 hours in a water bath. After cooling, the complex was washed with ethanol and dried for 24 hours at 60 °C in a vacuum.

2.3. Polymer Blend preparation

The polymer blends were prepared by solvent casting method. Polyacetal-Co complex solutions were prepared by dissolving in H_2O at room temperature with stirring. The nano Chitosan was dissolved in 2 % acetic acid to form 5 wt % polymer solutions.

Table 1: The weight fraction of PA-Co/Nano Chitosan Polymer blend.

Polymer blend	PA-Co %	Nano Ch. %
B1	25	75
B2	50	50
B3	75	25

3. Results and Discussion

3.1. FT-IR analysis for polyacetal

Polyacetal FT-IR spectrum that illustrated in figure 2 shows a broad band that located at 3444 cm^{-1}, which corresponds to the (O-H) stretching vibration, 2881 cm^{-1} to the (C-H) symmetric stretch, 1639 cm^{-1} to the (C-C) aromatic vibration, 1344 cm^{-1} to the (CH_3) bending vibration, and at 1105 cm^{-1} that due to the (C-O-C) acetal group of the ligand.

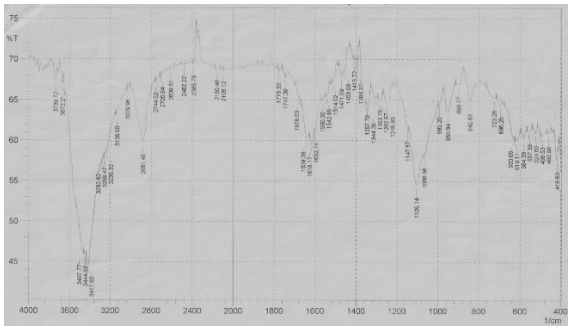

Figure 2: The FT-IR spectrum for Polyacetal.

3.2. Scanning electron microscope studies (SEM)

Figures 3-6 show SEM micrograph for the PEG acetal, PEG-Co complex, and nano chitosan polymer blend. The surface appears to have some inclusions and to be porous. In the presence of *p*-nitro benzaldehyde, the surface morphology of polyacetal exhibits a rough surface appearance. However, on the surface of the matrix, cobalt is present and is seen to be distributed uniformly. The average nano size of the particles in the polymer blend is between (23-47) nm, and (24-58) nm for polymer blend B1 and B2, respectively. After the interaction between the polymers, the surface of the produced blends showed considerable changes as seen in the FESEM figures.

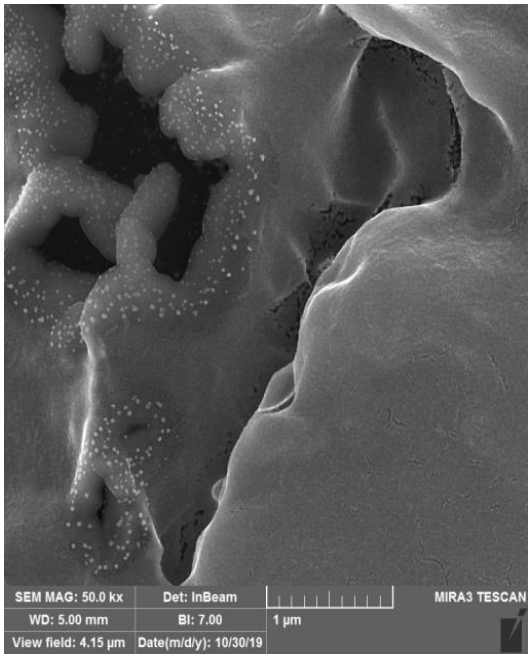

Figure 3: The SEM image of Polyacetal.

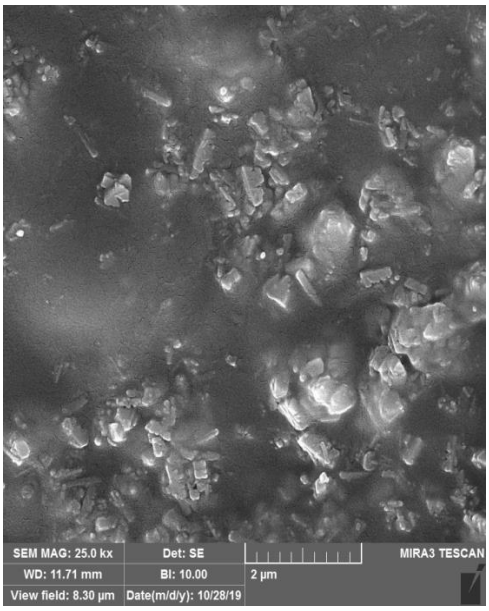

Figure 4: The SEM images of PA-Co.

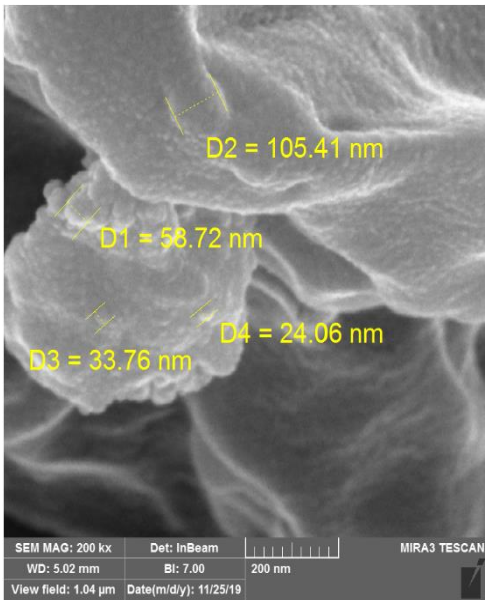

Figure 5: The SEM images of blend 1.

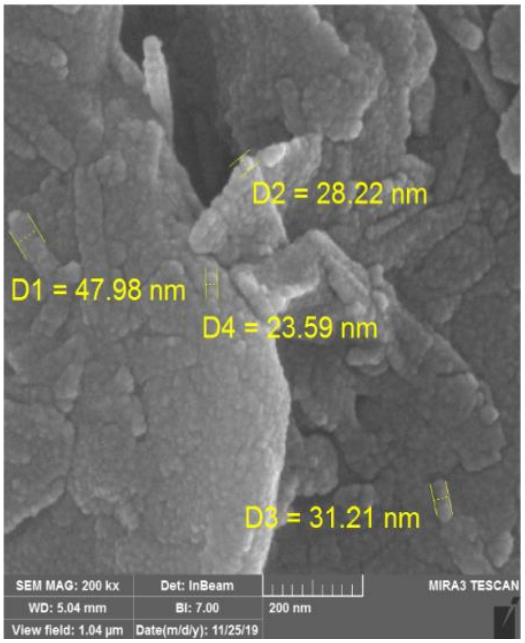

Figure 6: The SEM image of blend 2.

3.3 Thermal analysis

Thermal gravimetric analysis (DSC⁄ TGA) for PA, PA-Co metal complex and PA-Co/nano chitosan polymer blend were measured at temperatures in range from 0 to 600 °C with constant rate of 10 °C per minute. There are three steps concerning continuing mass loss, according to the TGA curve related to polyacetal (figure 7). The first stage is at 318.77 °C with a mass loss of the volatile compounds of -55.84 %. The second step is given at 364.45 °C with a mass loss of 2.981 %. The third step involves the decomposition of the polymer's main chain, at 594.94 °C, and results in a weight loss of approximately -42.798 %. Glass transition temperature Tg for the polyacetal was demonstrated by the DSC curve in the figure at 58.8 °C. Melting temperature point Tm matches with an endothermic peak at a temperature of (233.8 °C). Td at (558.7 °C), thermal decomposition of polymer backbone. The TGA curve for the polymer blend shown in figures 7 and 8 shows four steps for continuous mass loss. The initial step involves a mass loss of -9.475 % for the volatile compounds at (156 °C). The second step is (221 °C) with a mass loss of -4.716 %, and the third step is (338 °C) with side chain decomposition and a weight loss of approximately 17.77 %. The last step at (595 °C) is decomposition, which results in polymer degradation and weight loss of approximately -24.76 %. Glass transition temperature Tg for the polymer blend is illustrated by a DSC curve in at 89.4 °C. Exothermic peak at a temperature of (270.8 °C) related to melting temperature Tm. Thermal decomposition of main chain Td at a temperature of (465 °C). It was observed that after blending all temperatures are shifted slightly and the blend film show only one Tg on its thermogram, this indicates the presence of hydrogen bonding interactions between PA-Co and nano Ch polymer blend and that the two polymers are well blended together.

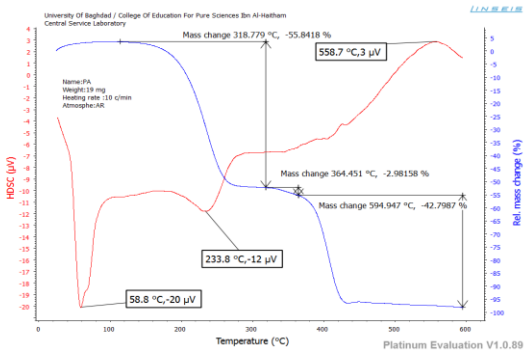

Figure 7: Thermal analysis of Polyacetal.

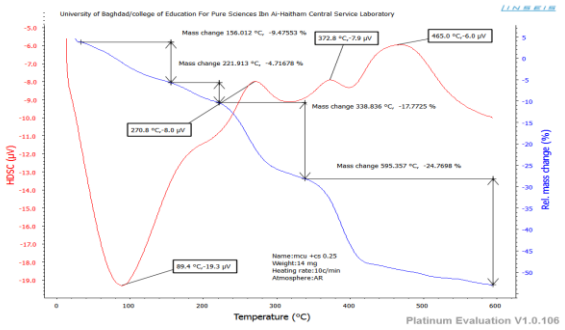

Figure 8: Thermal analysis of PA-Co/Nano Chitosan.

3.4. Biological activity

Through the diffusion inhibition method, the polymer blends' biological activity was evaluated against four different kinds of bacterial pathogens. Table1 illustrates the results of antibacterial activity. Gram positive bacteria (Bacillus subtilis and Staphylococcus aureus) and Gram-negative bacteria (Escherichia coli and Pseudomonas aeruginosa) were used to test the samples' antibacterial activity. Table 1 indicates evident that all the investigated substances have effective antibacterial properties against the growth of both Gram +ve and Gram-ve bacteria, that result in an inhibition zone with a diameter of (28 mm). The prepared polymer blend B3 has comparatively higher antimicrobial activities toward the tested microorganisms, which can be attributed to the higher percentage of PA-Co in the polymer blend.

The mode of action of polyacetal metal complex may be as follows: the protein interactions are mainly responsible for the antibacterial activity for the metal complex compounds because of the electrostatic interactions with proteins. Therefore, proteins are potential targets for the polyacetal metal complex as they normally bear positively charged regions. Besides the (possibly) reversible electrostatic interactions, polyacetals are also able to covalently bind to proteins [12]. This demonstrates the wide applicability of PA in biological fields. Due to the polyacetal ability to inhibit a series of biologically relevant proteins and enzymes, the mode of action of antibacterially active polymer might not be explained by one strict mechanism with one single target but rather by multiple PA–protein interactions affecting several biological pathways at the same time and the sum of these disturbances ultimately leads to the death of the bacterial cell [13].

Additionally, the presence of nano chitosan enhances the activity because the action of the nanoparticles is typically attributed to their small size, which allows them to penetrate through the bacteria's cell membrane. Moreover, the negatively charged lipidic bacterial membrane may interact with the positively charged (PA-Co/Nano Ch), preventing the cells from absorbing nutrients and limiting both cell growth and survival [14].

Table 2: Inhibition circle diameter in mm for the polymer blends.

Compound	*Escherichia Coli*	*Staphylococcus aureus*	*Bacillus cereus*	*Pseudomonas aeruginosa*
B1	20	20	21	23
B2	22	23	22	26
B3	23	24	22	28

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