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Preparation and Characterization of Polymer Blends/ Kaolinite Nanoclay

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Abstract

In this research, we prepared a polymer blend of polyvinylalcohol (PVA)/carrageenan/kaolinite by means of the solution cast approach. The composition of the blend was PVA in 1 gm by weight with 0.2 gm carrageenan as a plasticizer. The ratio of nanoclay varied between 1 and 5 wt%. Different properties were investigated in this study such as water vapor permeability, hardness, tear strength, color stability, thermal stability, and antibacterial activity. Water vapor permeability was decreased with increasing the ratio of nanoclay, while the values of hardness, tear strength, color stability, and thermal stability were increased. Also, the antibacterial activity examination with two types of bacteria, *e.g.* Gram positive (*Staphylococcus aureus*) and Gram negative (*Klebsiella pneumonia*), showed inhibition zone diameter which was increased with increasing nanoclay ratio. Moreover, it was found that nanoclay has the ability to kill both Gram positive and negative kinds of bacteria. It was found that the preparation of such films is suitable for food packaging.

Keywords: PVA, Carrageenan, KaoliniteNanoclay, Packaging food, Mechanical properties, Thermal, and color stability.

تحضير وتوصيف خلائط بوليمرية – اطيان الكاولين النانوي

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الخلاصة

في هذا البحث تم تحضير خلائط بوليمرية من بولي فينيل الكحول – كارجينان – طيان االكاولين النانوي باستخدام طريقه الصب . المتراكب المحضر يتكون من 1 غرام بولي فينيل الكحول مع 0.2 غرام كارجينان كملدن ونسب من 1−5 نسب وزنية من الكاولين . اجريت عدة فحوصات مختلفة لهذه الدراسة منها نفاذية الماء , الصلادة , متانة التمزق , استقرارية اللون , الاستقرارية الحرارية , والفعالية البكتيرية . وجد ان نفاذية الماء تقل بزيادة النسب الوزنية للكاولين النانوي وكذلك الصلادة ومتانة التمزق واستقرارية اللون والاستقرارية الحرارية . الفعالية البكتيرية تم اختيار نوعين من البكتريا الموجبة والسالبة وجد ان قطر التثبيط يزداد بزيادة النسب الوزنية وهذا يعني ان الكاولين له القابلية على قتل البكتريا وبكلا النوعين وقد وجد ان الاغشية المحضرة مناسبة للاغلفة الغذائية .

1. Introduction

Composites materials of polymer/nanoclay are employed in manufacturing applications, such as construction (building sections and structural panels), food and textiles packaging, automotive (gas tanks, bumpers, interior and exterior panels), pharmaceutical, parts (flame agent panels and

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high-performance components), and chemical (catalysts) processes [1]. In addition, food packaging materials with sufficient mechanical strength, barrier properties, thermal stability, unit area, bio-degradability, bactericidal actiivity, and inhibitory properties are necessary for food safety and increasing the shelf time of packaged foods [2]. Natural compound materials such as polyvinyl alcohol (PVA) gained a remarkable attention as perishable products owing to their low value and potential advantages. However, their poor barrier properties and sensible mechanical properties as compared to plastic materials, raise a serious limitation to the use of biopolymer films for food packaging applications [3]. Nanoparticle crammed composites, a category of nanostructured materials composed of assorted polymers and fillers, have superior physical, mechanical and alternative properties [4]. Clay raw materials and structures are those with the dominant morphology. Depending on the clay kind, the individual layers can be composed of multi (two to four) sheets of either $[AlO_3(OH)_3]^6$ octahedra or $[SiO_4]^-$ tetrahedra. The alumino-silicate layers organize themselves with a daily Van der Waals gap between them that is known as the associate interlayer [5]. Nanoclays are environment-friendly, of low-cost, and easily provided; therefore, they are utilized in completely different applications in several fields, such as medical and biomaterial applications [6]. Nanocomposites are new materials where a minimum of one-dimensional filler is distributed within the micromillimeter point of an eternal matrix. They need to be gained excellence and success when the primary booming development of composite nylon compounds with improved mechanical properties [5]. Since then, nanocomposites are a serious space of analysis. The nanocomposites have shown improved mechanical and thermal properties; shrunken flammability and barrier properties than each micro- and macro-composite materials. The filler loading; their form, ratio and their affinity towards matrix material are among distinctive parameters that play a significant role in modifying the properties of composites [7]. The nanocomposites may well be ready by many strategies like the direct combination, in-situ chemical process, and melt interaction [4]. The dispersed filler can be of the shape of the sphere, tube, fiber or lamellae [7].

In the current investigation, we have prepared packaging film from blend polymers with nanoclay and improved some mechanical, thermal, and biological properties.

2. Experimental details

Both PVA and Carrageenan are bought from Shanghai kudu Industrial development comb., Ltd China (mainland), while Nanoclay [Kaolinite nanoclay $Al_2Si_2O_5(OH)_4$], with purity> 99%, purchased from Shanghai kudu Industrial development comb., Ltd China (mainland).

The surface morphology of nanoclay powder was detected with AFM micrographs as shown in Figure-1. It emerges that the average diameter for nanoclay particles is 60 nm.

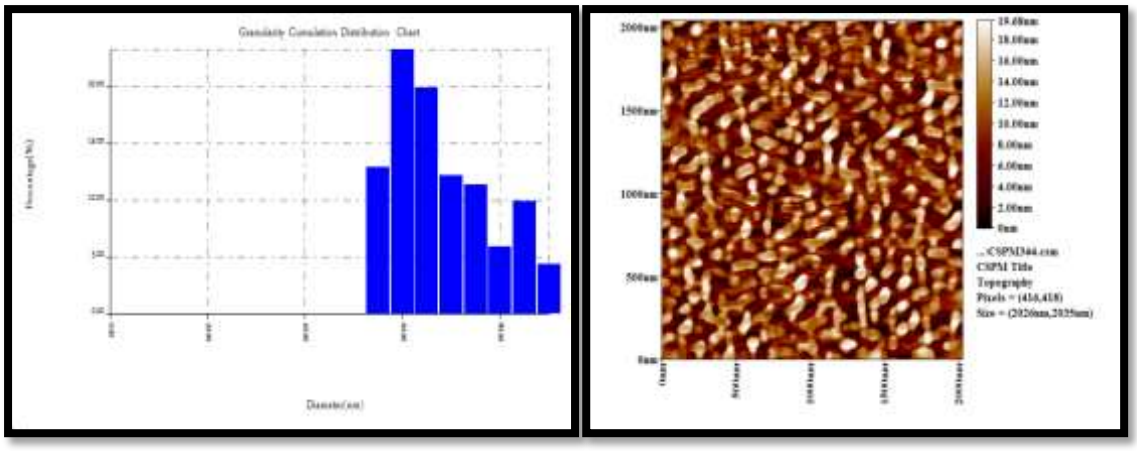

Figure 1-Granularity normal distribution diagram for Kaolinite nanoclay particles.

Polymer blend of PVA/carrageenan was made via a solution cast technique. The composites consist of PVA in 1 gm by weight with carrageenan 0.2 gm as a plasticizer. The ratios of nanoclay are 1,3,

and 5 wt%, where each of these ratios was cast on the bases of glass (petri dish) and left to dry at room temperature as shown in Figure-2.

Figure 2-Specimens of blend PVA/carrageenan/nanoclay nanocomposites.

Tear resistance referencing"ASTM D624" a customary check to understand the tear properties of a cured material check specimen to that a particular "cut" has been created to initiate the "tear". The tear could be a smart description, however well the fabric would possibly wear below physical demands. Again, attributable to the low crosslinking, cured gels exhibit terribly low tear strength [8]. Critical tearing energy (N/m), T_c, computed from the following equation [9]:

$$\boldsymbol{T_c = \frac{2F}{t}}$$

Where $\boldsymbol{F}$ is the tearing force and $\boldsymbol{t}$ is the specimen thickness. Additionally, the hardness of the cured material tested as penetration, Type "A". Penetration, the softest durometer, is tested on a penetrometer. The penetrometer permits an outlined foot, or probe, to push into the cured specimen at an outlined force manufacturing an activity. Referencing ASTM D 2240, kind "A" durometer is measured by solidifying a specimen a minimum of 0.25 thick and putting it on a take a look at the stand with kind "A" indenter. The indenter is forced down into the fabric at a continuing force and activity is obtained.

The disk diffusion assay method was used to detect the antibacterial activity of the prepared polymers and their various concentrations against a group of Gram-negative and positive pathogenic bacteria, which were previously identified by biochemical methods at the biology department/college of Science-Baghdad university. All bacterial strains were previously inoculated in nutrient broth and incubated at 37 °C for 18 hr. From each nutrient broth culture, 0.1 ml (1×10^8 CFU/ml) was transferred and inoculated on Muller-Hinton agar plates by using a glass spreader, then the polymer disks of different concentrations were placed on the surface of the inoculated plates and were then incubated at 37 °C for 24 hr. Inhibition zones around the disks were measured in millimeters.

Water Vapor Transmission Rate study of the steady vapor flow transmitted in the future (24 h) through a vicinity of a body around 50 cm^2 and thickness is a smaller amount than three metric linear units, with unit g/m^2 for 24 h [10]. Film specimens were mounted horizontally on poly (methyl methacrylate) crammed with water up to 1 cm beneath the film. The cups were placed in associate degree environmental chamber at 25 °C and five hundredth ratio (RH) with atmospheric condition movement at 60 cm^3/min exposed to an eternal flow of air across the top side, whereas bottom facet was exposed to vapor from the moistened pad within the wet cavity. The cups were weighed each hour for an amount valuable was noted typically when 6-8 h.

Thermogravimetric analysis (TGA) is a thermal analysis technique that consists of mensuration mass changes of a specimen at the identical time with increasing temperature in an exceedingly controlled atmosphere. The temperatures vary 50-500°C and also the heating rate was 10 °C/min.

3. Results and discussion

Nanoclay is ready by adding 1–2 mg clay in an associate equal quantity of KBr and ground to fine powder, the ranges from four hundred to 4000 cm^{-1}. In Figure-3 it's been according to that peak intensity at 3421 cm^{-1}, 3340 cm^{-1} resembling O-H stretching for the silicon oxide and water and 1633 cm^{-1} connected to (O-H bending) could also because of the presence of water molecules from wetness. Si-O-Si bond is confirmed from 1043 cm^{-1}. The peaks at 920 cm^{-1} to from Al-OH-Al deformation of alumina octahedral sheet, there are distinctive bands because of tetrahedral sheet SiO_4 close to 700 cm^{-1} in layer salt that's used for specific mineral identification. Bands at 2930 cm^{-1}, 1314 cm^{-1} to C-H vibrations of methylene group teams (asymmetric starching and bending) and 484 and 520 cm^{-1} attribute the presence of bonds like Si-O-Al and Si-O-Si. which agree with [5].

As well characteristic vibrations and attributed vibration modes for pristine PVA-carrageenan were ascertained as 3339 cm^{-1} (O-H stretching), 2942, 2912 cm^{-1} (alkyl C-H stretching), 1436, 1424 cm^{-1} (C-H bending), 1093 cm^{-1} (C–O stretching). Signals associated with residual acetate teams within the compound were ascertained at 1707 cm^{-1} (C=O stretching with unit H-bond), 1377 cm^{-1} (CH3 group) and 1238 cm^{-1} (C-O bending) [11].

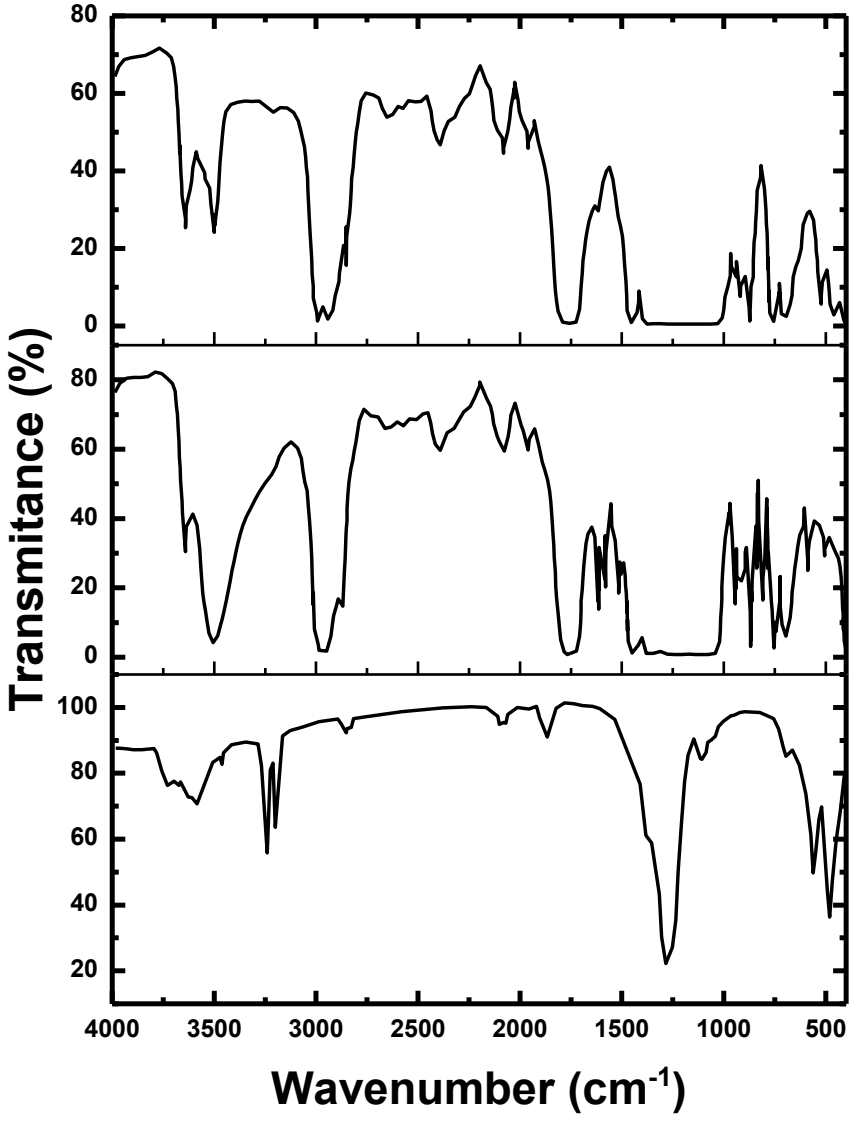

Figure 3-FTIR of Blends/Kaolinite nanoclay polymer with different content of nanoclay.

FTIR of blend PVA with carrageenan was shown in Figure-3. The film shows a broad peak at 3200-3300 cm^{-1} which is attributed to the strong inter and an intramolecular hydrogen bond between PVA-carrageenan and nanoclay. The peak at 2880 cm^{-1} corresponds to C-H stretching vibrations. The absorption peak at 1016 cm^{-1} is attributed to the stretching vibration of Si-O-Si bond. Characteristic peaks of C-O and C-C vibration bands of glycosidic bonds appear in 1200-800 cm^{-1}.

Tear strength is outlined because the resistance force that a specimen, changed by cutting or slitting, offers to the propagation of the tear. a mess of taking a look at specimen configurations has been conferred for tear take a look at Ref. [12]. The values for the tear strength of elastomeric materials with good tear properties are in the range 50-100 kN/m, and values over 100 kN/m are excellent. As ascertained from Figure-4, tear strength for 0.5-millimeter thickness of the composites increases from 67.21 to 75.30 kN/m because of the nanoclay content accumulated from 0 to 5%.

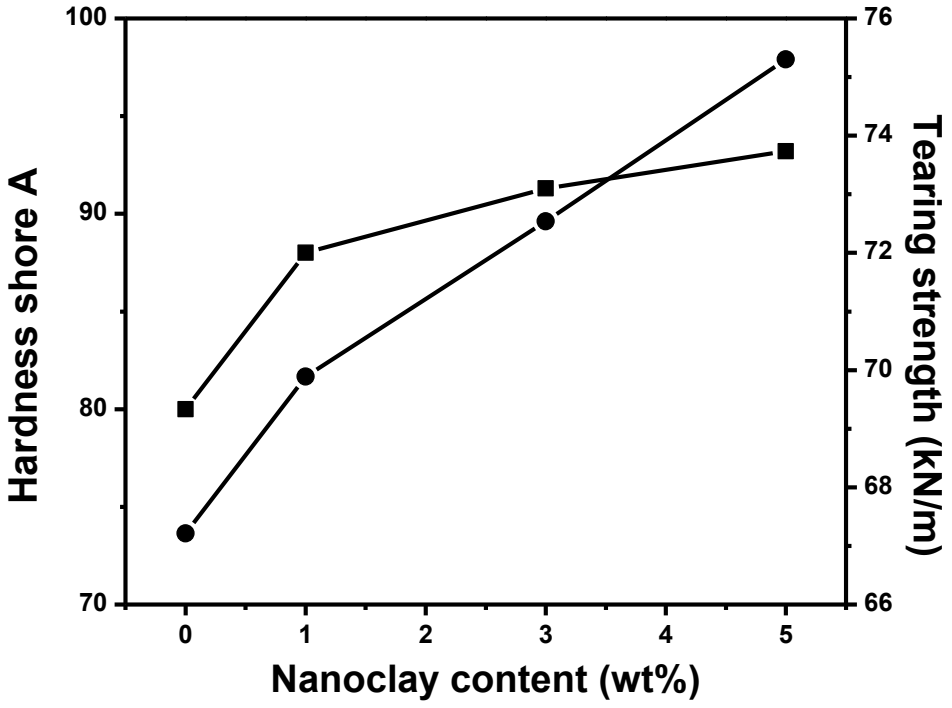

Figure 4-Values of hardness shore A (■) and tear strength(●)of the blend and nanocomposite as a function of nanoclay content.

The hardness knowledge of nanocomposite is shown in Figure-4. It is seen that the hardness depends on the amount of nanoclay additional to the chemical compound mix. The addition of just 1% by weight of nanoclay increases the hardness of pure polyvinyl acetate and carriage by 10% whereas the hardness increment will reach 16.5% by adding 5% by weight of nanoclay. The hardness results show that the incorporation of nanoclay to the PVA/KC mix causes dressing with higher hardness, which in good agreement with published work by Kokabi et al. [13].

Color is important factors to be considered in food packaging since it could influence consumer acceptance and commercial success of a food product, PVA/KC blend is highly transparent and colorless in the visible region of the spectra (wavelength (λ) =400–700 nm) that have transparent is 92.4% appear in Figure-6 shows Color parameter of blend PVA/KC and PVA/KC/nanoclay composites. When nanoclay is added to the film specimen, a slight decrease in lightness values (L^*) was observed when increasing nanoclay content and about 74.1% for nanocomposites with 5% nanoclay and 92.4for blend PVA/KC. Brightness is percentage reflectance of light at wavelength 457 nm show that high brightness in blend PVA/KC that is 79.2% and for nanocomposites is ranged (40.3-

57.2) % that appear high transparency of blend PVA/KC compare with blend/clay nanocomposites because the structure of nanocomposites being optically clear that is copied to the thickness of every clay layer that's smaller than the wavelength of visible radiation that agrees with [14].

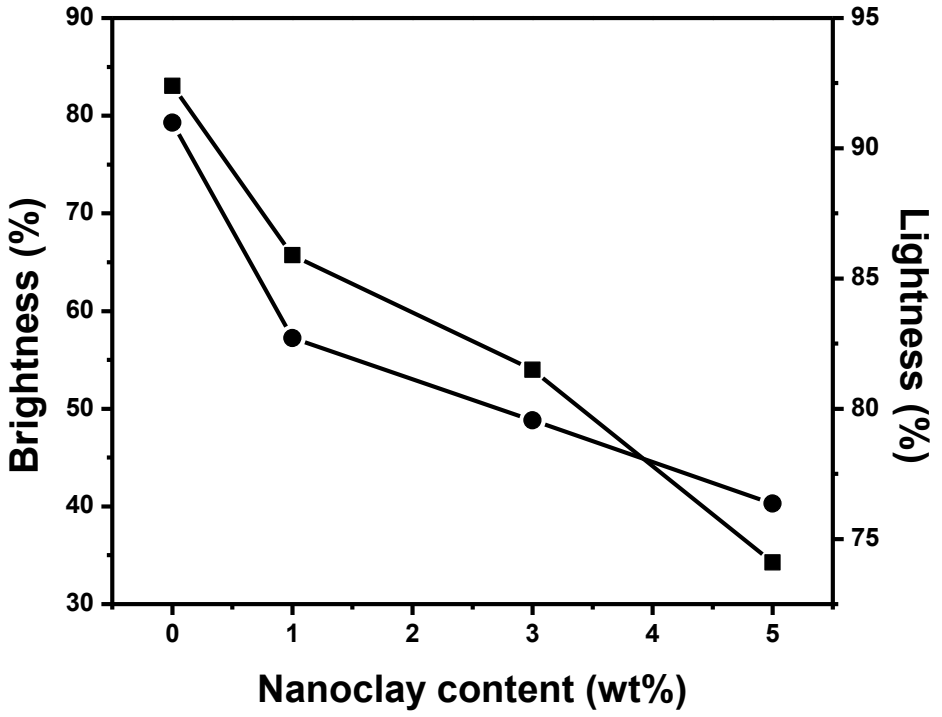

Figure 5-Brightness (●) and Lightness(■) of blend and nanocomposite as a function of nanoclay content.

The antibacterial activities of blend PVA/KC and PVA/KC/ nanoclay films were examined for their inhibitory effects against the growth of Gram-positive bacteria (Staphylococcusaureus) and Gram-negative (Klebsiella pneumonia) to find the antibacterial increase with increasing ratio of nanoclay due to the nanoclay it has the ability to kill bacteria both positive and negative shows in Figure-6 and Table-1, which agree with [15].

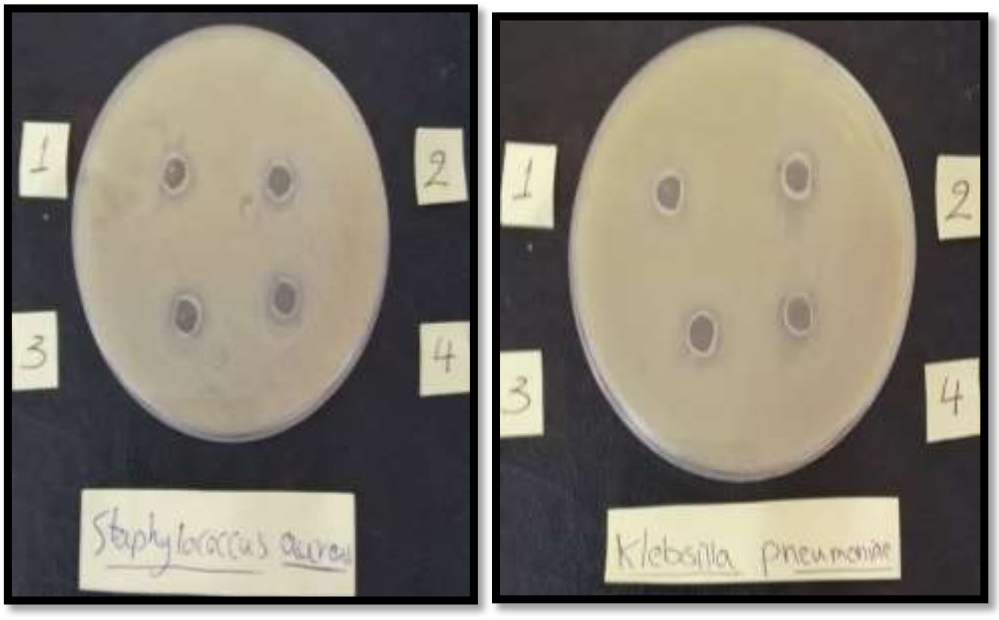

Figure 6-Antibacterial activity of blend PVA/KC and nanocomposites

Table 1-Antibacterial activity as the inhibition zone diameter (mm) of blend film and nanocomposites.

Specimens	N	Staphylococcus aureus (mm)	Klebsiella pneumonia (mm)
0	1	10	-
1%	2	12	10
3%	3	14	11
5%	4	15	12

Nanoparticles filling the pores within the macromolecules structures will decrease water vapor porousness [16]. Figure-7 shows the result of nanoparticle additions on the water vapor transmission rate through mix and nanocomposites films. for sure, the introduction of nanoparticles considerably weakened water vapor porousness (WVP) of mix films. Also, alternative researchers have shown the positive effects of nanoparticles on WVP. In fact, nanoclay improves the barrier properties of chemical compound films to water vapor transmission, which agree with [17].

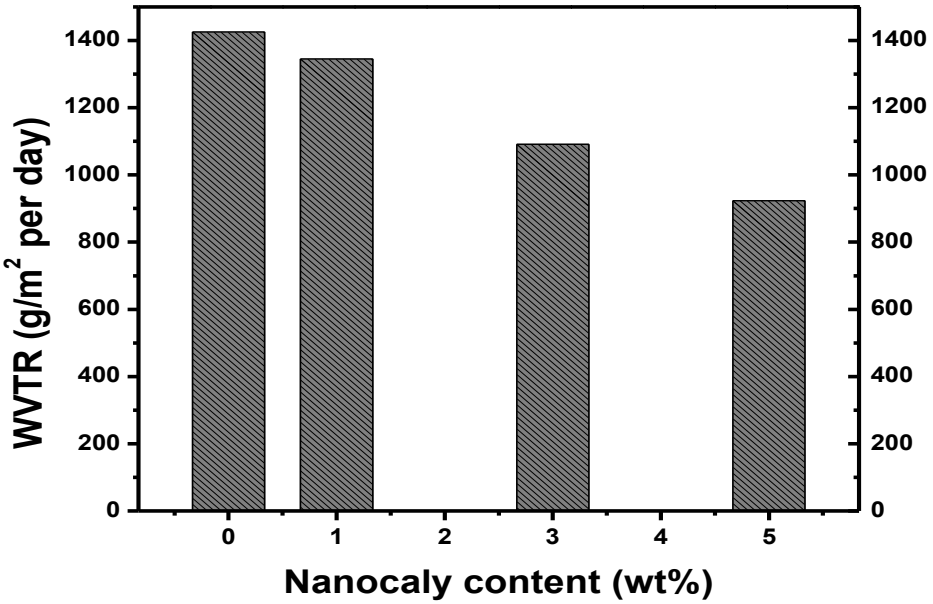

Figure 7-Water vapor transmission rate (WVTR) of blend and nanocomposite as a function of nanoclay content.

The thermal stability of PVA and nanocomposites was investigated victimization TGA below the chemical element. the information obtained area unit is shown in Figure-8 there are unit 3 steps of thermal degradation of the nanocomposites within the temperature vary of 100 ºC – 500 ºC. The temperature varies for the primary step of thermal degradation (Td) is 100 ºC–200 °C. This corresponds to the loss of water from the PVA and nanocomposites. The temperature varies for the second step of Td is 250 ºC – 400 ºC. This corresponds to the decomposition of fillers nanoclay and weight loss of vinyl resin from the nanocomposites. There is the third step of Td within the temperature vary of 400 ºC–500 °C below the chemical element. This could be thanks to the oxidization of partly rotten fillers below the chemical element. in keeping with the TGA analysis, adding of fillers improved the thermal stability and thermal stability of the vinyl resin matrix was found to extend with filler reinforcement.The weight loss of PVA & carrageenan blend, 1% nanoclay, and 5% nanoclay 47.04%, 45.12 %, 26.37%, respectively at 496.5 ºC, which agree with [18].

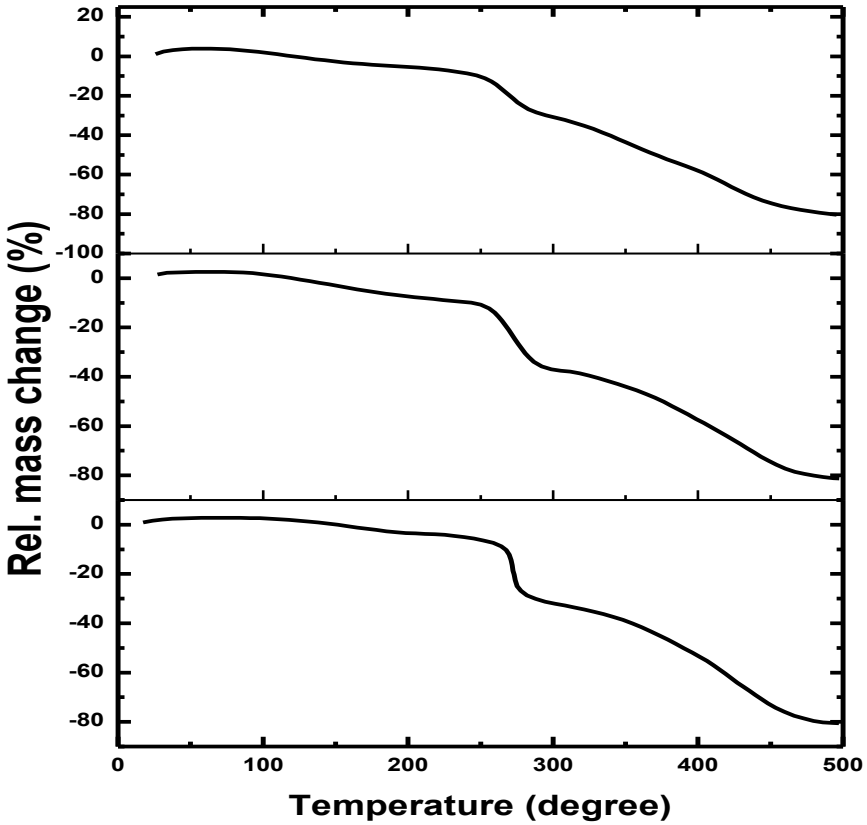

Figure 8-TGA of (a) PVA & carrageenan blend,(b) PVA/carrageenan/1% nanoclay and (c) PVA/carrageenan/5% nanoclay.

4. Conclusion

From the above we can write:

- Kaolinte nanoclay enhances some mechanical strength (hardness, and tear strength) and the best value of the weight ratio of nano was observed at 5 % wt.
- The water vapor permeability, color stability, thermal stability, enhancement when addition of nano with blends PVA& KC.
- Kaolinite nano clay killing bacteria in both types (positive Staphylococcusaureus) and (negative Klebsiella pneumonia) and increased the inhibition diameter by increasing the weight ratio of nanoclay.

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