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Effect of Potassium Dichromate on Properties and Biodegradation of Gum Arabic Based Bioplastic Membranes

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Abstract Gum Arabic (GA) collected from *Acacia senegal* trees was used with polyvinyl alcohol (PVA) to prepare of a series of biodegradable membranes doped and non-doped with potassium dichromate ($K_2Cr_2O_7$). Adding the $K_2Cr_2O_7$ to the GA/PVA blends slightly decreased their crystallinity index (CI) by about 2 %. Increasing the PVA concentration in the chromated GA/PVA blends was responsible for increasing the CI. Adding the $K_2Cr_2O_7$ to the pure GA solution modified its differential thermal behavior whereby the exothermic reactions occurred between 321°C and 433°C were disappeared. The $K_2Cr_2O_7$ increased the heat change drastically for all the bioplastic blends with the highest increase for the pure GA. Adding $K_2Cr_2O_7$ to the pure PVA increased the nanometric particle size (NPS) significantly. Increasing the PVA concentration in a blend had a greater effect than did the $K_2Cr_2O_7$ on the NPS. The buried bioplastic membranes in the control soil had different count and species of microbial communities. The numbers of bacteria and fungi in the initial soil sample were lower than those for chromated GA membranes and were greater than those for the chromated PVA. All bacterial and fungi species had growth ability and are expected to be detoxification tools of chromium ion-doped blends of GA and PVA leading to a green environment.

Keywords: *arabic gum, polyvenyl alcohol, potassium dichromate, bio-degradation*

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1. Introduction

Potassium dichromate ($K_2Cr_2O_7$) known as chromic acid, has a wide range of uses including oxidization in many chemical applications such as dyeing, staining tanning of leather as well as in composite materials. It is also used medically as an external antiseptic or astringent and is present in some veterinary medications. It was found that treating jute fabrics-composites with 0.005-0.03% w/v $K_2Cr_2O_7$ showed better performance, higher thermal stability and superior mechanical properties than those of the control composite. In addition, the tendency of water uptake of the composite was also reduced due to $K_2Cr_2O_7$ treatment. The great improvement in the thermal stability of the composite was attributed to the development of strong fiber-matrix interface [1]. Potassium dichromate solution was used to improve the hydrophilicity of polyglycolide or polyglycolic acid and poly(lactic-co-glycolic acid) fibers by compensating the lack of hydrophilic groups on their surfaces and preserving fiber mechanical property at the same time [2].

Crystallinity is a case of molecular structure among a long range periodic geometric pattern of atomic spacings. In semicrystalline polymers, the degree of crystallinity (crystallinity index, %) influences the degree of stiffness, hardness and heat resistance. In semicrystalline polymers, some of their macromolecules are arranged as crystallites immersed in an amorphous matrix. The greater the concentration of these crystallites, the greater the crystallinity and subsequently more rigidity were obtained for the polymer [3].

Many researchers have reported the capability of bacterial and fungi species to degrade the polyvinyl-alcohol or gum Arabic easily [4,5,6,7,8]. It was showed that GA and PVA may blended together or with other natural polymers to improve their biodegradability, properties, and for producing nontoxic phytochemical scaffold which have therapeutic and diagnosis treatments applications [9,10,11,12,13]. Moreover, in the industrial applications field, solution of gum Arabic is mixed with either potassium or ammonium dichromate as a way of making photographic reproductions, and this is called gum printing [14]. Chromium compounds are used

commercially in industrial welding, metal finishes, leather tanning, and wood preservation [15]. The chromium ion is considered as one of heavy metals that are very essential for biochemical and physiological functions in plants and animals [16]. Although chromium is an essential micronutrient for the growth of many organisms, but at high concentration it is toxic, carcinogenic and cause allergic [17,18,19,20]. Potassium dichromate has many harmful and toxic effects on mammals and rats [16]. For example, toxic effects of potassium dichromate on sex hormones of female albino rats [21], respiratory cancers [17,22], and ototoxicity that cause a wide range of fetal effects [23]. Fortunately, many microbial species have the ability to breakdown a variety of chemical compounds, including aliphatic and aromatic hydrocarbons, fatty acids, insecticides and potassium dichromate, which make them useful for a bioremediation of environmental pollutants [24]. This means that microorganisms can play an important role in the detoxification of potassium dichromate from the polluted places by modifying their chemical and/or physical characteristics and that because the bacteria and fungi species can use chromium (VI) as terminal electron acceptor during oxidation of organic compound [25,26,27]. It was reported that *Bacillus* sp. [25,28], *Escherichia coli* [29], *Pseudomonas* sp. [30,31], *Staphylococcus aureus* IFR-2, and *Pediococcus pentosaceus* IFR-3 [32], are the most bacterial strains having the abilities for detoxification of potassium dichromate, while *Penicillium* sp., *Rhizopus* sp., *Aspergillus* sp. were the most strains of fungi possessing this ability [33,34].

1.1. Objectives

The aim of the current research is to study the effects of potassium dichromate on crystallinity index, mass loss, thermal stability, nanoparticle size and biodegradation of gum Arabic based bioplastic membranes with different ratios of GA and PVA treated and untreated with potassium dichromate.

2. Experimental

2.1. Raw Material

Gum Arabic (GA) with molecular weight (about Mw: 1.827×10^6 g/mole) was collected from *Acacia senegal* trees habitated at Hada Al-Sham (about 120 km apart from Jeddah). The GA was used to prepare of twelve bio-plastic membranes beside ACS reagents of polyvinyl alcohol (PVA, Mw 88000, 88% deacetylated) and potassium dichromate ($K_2Cr_2O_7$, 99%) that were purchased from Sigma-Aldrich, USA. Deionized water was used throughout.

2.2. Preparation of Precursor Solutions

5wt% aqueous solutions of each of AG, PVA and $K_2Cr_2O_7$ were prepared in deionized water as shown by Hindi *et al.* [35].

For the aqueous solution of the GA, the crude granules of the GA were dissolved in deionized water at 80 °C with continuous stirring until all the granules were disappeared. The clear solution was obtained by removal of insoluble components by vacuum filtration using 120 mesh standard screen.

Two groups of blends were synthesized by mixing different ratios of GA/PVA, namely chromated nonchromated bioplastic membranes by using 5wt% aqueous solutions according to the different weight ratios shown in Table 1. The stirring process must be calm to ensure non-introducing much air bubbles into the solution and be extended until obtaining the adequate homogeneity. The bubble free ternary blend solution was poured onto a cleaned acrylic panel (polymethyl methacrylate) with a prominent frame and allowed to be evaporated at room temperature. The membrane thickness was controlled by pouring a definite quantity of blend solution. The acrylic panel was chosen due to its non-sticky characteristic with the blended polymers and the membranes can be easily peeled off the panels after curing and drying. The peeled membranes were kept in vacuum desiccators until utilization.

Table 1. GA/PVA ratio and precursor allocation in 100 mL-blend of bioplastic membrane synthesized from three 5% wt/wt-aquous precursors of gum Arabic (GA), polyvinyl alcohol (PVA) and potassium dichromate ($K_2Cr_2O_7$)

Formula No.	AG/PVA ratio	Precursor allocation in 100 mL		
		GA (mL)	PVA (mL)	$K_2Cr_2O_7$ (mL)
1	1:0	100	0	0
2	1:0.25	80	20	0
3	1:0.5	66.7	33.3	0
4	1:0.75	57.1	42.9	0
5	1:1	50	50	0
6	0:1	0	100	0
7	1:0	85	0	15
8	1:0.25	68	17	15
9	1:0.50	56.7	28.3	15
10	1:0.75	48.57	36.43	15
11	1:1	42.5	42.5	15
12	0:1	0	85	15

2.3. Characterization

2.3.1. X-Ray Diffraction (XRD)

The XRD spectra of the bioplastic membranes were measured by using XRD 7000 Shimadzu diffractometer (Japan) according to Hindi [36]. The system has a rotating anode generator with a copper target and wide angle powder goniometer. The system was performed using CuKα radiation generated at 30 kV and 30 mA. The CuKα radiation consists of $K\alpha_1$ (0.15406 nm) and $K\alpha_2$ (0.15444 nm) components, and the resultant XRD data has both components. The CuKα radiation is separated from the data using a single-channel analyzer on the output from the semiconductor detector. Each of the divergence and scatter slits was 1° and the receiving slit was 0.15 mm at the same radius. Dried bioplastic samples (about 0.5 g) were mounted onto a quartz substrate using amorphous glue. All samples were scanned in 2Θ° range differed from 10° to 30°. All the measurements were performed in the reflection mode at a scan speed of 4° /min in steps of 0.05°.

2.4. Thermal Analysis

This characterization was done for the six formulas. The Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for each formula was performed by using a Seiko & star 6300 analyzer, Central Laboratory, Faculty of Science, Alexandria University, Egypt. Heating scans from 30 up to 550°C at 20°C/min in nitrogen atmosphere were performed for each sample [37].

2.4.1. Surface Roughness (SR)

The SR was investigated by atomic force microscopy (AFM) to study the surficial roughness by Omicron VT AFM. XA [35].

2.4.2. Biodegradation by Bacteria and Fungi

The bioplastic samples were buried in a soil that obtained from Hada Al-Sham at the Agricultural Research Station (ARS) of the Faculty of Meteorology, Environment and Arid Land Agriculture of King Abdullaziz University. The pH of soil in this site is ranging from 7.1 to 7.9, and the organic matter, $CaCO_3$ and cation exchange capacity were low.

2.4.3. Isolation of Microbial Communities

Only one gram of each soil sample was suspended in sterile distilled water. Then, the supernatant was diluted among six tubes by serial dilution method and 1 ml from each dilution was plated in nutrient agar medium NA (Oxoid) for bacterial isolation while using potato dextrose agar medium PDA (Oxoid) for fungi isolates. After that, all the plates were incubated at 30 °C for 2-4 days for the bacterial count and for 3–5 days at 25°C to the fungal count. The isolated microorganisms were identified based on the cultural and morphological characters by using standard biochemical tests [38].

2.4.4. Sample Preparation and Soil Burial Studies

At a depth of 10 cm, the different bioplastic samples were cut into 2 × 2 cm pieces and buried in the soil that wear in boxes (1L) /sample. The weight for all pieces was between 0.040- 0.038 mg before being placed in the soil. All the soil boxes were placed in the laboratory, and the deionized water was added to adjust the soil moisture. Also, the excess water was excluded by a hole at the bottom of the boxes. After 30 days and 60 days, soil samples were taken carefully to isolate, count the microorganism's community, and to observe the degradation by morphological change in the samples surface [13,39].

2.5. Statistical Design and Analysis

Randomized complete block design was used to evaluate the different properties of the bioplastic blended from twelve different formulas constituted from three aqueous solutions of Arabic gum (AG), Polyvinyl alcohol (PVA) and Potassium dichromate ($K_2Cr_2O_7$). Statistical analysis of the recorded data was done using the analysis of variance procedure and least significant difference test (LSD) at 0.05 according to El-Nakhalawy [41].

3. Results and Discussion

3.1. X-Ray Diffraction (XRD)

All the maximum intensities of the bioplastic membranes doped with $K_2Cr_2O_7$ were obtained around 2θ=19° except for the GA-diffractogram that was shifted to 2θ=22.34° (Table 2) In addition, pure PVA known as a semi-crystalline polymer [42,43] exhibited a sharper peak at 2θ=19.9° (Figure 1 and Table 2).

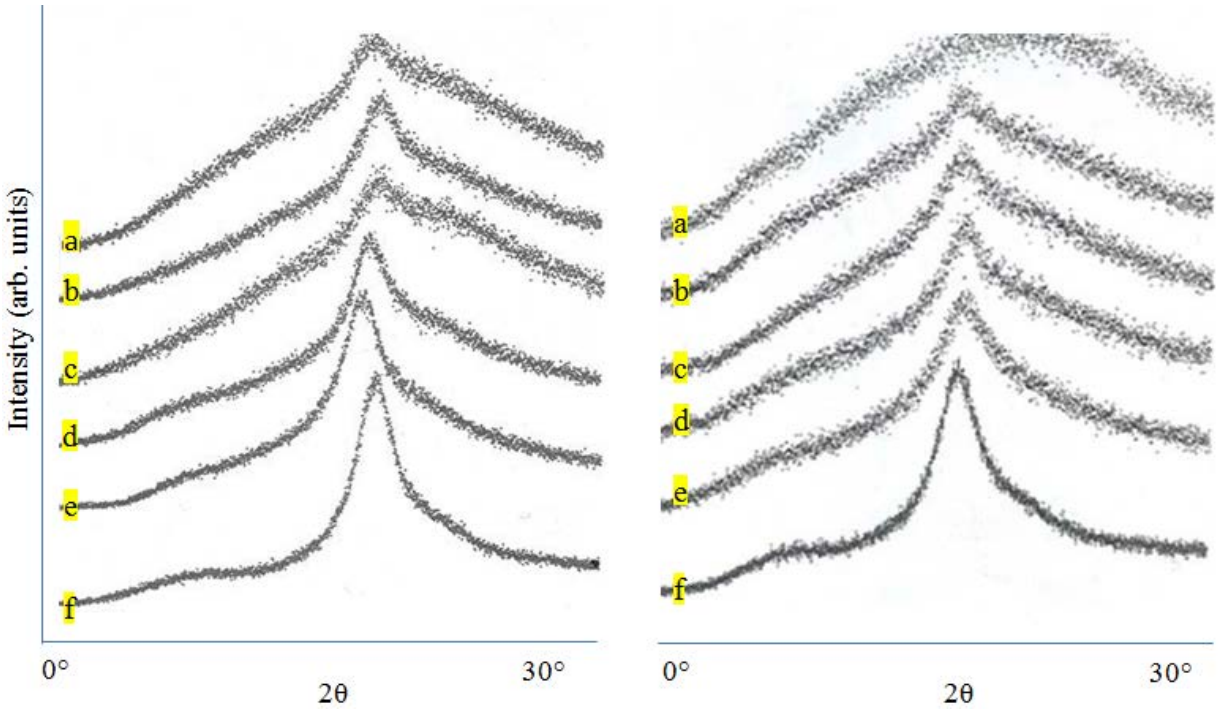

Figure 1. XRD dffractograms of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with different ratios, namely GA/PVA of: a) 1/0, b) 1/0.25, c) 1/0.5, d) 1/1.75, e) 1/1, and f) 0/1 in absence and presence of potassium di-chromate ($K_2Cr_2O_7$).in wavenumber range of 3500 to 500 cm^{-1}

Table 2. XRD results[1,2] of the principle peaks of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with different ratios, namely GA/PVA of: a) 1/0, b) 1/0.25, c) 1/0.5, d) 1/1.75, e) 1/1, and f) 0/1 in absence and presence of potassium dichromate ($K_2Cr_2O_7$).in wavenumber range of 3500 to 500 cm^{-1}

AG/ PVA/ $K_2Cr_2O_7$ ratio	Two Theta		Maximum Intensity (Counts)	
	Non-chromated	Chromated	Non-chromated	Chromated
1/0	19.989[b]	22.34[a]	977[a]	518[b]
1/ 0.25	19.88[a]	19.189[a]	1768[a]	1137[b]
1/ 0.5	20.231[a]	19.637[a]	1071[a]	638[b]
1/ 0.75	19.843[a]	19.443[a]	845[a]	745[a]
1/1	19.722[a]	19.964[a]	1272[a]	673[b]
0/1	19.14[a]	19.455[a]	1622[a]	779[b]

[1]Each value is an average of 3 samples.
[2]Superscripted small letters for comparisons between temperature zones.

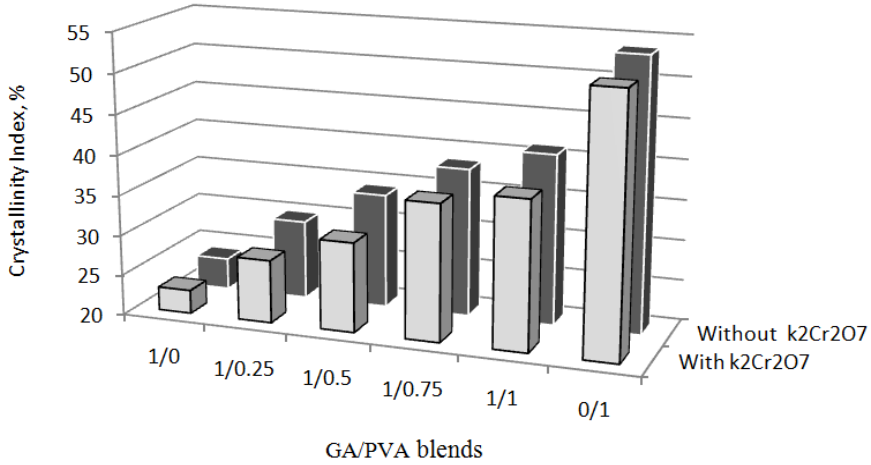

Figure 2. Crystallinity index (CI) of the various bioplastic membranes made from the different gum Arabic (GA)/polyvinyl alcohol (PVA) and potassium dichromate ($K_2Cr_2O_7$) blends

3.2. Crystallinity Index (CI)

The XR-dffractograms presented in Figure 1 were used to determine the crystallinity indices of the bioplastic blends. For the bioplastic blends free of $K_2Cr_2O_7$, the CI values were found to be increased from 22.9% (for pure GA) up to 51.9% (for pure PVA) as shown in Figure 2. Accordingly, it is clear that the increasing in the CI of the bioplastic blends can be attributed to the increasing of the PVA allocation in the blend. In addition, for the bioplastic blended with $K_2Cr_2O_7$, the CI values exhibited the same trend of those free of the $K_2Cr_2O_7$ in which they increased from 22.9 % for pure GA up to 51.9% for pure PVA. Comparing the two groups of bioplastic membranes (with and without $K_2Cr_2O_7$) for their CI property revealed that adding the $K_2Cr_2O_7$ to the GA/PVA blends decreased their CI by about 2 % although there are no statistical difference between them (Figure 2). Within each group of the bioplastic blends, the increase occurred in the crystallinity of blends can be attributed to the increasing the allocate of the PVA in the bioplastic membranes [35] as shown in Figure 2.

3.3. Thermal Analysis

Thermal Analysis (TGA and DTA) was applied to detect the thermal behaviour of the twelve bioplastic membranes as affected by an external change in temperature.

3.4. Thermogravimetric Analysis (TGA)

The TGA measures the mass loss of the bioplastic membranes as a function of temperature and time, in a controlled atmosphere. It was to determine thermal stability and degradation characteristics of the materials examined.

For the bioplastic samples free of the $K_2Cr_2O_7$, it is clear from Table 3 that thermal degradation of the bioplastic samples occurred at the higher temperatures (300-500°C) was higher than that at the lower temperatures (25-300°C). Comparing the mass losses within the temperature regions showed that PVA lost more weight (37.18 % and 32.4%) than that for the GA (18.9% and 16.4%) at the higher temperature zones (300°-400°C and 400°-500°C, respectively). The mass loss occurred up to 100°C can be attributed to evaporation of free water from the samples [35,44]. On the other hand, evaporation of hygroscopic water is responsible to the mass loss occurred at about to 150°C [35,44]. In addition, for the bioplastic samples doped with $K_2Cr_2O_7$, the mass loss property had the same trend for those samples blended without $K_2Cr_2O_7$ whereby they lose more weight at the higher temperatures (Table 3). In addition, adding the $K_2Cr_2O_7$ to the bioplastic blends enhances the mass loss at the higher temperatures. Comparisons within each group of the blends (without and with $K_2Cr_2O_7$), doping the $K_2Cr_2O_7$ in the formulas enhances the mass loss for the GA-based membranes, while the inverse result was obtained for the pure PVA membranes except for the temperature region 200°-300°C (Table 3).

3.5. Differential Thermal Analysis (DTA)

The DTA measures the temperature difference of the sample versus a reference, caused by thermal events in a material. It provides similar information to DSC. DTA usually complements TGA with phase transition information.

The DTA results of the six bioplastic are presented in Table 4 and Figure 3. Comparing the thermograms of pure GA and PVA membranes (GA/PVA=0/1 and 1/0, respectively) revealed that the GA thermogram was differentiated into two distinct regions (endotherm and exotherm), while the PVA thermogram had a unique thermal state termed as endotherm. In addition, the bioplastic thermograms of GA/PVA of 1/0.5, and 1/0.75 had both endo-and exotherms, while GA/PVA blends of 1/0.25, and 1/1 had a unique endotherm. For more details, the temperature range of each thermogram and the maximum temperature of the six bioplastic blends are presented in Table 4. In addition, the absolute values of the heat change values for the endotherms ranged from 1017.3 µVs/mg to 2268.8 µVs/mg and were higher than those for the exotherms (16 µVs/mg -52.4 µVs/mg). In addition, the endotherm of the pure PVA (Formula no. 6) absorbed the highest energy (2119.7 µVs/mg) among the other bioplastic blends, while the GA had the lowest value of the heat change (-1017.3 µVs/mg). The overall energy absorbed up to 500°C and subsequently thermal stability of the bioplastic membranes were increased as the PVA allocation in the blend is increased although the mass loss has the same trend. Accordingly, the PVA is more thermally stable than the GA due to its higher absorption of the heat released that prevents the bioplastic sample from probable thermal degradation caused by increasing temperature. In addition, the thermal stability of the bioplastic membranes was increased with the increasing in the PVA allocation in the blends.

Comparing the heat change extracted from the DTA-thermogram of pure GA (Figure 3a, and Table 4) revealed that without $K_2Cr_2O_7$, the thermogram was divided into two divisions, namely exothermic sub-peak (arisen between 321°C-433°C) and endothermic sub-peak appeared at 31°C and 321°C). In addition, the DTA-thermogram doped with $K_2Cr_2O_7$ exhibited one endothermic sub-peak arisen from 32°C to 487°C (Figure 3b). Accordingly, adding the $K_2Cr_2O_7$ to the pure GA solution modified its differential thermal behavior whereby the exothermic reactions occurred between 321°C and 433°C were disappeared.

In addition, as shown in Table 4, the $K_2Cr_2O_7$ increased the heat change formed upon heat exposure drastically for all the bioplastic blends. For more illustration, the absorbed heat by the endotherms due to addition of the $K_2Cr_2O_7$ were increased from 1017 to 6310, from 2269 to 4062, from 1128 to 3600, from 1276 to 3500, from 1467 to 3309, and from 2120 to 2952 for the AG/PVA formulas of 1/0, 1/0.25, 1/0.5, 1/0.75, 1/1, and 0/1, respectively. Increasing the heat absorbed by such a bioplastic blend is useful to prevent its enthalpy to proceed into its thermal degradation point and subsequently enhance its thermal stability.

Table 3. Mean values of mass loss (%) of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with the different ratios in absence and presence of potassium dichromate ($K_2Cr_2O_7$).occurred upon thermal exposure up to 500°C

AG/PVA	100°-200°C		200°-300°C		300°-400°C		400°-500°C	
	Non-chromated	chromated	Non-chromated	chromated	Non-chromated	chromated	Non-chromated	chromated
1:0	15.7	14.9	13.1	14.9	18.9	22.8	16.4	28.6
1:0.25	10.4	10.3	12.5	17.9	25.4	23.9	18.7	28.8
1:0.5	12.1	10.4	12.7	17.1	23.6	24	26.7	29.8
1:0.75	12	10.8	9.4	16.3	34.5	24.4	22.6	33.9
1:1	10.6	12.2	12.7	19.6	37.2	18.5	24.1	33.3
0:1	16.6	9.9	8.7	33.7	37.18	7.6	32.4	30

Table 4. Differential thermal analysis (DTA) output for temperature range (TR), maximum temperature (MT) and heat change (HG) of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with different ratios in absence and presence of potassium di-chromate ($K_2Cr_2O_7$) upon thermal exposure up to 500°C

Formula AG/PVA	Sub-peak No.	TR (°C)		MT (°C)		HG (µVs/mg)	
		Without $K_2Cr_2O_7$	With $K_2Cr_2O_7$	Without $K_2Cr_2O_7$	With $K_2Cr_2O_7$	Without $K_2Cr_2O_7$	With $K_2Cr_2O_7$
1:0	Endotherm	31 - 321	32 – 487	106	280	-1017	-6310
	Exotherm	321 - 433	-	407	-	+52	-
1:0.25	Endotherm	32 - 500	43 - 471	114	275	-2269	-4062
1:0.5	Endotherm	45 - 421	43 - 468	119	275	-1128	-3600
	Exotherm	421 - 500	468 - 500	465	443	-17	+189
1:0.75	Endotherm	48 -389	32 - 430	127	276	-1276	-3500
	Exotherm	3089 - 500	430-491	422	450	-29	+177
1:1	Endotherm	41 – 384	32 - 433	123	273	-1467	-3309
	Exotherm	-	433 - 500	-	458	-	+132
0:1	Endotherm	45 – 438	136 - 422	220	228	-2120	-2952
	Exotherm	-	422 - 500	-	467	-	-108

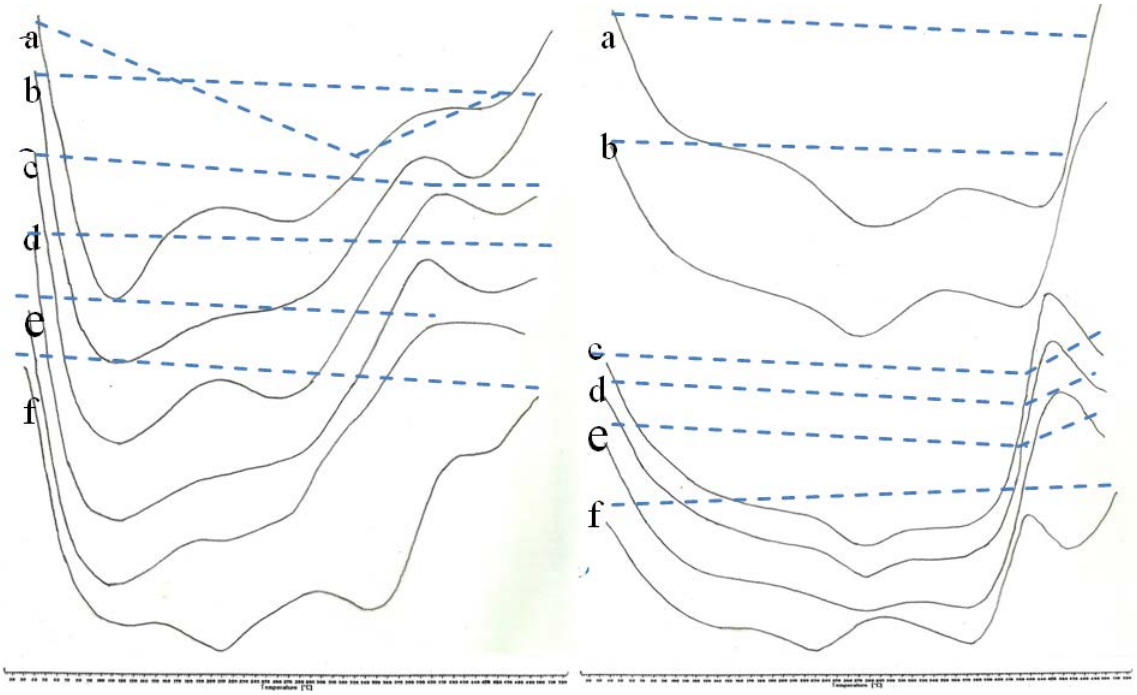

Figure 3. Differential thermal analysis (DTA) thermograms of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with different ratios in absence and presence of potassium dichromate ($K_2Cr_2O_7$) in temperature range from 25-500°C: a-f) GA/PVA ratios: a) 1/0, b) 1/0.25, c) 1/0.5, d) 1/0.75, e) 1/1 and 0/1

Table 5. Some statistic parameters, namely maximum value (Max.), mean, observations number (ON) and standard deviation (SD) of particle size and void volume of the bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with and without potassium dichromate ($K_2Cr_2O_7$)

AG/PVA ratio	Statistic parameters	Particle size (nm)		Void Volum (nm^3)	
		Without $K_2Cr_2O_7$	With $K_2Cr_2O_7$	Without $K_2Cr_2O_7$	With $K_2Cr_2O_7$
1:0	Max.	55.4	71.3	8989	6828
	Mean	13.7	15.7	101.9	92
	SD	7.71	8.8	468	394
	ON	1293	986	1111	986
1:0.25	Max.	76.9	93.5	1886	5458
	Mean	14.2	19.2	89	229
	SD	8.7	13.8	209	483
	ON	1153	572	1231	572
1:0.5	Max.	67	79.9	5219	3392
	Mean	14.4	13.89	73	120
	SD	8.15	9.6	282	250
	ON	1167	1117	1175	1117
1:0.75	Max.	72.3	56.8	10081	1033
	Mean	16.9	12.2	138	61
	SD	9.25	7.1	647	96
	ON	865	1600	697	1600
1:1	Max.	77	52.6	74927	2827
	Mean	19	12.3	520	55
	SD	12	6.3	3660	174
	ON	634	1667	580	1667
0:1	Max.	89.8	116	24725	11541
	Mean	18.9	47.2	415	2793
	SD	14.5	24.8	1705	2491
	ON	564	113	530	113

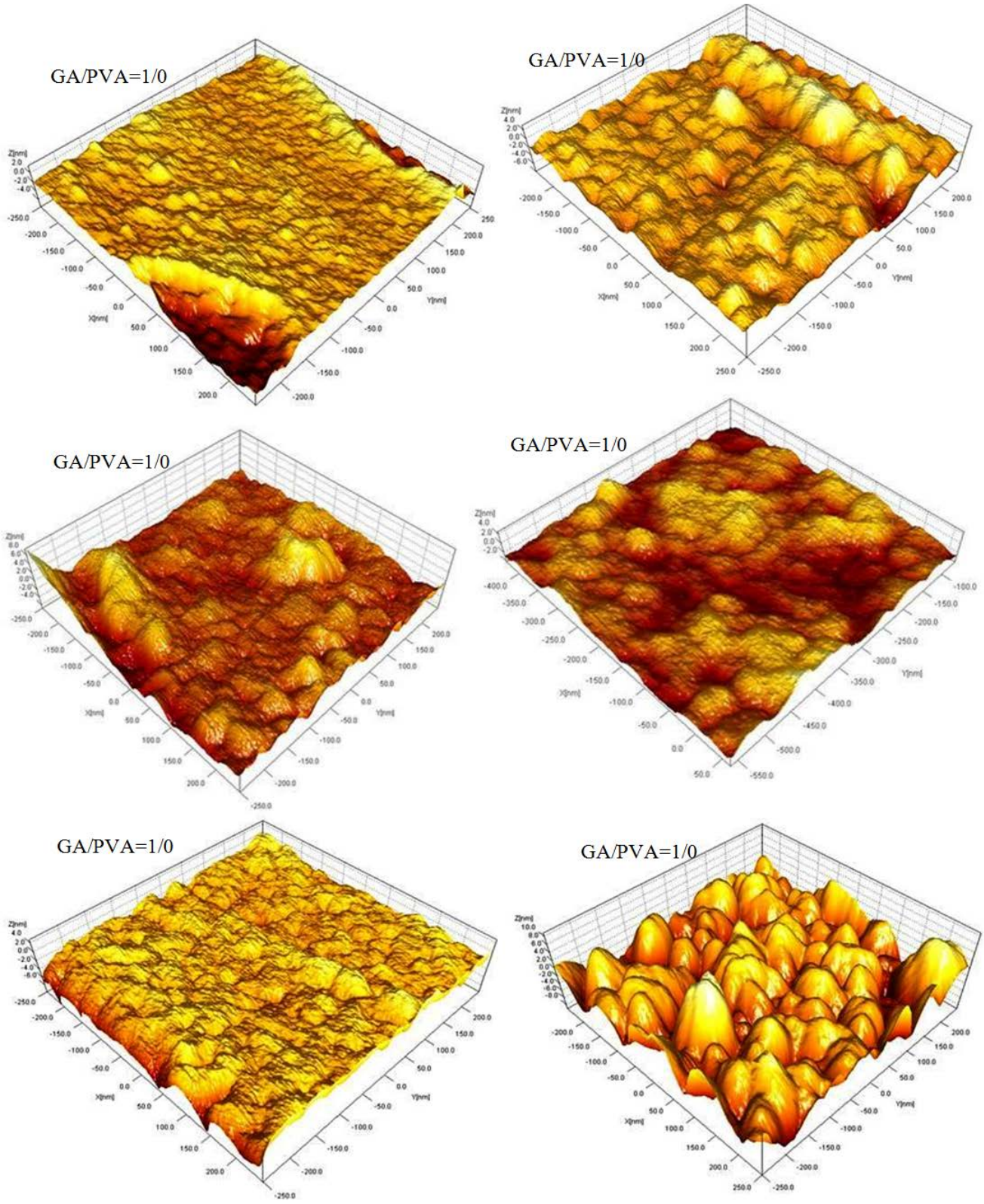

Figure 4. AFM images showing surface roughness of the twelve bioplastic membranes blended from gum Arabic (GA) and polyvinyl alcohol (PVA) with the different ratios in absence and presence of potassium di-chromate ($K_2Cr_2O_7$): a-f) GA/PVA ratios: a) 1/0, b) 1/0.25, c) 1/0.5, d) 1/0.75, e) 1/1 and 0/1

3.6. Nanometric Particle Size (NPS)

For the nanometric particle size (NPS) of the two groups of bioplastic membranes (doped and non-doped with $K_2Cr_2O_7$) presented at Table 5, comparisons between groups revealed that the non-doped-K_2Cr_2O pure GA membrane had slightly lower NPS than that for the doped one each of mean (13.69 nm and 15.7 nm, respectively) and maximum values (55.4 nm, 71.3 nm, respectively). In addition, the non-doped-K_2Cr_2O pure PVA membrane had lower NPS values (18.9 and 89.8 nm for mean and maximum values, respectively) than that for doped one (47.7 and 116 nm for mean and maximum values, respectively). Accordingly, adding $K_2Cr_2O_7$ to the pure

PVA-based bioplastic blends (GA/PVA-0/1) increased the NPS significantly, while this effect is not clear for the other blends.

Comparisons within the group revealed that increasing the PVA concentration in a blend had a greater effect than did $K_2Cr_2O_7$ on the NPS. Accordingly, increasing the PVA concentration in the bioplastic blends increased the NPS gradually. This can be confirmed by the surface roughness features investigated by atomic force microscope (AFM) as shown in Figure 4.

3.7. Biodegradation Bacteria and Fungi

The microbial population's species data of the colony forming units (CFU) are presented in Table 6. The numbers of bacteria and fungi in the initial soil sample were found to be 2.11×10^5 and 1.3×10^2 CFU/ml, respectively and were lower than that for the chromated GA and greater than that for the chromated PVA (Table 6). The CFU of the chromated pure GA (GA/PVA=1/0) was greater than that for the chromated pure PVA (GA/PVA=0/1) after 30 and 60 days. This means that the GA substrate is more preferred as a nutrient supply for these microorganisms. Also, there were no clear differences in the CFU values obtained after 30 and 60 days for all the six bioplastic membranes.

Table 6. Colony forming units (CFU) of microbial populations for bacterial and fungal species in the six buried bioplastic membranes blended from chromated gum Arabic and polyvinyl alcohol with the different GA/PVA ratios of 1/0, 1/0.25, 1/0.5, 1/0.75, 1/1 and 0/1 as compared with the control soil samples

Chromated AG/ PVA ratio	CFU/ml			
	After 30 days		After 60 days	
	Bacteria	Fungi	Bacteria	Fungi
1/0	2.51×10^5	1.51×10^2	2.33×10^5	1.42×10^2
1/ 0.25	2.11×10^5	1.35×10^2	1.98×10^5	1.37×10^2
1/ 0.5	2.14×10^5	1.37×10^2	2.00×10^5	1.38×10^2
1/ 0.75	2.22×10^5	1.44×10^2	2.32×10^5	1.41×10^2
1/1	2.43×10^5	1.47×10^2	2.45×10^5	1.43×10^2
0/1	1.89×10^5	1.4×10^2	1.73×10^5	1.16×10^2
0/0	2.11×10^5	1.3×10^2	2.18×10^5	1.5×10^2

The buried bioplastic membranes in the initial soil samples had different number and species of microbial communities. There were different species of bacteria and fungi according to the type of buried membrane and the concentration of the polymer. The buried chromated pure PVA membrane, the dominant species were *Bacillus* spp [25,45,46,47,48,49], *Pseudomonas* spp [27,31,50,47,48], *Aspergillus* spp [51] and *Penicillium* spp [27,47]. In addition, for the buried GA, the major species were *Bacillus* spp [6,12,45], *Penicillium* spp, *Aspergillus* spp, *Rhizorpous* spp, [6,33,34]. This results agree with Coleman and Paran [52] who concluded that Gram-negative chromium reducing-bacteria tend to be more sensitive to chromium ion, while Gram positive bacteria are significantly tolerant to chromate ion toxicity even at relatively high concentration of the ion [25,52]. Moreover, the microbial communities of the bioplastic blends, namely (chromated GA/PVA=1:1), (chromated GA/PVA=1:0.75), (chromated GA/PVA=0.5) and (GA/PVA=1:0.25) contained *Bacillus* spp [25,45,46,49,53], *Pseudomonas* spp [27,31,47,48,50], *Aspergillus* spp, *Rhizorpous* spp, and *Penicillium* spp. [33]. It is worth to mention that *Pseudomonas* spp. are well-characterized heterotrophs known to degrade several hydrocarbons [5,6,7,40], and reduce metals such as Cr (VI) due to these bacteria can use the PVA as a source of carbon.

Also, it is very clear that the detected bacterial species were more than fungal which is not agreed with Mergaert *et al*. [38] who found that the fungal isolates had high capability of utilizing his the membranes as a growth substrate than bacterial isolates. The PVA is a vinyl polymer where the main chain is joined by only one carbon-carbon linkage $(-CH_2-CHOH-)_n$ and this considered to be a good source of carbon for different bacterial and fungi species which leads to increase in cell growth and number [54]. On the other hand, GA is a branched-chain, complex polysaccharide which also is considered to be a good source of carbon for microorganisms [6]. Furthermore, PVA and GA may blended together or with other polymers to improve their biodegradability and mechanical properties which is explain the high numbers of bacterial and fungal species on the blended membranes respectively (chromated GA/PVA=1:0.25), (chromated GA/PVA=1:0.5), chromated GA/PVA=1:0.75), and (chromated GA/PVA) comparing to the number of different microorganisms on the initial soil sample. In addition, the most number of microorganisms species was appeared with GA, and the low number was with PVA [9,10,11,12,55]. In this study, all bacterial and fungi species had a growth ability and are expected to be detoxification tools of potassium dichromate that blended with GA and PVA or both which leads to reduce the high absorption rate of chromium ion by animal, plant, and algae cells in the soil and enhancing the biodegradation of bioplastic membranes [25]. No yeast cells found in our samples and this is not agree with Jadhav *et al*. [33] who proved that yeast are capable to reduce the toxicity of the dye in the environment to the permissible limit of discharge.

4. Conclusions

- All the maximum intensities of the bioplastic membranes doped with $K_2Cr_2O_7$ were obtained around $2\theta=19°$ except for the gum Arabic-diffractogram that was shifted to $2\theta=22.34°$.
- Pure polyvinyl alcohol known as a semi-crystalline polymer exhibited a sharper peak at $2\theta=19.9°$.
- Adding potassium dichromate to the gum Arabic/polyvinyl alcohol blends had a minor effect on reducing their crystallinity index and the increase in the crystallinity of blends can be attributed to the increasing the concentration of the polyvinyl alcohol in the bioplastic membranes.
- Adding potassium dichromate to the pure gum Arabic solution modified its differential thermal behavior whereby the exothermic reactions occurred between 321°C and 433°C were disappeared.
- Potassium dichromate increased the heat change formed upon heat exposure drastically for all the

bioplastic blends with the highest increase for the pure gum Arabic samples.

- Adding potassium dichromate to the pure polyvinyl alcohol blends increased the nanometric particle size significantly, while this effect is not clear for the other blends.
- Increasing the polyvinyl alcohol concentration in a blend had a greater effect than the potassium dichromate on the nanometric particle size of the bioplastic samples.
- The buried bioplastic membranes in the initial soil samples had different number and species of microbial communities.
- The numbers of bacteria and fungi in the initial soil sample were lower than those for chromated gum Arabic membranes and were greater than those for the chromated polyvinyl alcohol.
- The buried chromated pure polyvinyl alcohol membrane, the dominant species were *Bacillus* spp, *Pseudomonas* spp, *Aspergillus* spp and *Penicillium* spp.
- For the buried chromated pure gum Arabic, the major species were *Bacillus* spp, *Penicillium* spp, *Aspergillus* spp and *Rhizorpous* spp
- The colony forming unit of the chromated pure gum Arabic was greater than that for the chromated pure polyvinyl alcohol which means that the GA substrate is more preferred as a nutrient supply by these microorganisms.
- There were no clear differences in the colony forming units obtained after 30 and 60 days for all the six chromated bioplastic membranes.
- All bacterial and fungi species had a growth ability and are expected to be detoxification tools of chromium ion that blended with GA and PVA which leads to reduce the high absorption rate of this ion by animal, plant, and algae cells in the soil and enhancing the biodegradation of bioplastic membranes.

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