



Copper(II) and Vanadium(IV) Complexes of New Modified Poly(vinyl chloride) Schiff Base for Catalytic Studies in Knoevenagel Condensation

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At first, new pendant Schiff base PVC-en-3MSSB was prepared by modification of PVC at the presence of ethylene diamine and 3-methoxy salicylaldehyde (3MS). Then, from the reaction of PVC-en-3MSSB and Cu(OAc)₂ or VO(acac)₂, PVC pendant complexes PVC-en-3MSSB-Cu (1) and PVC-en-3MSSB-VO (2) were prepared. All compounds were characterized by FT-IR, XRD, TGA, DTA and TEM. FT-IR and XRD results confirmed the preparation of all compounds. TGA results show that the stability of complex 1 is higher than 2 and PVC-en-3MSSB. In addition, the catalytic properties of the complexes in Knoevenagel condensation for synthesis of 4-hydroxysalicydenebarbituric acid are investigated and the results show that the vanadium(IV) complex has a better catalytic properties.

Keywords: Poly(vinyl chloride), Pendant Schiff base, Modification, Knoevenagel condensation

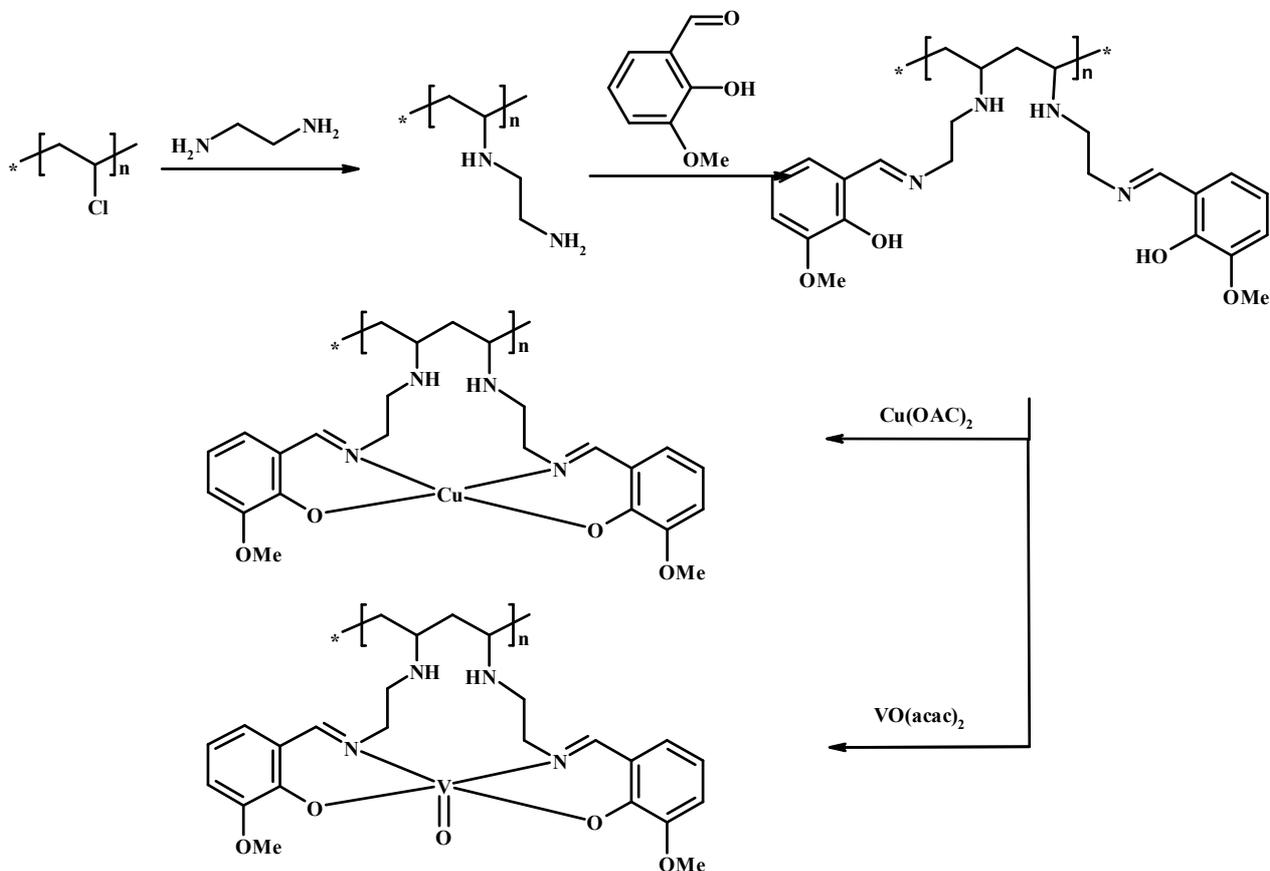
INTRODUCTION

Poly(vinyl chloride) and its modified compounds are one of the most extensive polymers and used in various application due to good properties and also low cost [1-8]. This polymer almost covers one-third of disposed plastic in the world [9]. PVC has poor heat stability and starts to degrade at 120 °C [10], prepared HCl gas and conjugated polyene [4]. Chemical modification is an effective route in reducing the degradability and producing more sustainable materials [11-13]. Yousif *et al.* [2] studied the influence of modification on the photochemical properties of PVC. They reported that the PVC-L-cu was found to be the most effective in the photostabilization process [2]. Theram stability of the vanillin-Schiff's base has been reported by Sabaa *et al.* [3]. Ahmed *et al.* [5] prepared new photostabilizers PVC-Schiff bases from condensation of biphenyl-3,3',4,4'-tetraamine and excess aromatic aldehyde in ethanol in the presence of acetic acid as a catalyst under reflux for 4 h. Elsharif *et al.* [10] reported modification of

PVC by N-phenylitaconimide derivatives. TGA results revealed that the products exhibited high thermal stability. Rajesh Krishnan *et al.* [14] prepared 8 complexes of various Schiff bases supported on PVC as heterogeneous catalysts in the synthesis of β -amino alcohols and in the following [15] reported modified PVC with pendant copper complex as an efficient heterogeneous catalyst in the three-component Mannich reaction. Dong *et al.* [16] reported a PVC supported tetraethylenepentamin (PVC-TEPA) as an efficient catalyst for the Knoevenagel condensation. The UV stability of the modified PVC-Schiff base containing 1,2,4-triazole ring has was tested by Yousif and Ahmed [17] and Ahmed *et al.* [18] and abdallh *et al.* [19]. The modification of PVC is accompanied by the elimination of hydrogen chloride with the insertion of polar groups had caused changes in the color of polymer from white to orange [14-18].

Herein we prepared new modified PVC supported Schiff base and its complexes of PVC-en-3MSSB-Cu (1) and PVC-en-3MSSB-VO (2) complexes (Scheme 1) and characterized by FT-IR, XRD, TGA, DTA and TEM. In addition, catalytic activity of the complexes has been considered in the synthesis of 4-hydroxysalicydene-barbituric acid.

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Scheme 1. General method for the synthesis of PVC-en-3MSSB, PVC-en-3MSSB-Cu (1) and PVC-en-3MSSB-VO (2)

EXPERIMENTAL

Materials and Methods

Poly(vinyl chloride), ethylenediamine, copper(II) acetate monohydrate, vanadium(IV) acetylacetonate, ethanol, 3-hydroxysalicylaldehydes, ethanol, barbituric acid and various aldehydes were purchased from Aldrich and Merck companies and used as received without further purification. Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin-Elmer spectrophotometer. X-Ray powder diffraction was done with a Bruker AXS diffractometer D8 ADVANCE with Cu-K α radiation in the range $2\theta = 10^\circ$ - 80° . TEM images were recorded on transmission electron microscope Philips with CCD camera Olympus Veleta. The TGA and DTA measurements were performed on a Perkin Elmer TG/DTA lab system 1

(Technology by SII) in air atmosphere with a heating rate of $20^\circ\text{C min}^{-1}$ in the temperature span of 30 - 600°C . PVC-en prepared by literature procedure [14,15].

Preparation of PVC-en-3MSSB

PVC-en (2 g) was dispersed in to 15 mL of ethanol and stirred for 5 min, then, an ethanolic solution of 3 g 3-methoxysalicylaldehyde (in 15 mL) was added and mixture was stirred for about 2 h at 70°C . The light-yellow precipitates were filtered, washed with water-ethanol mixture (2:1 v/v) and dried at 25°C (r.t.) for 3 days and characterized by FT-IR, XRD, TGA, DTA and TEM.

Preparation of PVC-en-3MSSB-Cu (1)

PVC-en-3MSSB (2 g) was dispersed in to 15 mL of ethanol in a 50 mL round-bottom flask and stirred for 5 min.

Then, an ethanolic solution of 1 g $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (in 15 mL) was added and mixture was refluxed for about 12 h. The light-brown precipitates were filtered, washed with water-ethanol mixture (2:1 v/v) and dried at 25 °C (r.t.) for 3 days and characterized by FT-IR, XRD, TGA, DTA and TEM.

Preparation of PVC-en-3MSSB-VO (2)

PVC-en-3MSSB (2 g) was dispersed in to 15 mL of ethanol in a 50 mL round-bottom flask and stirred for 5 min. Then, an ethanolic solution of 1 g $\text{VO}(\text{acac})_2$ (in 15 mL) was added and mixture was refluxed for about 12 h. The green precipitates were filtered, washed with water-ethanol mixture (2:1 v/v) and dried at 25 °C (r.t.) for 3 days and characterized by FT-IR, XRD, TGA, DTA and TEM.

Catalytic Activity

The catalytic activity of the complexes under optimal conditions has been investigated as follows: Barbituric acid (5 mmol) was dissolved in hot-water, followed by addition of 0.02 g complex and stirred for about 10 min. Then, the ethanolic solution of 4-hydroxybenzaldehydes (5 mmol) was added to the reaction mixture and stirred until the pale-yellow precipitates of the product has been prepared. The precipitates were filtered, dissolved in hot-ethanol, filtered off to separate the catalyst. Then, by slow evaporation of ethanolic solution after several days the product has been prepared, filtered off and characterized by FT-IR and UV-Vis spectroscopy. Also, melting points of the products were recorded.

RESULTS AND DISCUSSION

The solubility of these compounds in organic solvents is very low and can be said to be insoluble. Therefore the identification of compounds in solution such as NMR and UV has not been performed. The stability of solid compounds at room temperature and light is very high.

FT-IR Spectra

In the FT-IR spectrum of PVC, there are several peaks at about 2900-300, 1401, 1301 and 1223 cm^{-1} [20-22]. After modified the PVC with ethylene diamine and prepared PVC-en, new peaks at about 1471, 1591, 3377 and 3456 cm^{-1}

were appeared that assigned to the N-H vibration. In the FT-IR spectrum of PVC-en-3MSSB new peaks appeared at about 1634 cm^{-1} , is assigned to the -C=N- vibration and confirmed the preparation of Schiff base compound [15] and also the bands at about 3400 cm^{-1} disappeared and appeared new band around 3500 cm^{-1} concerning to the phenolic group (OH). In the FT-IR spectra of 1 and 2, the vibration band concerning to the -C=N- group shifted to the 1615 and 1603 cm^{-1} , respectively, confirmed the coordination of nitrogen iminic group to the Cu(II) and V(IV) ions.

XRD Patterns

XRD patterns of PVC-en-3MSSB and its copper(II) and vanadium(IV) complexes are shown in Fig. 1. In the XRD pattern of the prepared Schiff base PVC-en-3MSSB, the peaks appearing at angles 17, 17.6 and 23° indicate the presence of PVC, which is consistent with the peaks reported by Ammari *et al.* [23]. While, the peaks appearing at angles 35 and 38° can be a reason for the formation of the desired Schiff base compound PVC-en-3MSSB. The low intensity and high width of the peaks indicate that the resulting composition is amorphous. With the coordination of the recycled ligand into copper and vanadium centers and the formation of their complexes, many changes are seen in their X-ray diffraction pattern. These changes and the appearance of peaks with low width and high intensities, can be a reason for the formation of complexes and their crystallinity in the final products.

TEM Images

TEM images of PVC-en, PVC-en-3MSSB and its copper(II) and vanadium(IV) complexes are presented in Fig. 2. In TEM images, spherical shapes with different sizes related to PVC can be seen. By modifying the surface of PVC with amine and then preparing the Schiff base and its complexes, various other shapes with different sizes can be seen in TEM images, which indicate the formation of these compounds. Also, TEM images show that the particles in the complexes are more bonded and agglomerated, which can be attributed to the existence of better intermolecular interaction between the imine and hydroxy groups in these complexes.

TGA/DTA Curves

Thermal gravimetric technique can be used to investigate

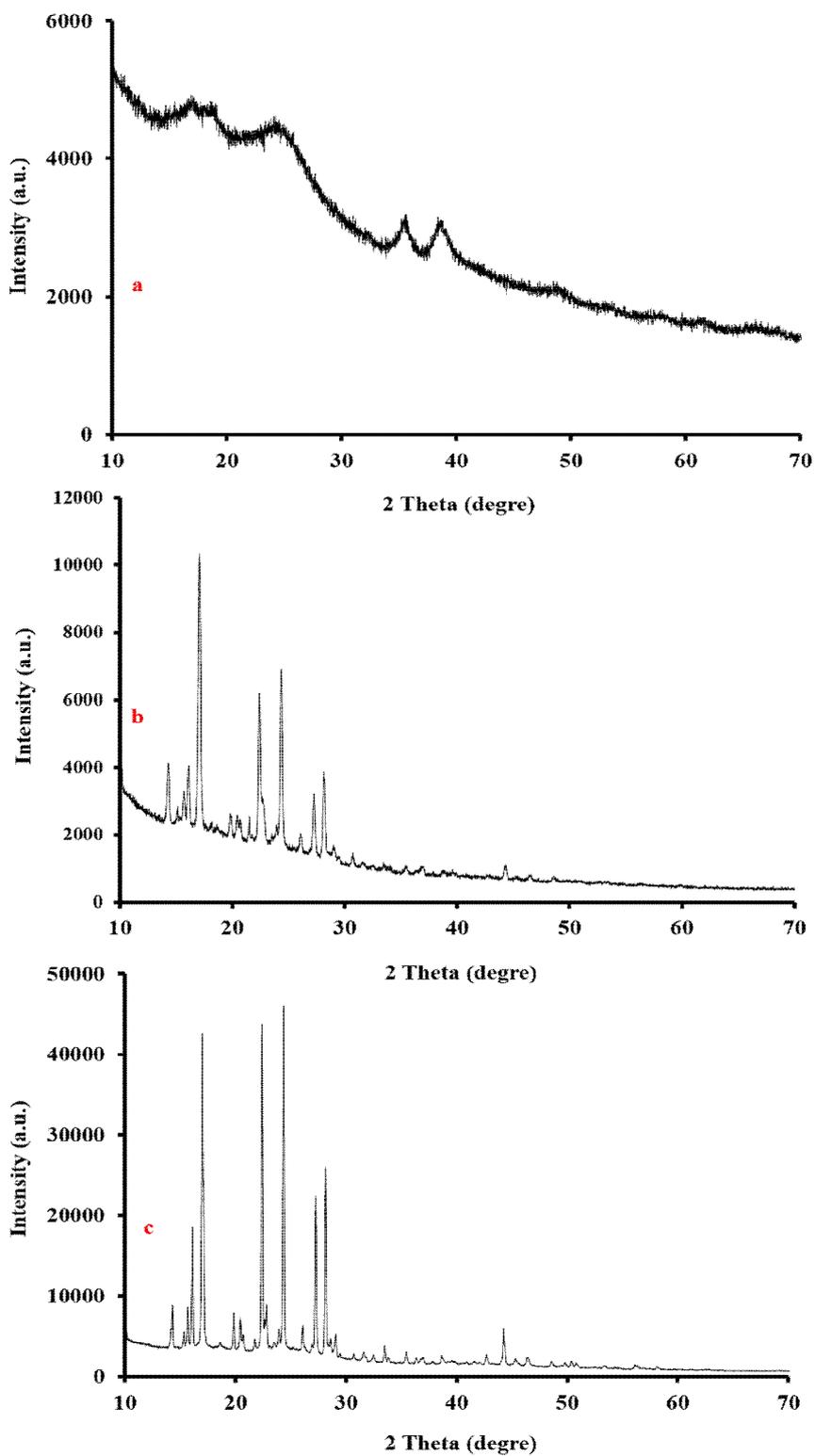


Fig. 1. XRD patterns of a) PVC-en-3MSSB, b) PVC-en-3MSSB-Cu (1) and c) PVC-en-3MSSB-VO (2).

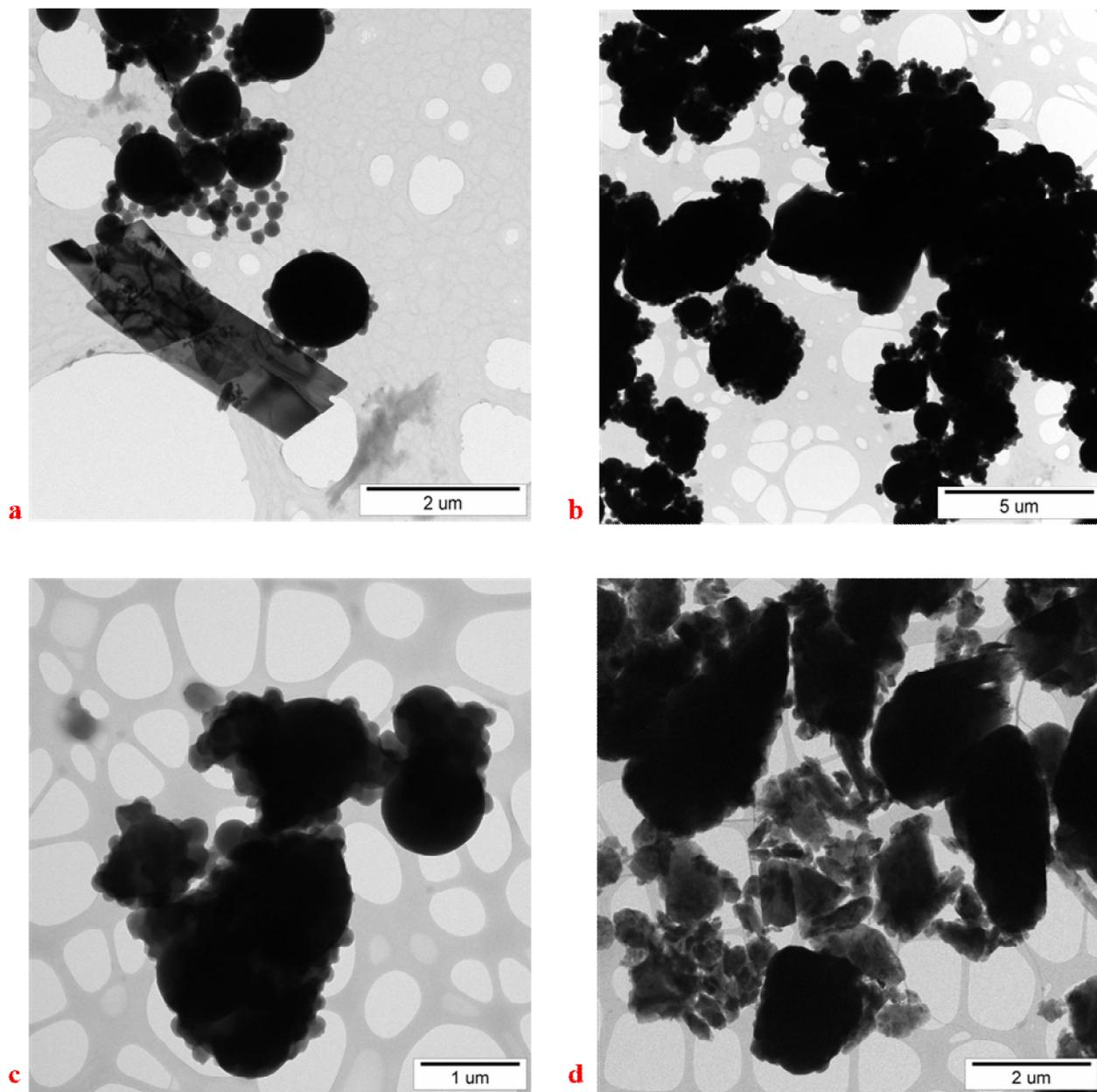


Fig. 2. TEM image of a) PVC-en, b) PVC-en-3MSSB, c) PVC-en-3MSSB-Cu (1) and d) PVC-en-3MSSB-VO (2).

the weight loss of polymers by increasing the temperature. TG/DTA curves of PVC-en-3MSSB and its copper(II) and vanadium(IV) complexes are shown in Fig. 3. TG/DTA curve of PVC-en-3MSSB (Fig. 3a) shows that this

compound lost only about 5.6% of its weight until 200 °C, may be due to the removal of the adsorbed solvent on the compound. Then, in a rapid stage from 200-360 °C, it shows a weight loss of 36.16%. After that, with a lower slope from

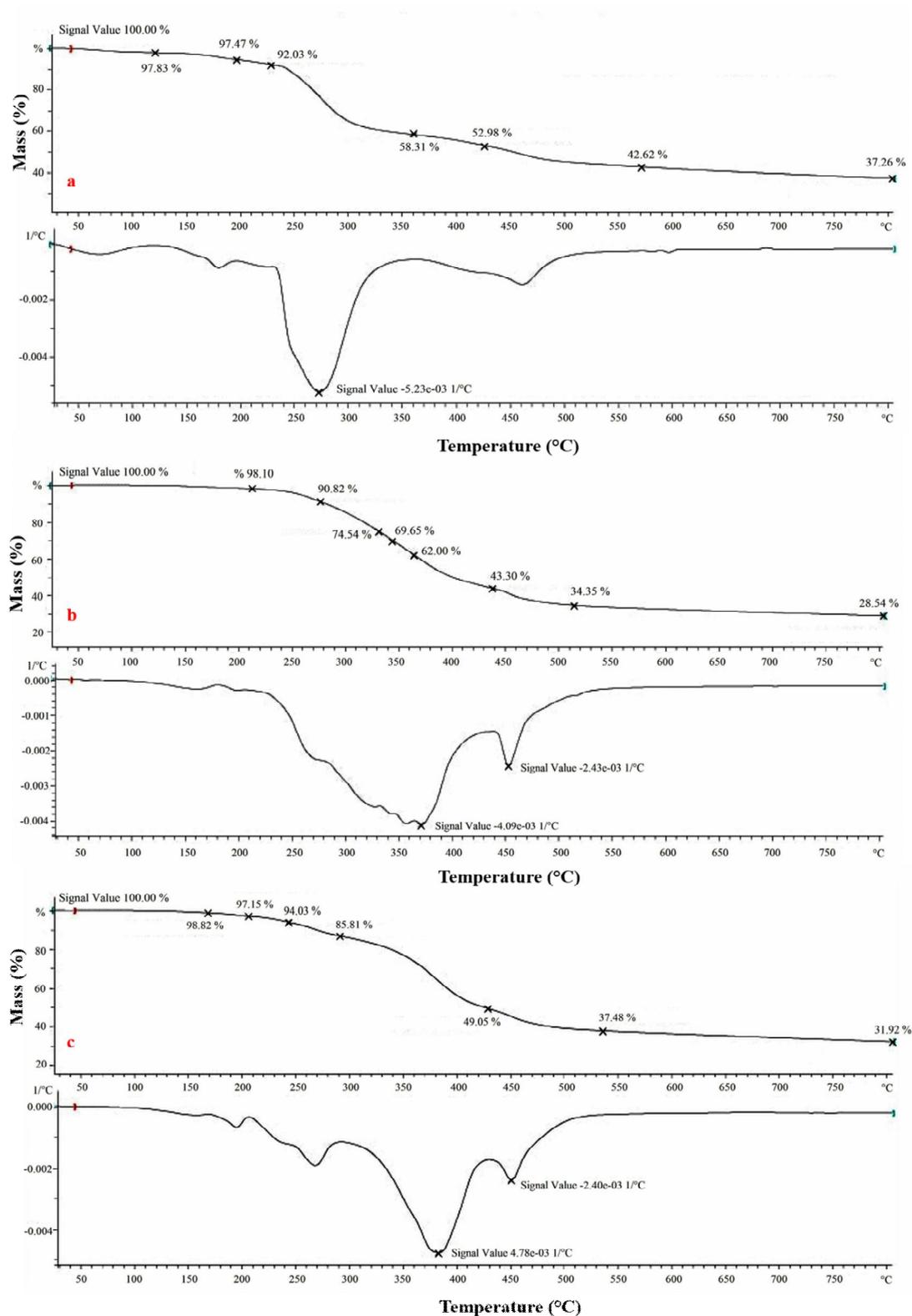
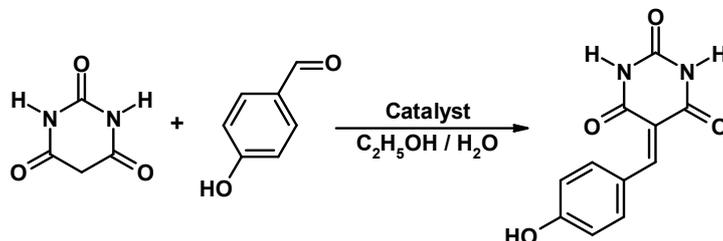


Fig. 3. TGA curves of a) PVC-en-3MSSB, b) PVC-en-3MSSB-Cu (1) and c) PVC-en-3MSSB-VO (2).



Scheme 2. General method for the preparation of 4-hydroxysalicylidene-barbituric acid

360-800 °C, it will lose another 21.05% of its weight. The residual amount of the compound at 800 °C is about 37.26%. In the DTA curve of this compound (Fig. 3a) there is a strong peak at 273 °C, confirmed the heat loss is exothermic. However, two weaker exothermic peaks can also be seen at temperatures around 180 and 460 °C. Figure 3b show that the copper complex has a weight reduction of 1.90% up to 210 °C. After that, in one step and up to 520 °C, it loses another 63.75% of its weight. From 520 to 800 °C, this compound also loses about 5.81% of its own weight. The residual amount of the compound at 800 °C is about 28.54%. In the DTA curve of this compound there is a strong, multiple and broad peak indicating that heat loss is exothermic at temperatures between 230-400 °C and one sharp exothermic peak can also be seen at 450 °C. TGA curve of the vanadium complex (Fig. 3c) show that the complex has lost about 2.85% of its weight by 200 °C. The complex then loses about 10.44%, 37.76% and another 11.57% of its weight in three different stages, from 200-290 °C, 290-430 °C and 430-540 °C, respectively. In the end, from 540 to 800 °C, this compound lost another 5.56% of its weight. The residual amount of the compound at 800 °C is about 31.92%. In the DTA curve of this compound, a strong peak is seen in the temperature range of 320-420 °C, which indicates that this step wishes to release a lot of heat weight. In addition, three other less intense exothermic peaks at 195, 270 and 450 °C are seen for this compound.

Catalytic Activity

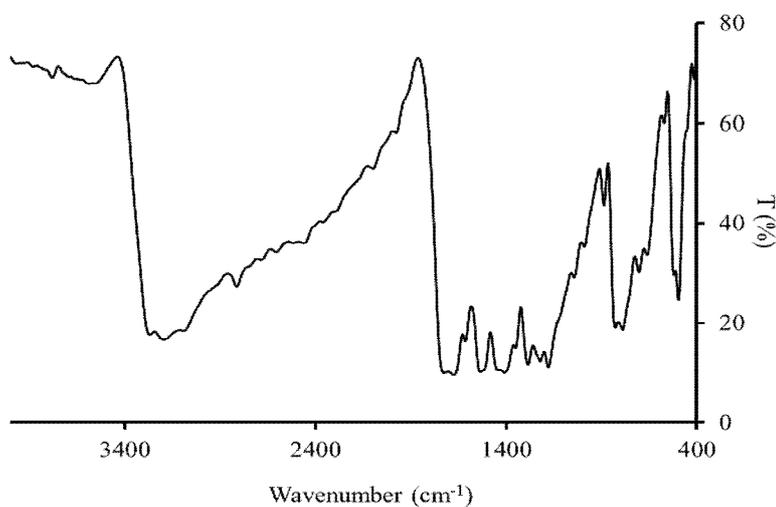
From the reaction of barbituric acid and 4-hydroxybenzaldehyde at the presence of complexes as catalyst at optimal conditions, pale-yellow precipitates of 4-hydroxysalicylidene-barbituric acid (Scheme 2) have been prepared. Melting point of 4-hydroxysalicylidene-barbituric

acid is about 325 °C and is similar to this compound reported [24]. Table 1 presents the different conditions for studying the catalytic properties of the complexes. Due to the low solubility of barbituric acid in solvents such as chloroform, dichloromethane and acetone, therefore the catalytic properties of the complexes in these solvents have not been investigated. Therefore, polar solvents such as acetonitrile, water, ethanol and dimethyl sulfoxide were used to investigate the catalytic properties of the complexes [24-26]. The high solubility of the compound prepared in the dimethyl sulfoxide as solvent and also high boiling point of it, a long time is required to prepare the product, so it can be said that this solvent is not suitable for investigating the catalytic properties of the complexes. According to Table 1, it can be said that the best conditions is mixture of water-ethanol (1:1, v/v) at the presence of 0.02 g of vanadium complex as catalyst. Finally, the 4-hydroxysalicylidene-barbituric acid was characterized by the FT-IR (Fig. 4) and UV-Vis (Fig. 5) spectroscopies.

FT-IR and UV-Vis spectra of 4-hydroxysalicylidene-barbituric acid are presented in Figs. 4 and 5, respectively. The sharp and multiple bands at about 3300 cm⁻¹ assigned to the symmetric and asymmetric N-H stretching. The band appeared at 2812 cm⁻¹ corresponding to the sp² C-H stretching. The sharp and broad band at about 1710 cm⁻¹ confirmed the presence of carbonyl groups. The aromatic C=C vibration are appeared at about 1536-1675 cm⁻¹. Finally, the band appeared at about 1220 cm⁻¹ is assigned to C-N stretching [26]. As shown in Fig. 5, there is one sharp band in visible region at about 390 nm, could be assigned to the n→π* of C=O groups. The pale yellow color of 4-hydroxysalicylidene-barbituric acid is due to the appearance of the end of this peak in the visible area. Two weak and broad bands at violet region at 291 and 257 nm, could be

Table 1. Optimization of the Preparation of 4-Hydroxysalicylidene-barbituric Acid

Entry	Complex	Time (min)	Yield (%)	Catalyst amount (g)	Solvent
1	Cu	10	78	0.01	Acetonitrile
2	Cu	10	82	0.01	Ethanol
3	Cu	10	80	0.01	Water
4	Cu	10	88	0.01	Ethanol-water (1:1)
5	Cu	10	93	0.02	Ethanol-water (1:1)
6	V	7	80	0.01	Acetonitrile
7	V	7	84	0.01	Ethanol
8	V	7	85	0.01	Water
9	V	7	91	0.01	Ethanol-water (1:1)
10	V	7	96	0.02	Ethanol-water (1:1)

**Fig. 4.** FT-IR spectrum of 4-hydroxysalicylidene-barbituric acid.

assigned to the $\pi \rightarrow \pi^*$ of C=C groups of phenyl and ethylene groups.

CONCLUSIONS

In this paper, we prepared copper(II) and vanadium(IV)

complexes of modified polyvinyl chloride-3-methoxy salicylaldehyde Schiff base, and characterized them. The results of XRD and TEM confirm the successful synthesis of the compounds. However, TEM results show that agglomerated in the Cu(II) and V(IV) complexes is more than Schiff base. TG results show different weight reductions

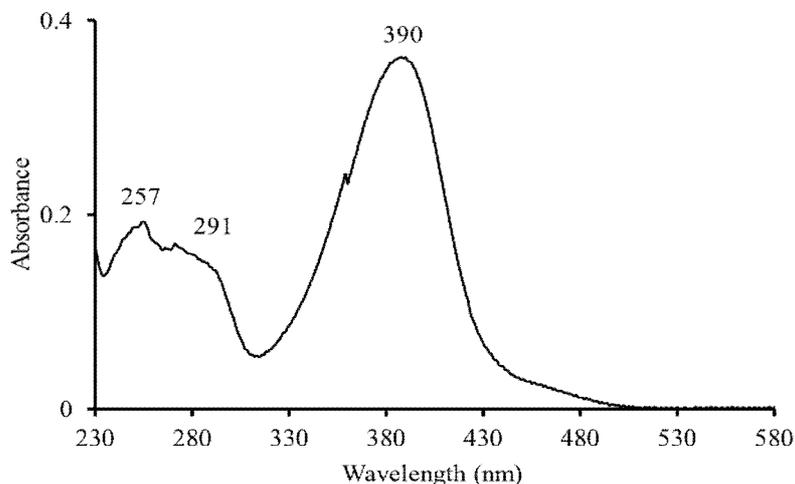


Fig. 5. UV-Vis spectrum of 4-hydroxysalicylidene-barbituric acid.

for the compounds and the stability of the complexes is higher than that of the Schiff base. However, the weight loss begins at the copper complex at higher temperatures than at the vanadium complex. Therefore, the complexes prepared in this paper can be used for application at higher temperatures. Investigation of the catalytic properties of the complexes shows that they show the best performance in the mixture of methanol-water (1:1, V/V) and with increasing the amount of catalyst, the production efficiency increases. Also, the results show that the catalytic activity of the vanadium complex is greater than the copper complex.

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