Synthesis and Characterization of New Polymeric-Schiff Bases and Their Complexes

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ARTICLE INFO	ABSTRACT
Keywords: Modification, Polyvinylalcohol(PVA), Styrene-allylalcohol copolymer(SAA), Morphology, Thermal analysis.	Complexations of three new polymeric Schiff base ligands to transition metals (Ni and Zn) were synthesized via the preparation of a Schiff base ligand on Styrene-allyl alcohol (SAA) and two types of polyvinyl alcohol (PVA). These polymers were a supporting agent for preparing Schiff base ligand on it, followed by complexation with transition metals. Modified SAA and PVA polymers with Ni (II) and Zn (II) have been synthesized in order to investigate some transition metal complexes roles in these polymer modifications. The prepared polymeric complexes were confirmed and characterized by FTIR spectroscopy and TGA instrument respectively. The transition metals (Ni and Zn) content was estimated using SEM-EDX analysis.

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1. Introduction

Schiff base ligands play an essential role in coordination chemistry due to their ease of synthesis and high stability [1]. Schiff base ligand and their metal complexes have been used in various areas of medical, industrial, biological, and catalytical applications [2], corrosion inhibitor [3], catalytic activity [4], antibacterial and antifungal activity [5]. Many researchers have been interested in polymer-metal complexes of Schiff bases because of their applications as semiconductors, electrical insulators, and adhesives [6-10]. Also, they have good thermal stability and photoluminescence activity [11,12]. In the literature, various polymer metal complexes result in Schiff base compounds, and their applications. Bilici et al. prepared polymer- Cu(II) and Co(II) complexes of Schiff bases base on diaminopyridine compound and applied them as a catalyst for oxidation of 2,7-dihydroxynaphthalene [13]. Dogan et al, synthesized polyphenols-metal complexes with Schiff base substitution [14]. Syrlybaeva et al, synthesized polymer-metal complexes of polyacrylonitrile [15]. Alshehri et al, synthesized an epoxy polymeric resin - metals complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions based on 4,7-dihydroxy-1,10-phenanthroline [16].In this work, we reported, herein, two types of polyvinyl alcohol (PVA) and Styrene-allyl alcohol copolymer (SAA) nickel and zinc metal complexes, which PVA and SAA were used as a support for the preparation of poly Schiff base ligand.

2. Material and Methods

2.1 Material

Two types of poly vinyl alcohol (PVA) with degree of polymerization 99% and 75% respectively and Styrene-allyl alcohol (SAA) copolymer supplied from Aldrich Co. Dichloro methylene (DCM), Nickel acetate Ni $(CH_3CO_2)_2.4H_2O)$ and Zinc nitrate Zn $(NO_3)_2.6H_2O$, Salicylaldehyde supplied from Sigma Aldrich Co. Methanol, epichlorohydrin (ECH) and ammonium chloride (NH_4Cl) supplied from Fluka Co. All chemicals were used without any purification.

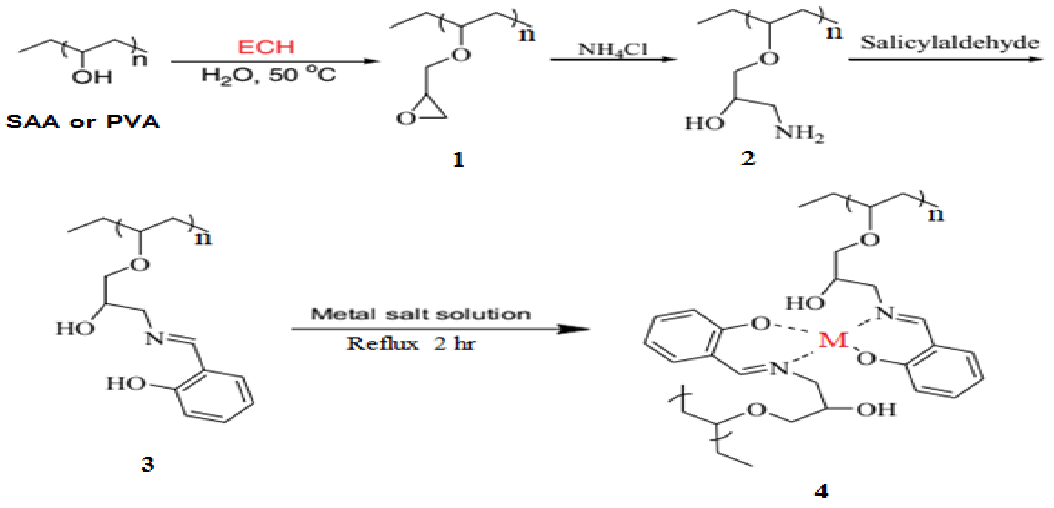
2.2 Characterization instruments

FTIR spectra were obtained using a Shimadzu FTIR 8300 spectrophotometer using a KBr pellet. Thermal studies (TGA) have been performed on a Perkin Elmer Pyris TGA (STA600) in a nitrogen atmosphere with a heating rate of 10°C/min in the 25-800 °C temperature range. SEM-EDX analysis was carried out ing a Carl Zeiss Auriga.

3. Experimental

3.1 Preparation of polymers Schiff base complex

Initially, the preparation of Schiff base ligand 3 (Figure 1), PVA (75% and 99%) (0.2 g) and SAA were added to 20 mL water as a solvent for dissolution of PVAPVA polymers and used DCM for dissolved SAA in a 50 mL round bottom flask at 50 °C and stirred for 20 min in order to complete dissolution. Then, 0.5 mL (5 mmol) ECH was added to the reaction mixture and refluxed at 80 °C for 24 h with stirring. product 1 (Figure 1) was precipitated with addition of 10 mL acetone. Filtered and washed with cold acetone. Product 1 was dissolved in 20 mL of water (for PVA polymers ,while SAA used methanol). Added NH4Cl (0.30 g, 5.60 mmol) to the reaction mixture and refluxed at 80 °C for 24 h to obtain product 2 (Figure 1). Product 2 was precipitated by the addition of acetone and dried in a vacuum oven overnight. For prepared product 3 (Figure 1), product 2 was supplied to a round bottom flask along with 20 mL of water and then salicylaldehyde (1.2 mL, 11.3 mmol) was added to the reaction mixture and stirred for 2 h. Then, 0.9 g of metal salts (Zn(NO3)2.6H2O and Ni(CH3CO2)2.4H2O) was added in 5 min to the reaction mixture and polymers Schiff base complexes 4 (Figure 1) was obtained as a bright green solid for nickel complexes and dark hazel for zinc complexes.



M = Ni(II) and Zn(II)

Figure 1: Preparation of PVA and SAA Schiff base complexes

4. Results and Characterization

4.1 Characterization of polymers Schiff base complex

The schematic diagram for preparing of Schiff base complex-based polymers 4 is shown in Figure 1. Product were characterized step by step by FTIR and thermal studies of complex products 4 were performed by TGA instrument to prove the preparation of product 4 and determine its thermal stability. Proton NMR ^{1}H spectra of polymers complex could not be recorded due to its partial paramagnetic nature of complex as noticed earlier [17]. Preparation and characterization of polymeric Schiff base complex was identified through FTIR instrument in each step (Figures not shown). Only, FTIR spectra of products 4 was shown in Figure 2-7. Epoxidation of PVA and SAA with ECH which represent products 1 in Figure 1, advent of peaks at 960 and 1173-1107 cm^{-1} were related to C-O in epoxy groups. The red shift of these peaks was due to the chelation of Ni and Zn in Schiff base ligand that was shown in FT-IR spectrum [18]. Characteristic peaks were included 3352 cm^{-1} and 3354 cm^{-1} for products 2 in Figure 1 that were related to stretching vibration of -NH$_2$ and 1404-1408 cm^{-1} for its bending [19]. Vibration of azomethine groups in products 3 and 4 in Figure 1 were appeared in 1637 cm^{-1} and 1662 cm^{-1} respectively. These peaks shift to higher wavelengths in the FTIR spectra of products 4 in Figure1, confirming the chelation of Ni and Zn in tetra dentate ligand 3. Also, characteristic peaks of metal bonds (M-O and M-N) appeared in the range 400-690 cm-1. A partial list of FTIR spectral data is presented in Table 1.

Table 1: FTIR spectral data (cm^{-1}) of polymeric complexes

Products	ν cm^{-1} (Stretching)				
	$(C{-}O)_{epoxide}$ ring st,sh	$-NH_2$ primary amino group	$(C{=}N)$ azomethine st,sh	M–O m	M–N M
PVA99[Ni]	1037 - 1103	3354 $1433_{bending}$	1637	420 – 690	
PVA99[Zn]	1037 - 1103	3354 $1433_{bending}$	1637	420 – 690	
PVA75 [Ni]	1037 - 1107	3352 $1404_{bending}$	1620 - 1660	424 – 563	
PVA75[Zn]	1037 - 1107	3352 $1404_{bending}$	1620 - 1660	432 – 650	
SAA[Ni]	960 w,sh	3151 $1408_{bending}$	1662	462 – 690	
SAA[Zn]	960 w,sh	3151 $1408_{bending}$	1662	420 – 690	
w = weak	st = strong	br =broad	sh =sharp	m = medium	

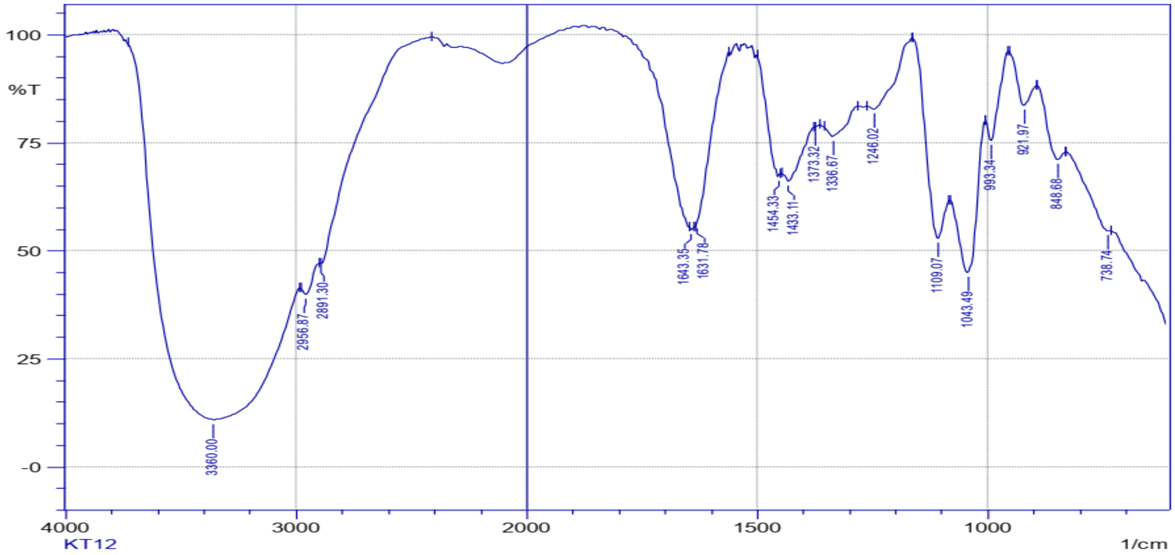


Figure 2: FTIR spectrum of PVA 99[Ni]

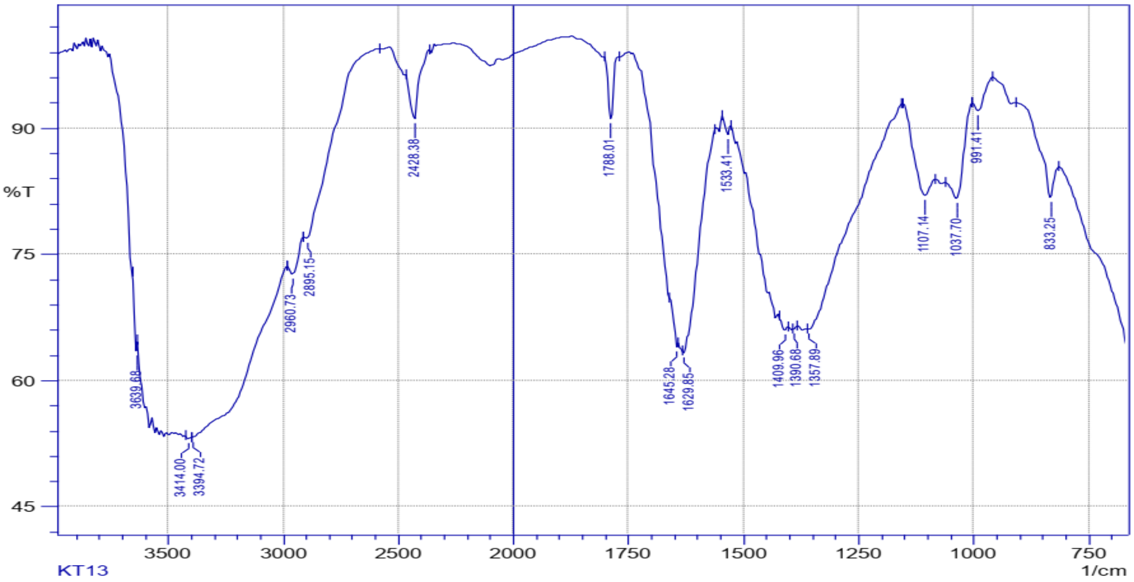


Figure 3: FTIR spectrum of PVA 99[Zn]

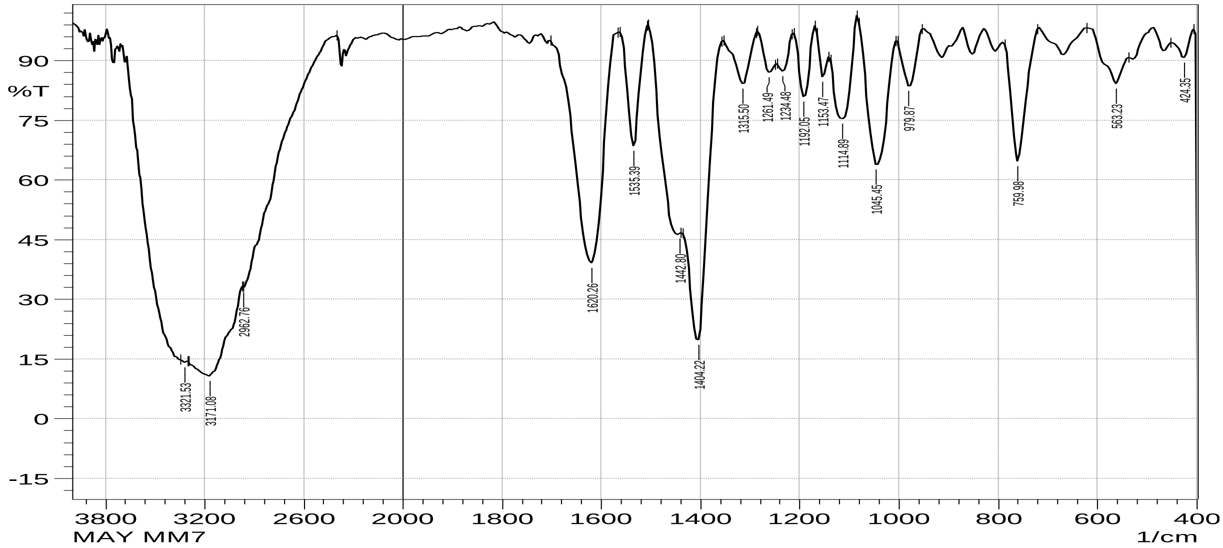


Figure 4: FTIR spectrum of PVA75[Ni]

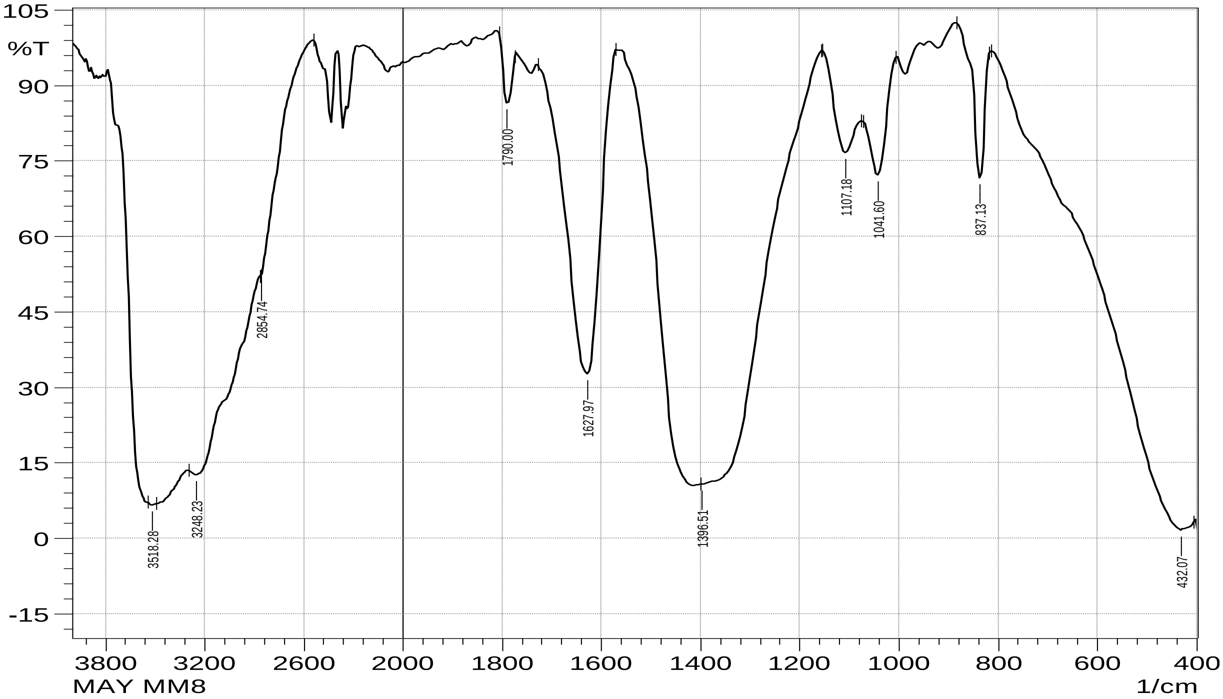


Figure 5: FTIR spectrum of PVA75[Zn]

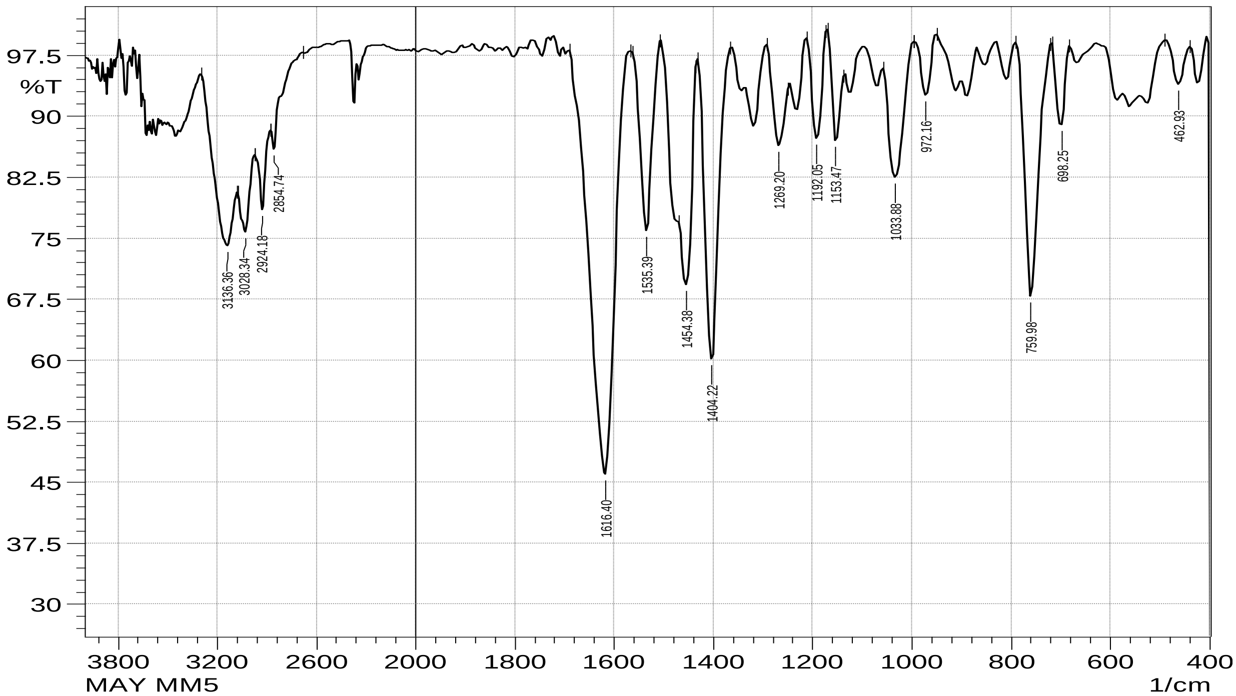


Figure 6: FTIR spectrum of SAA[Ni]

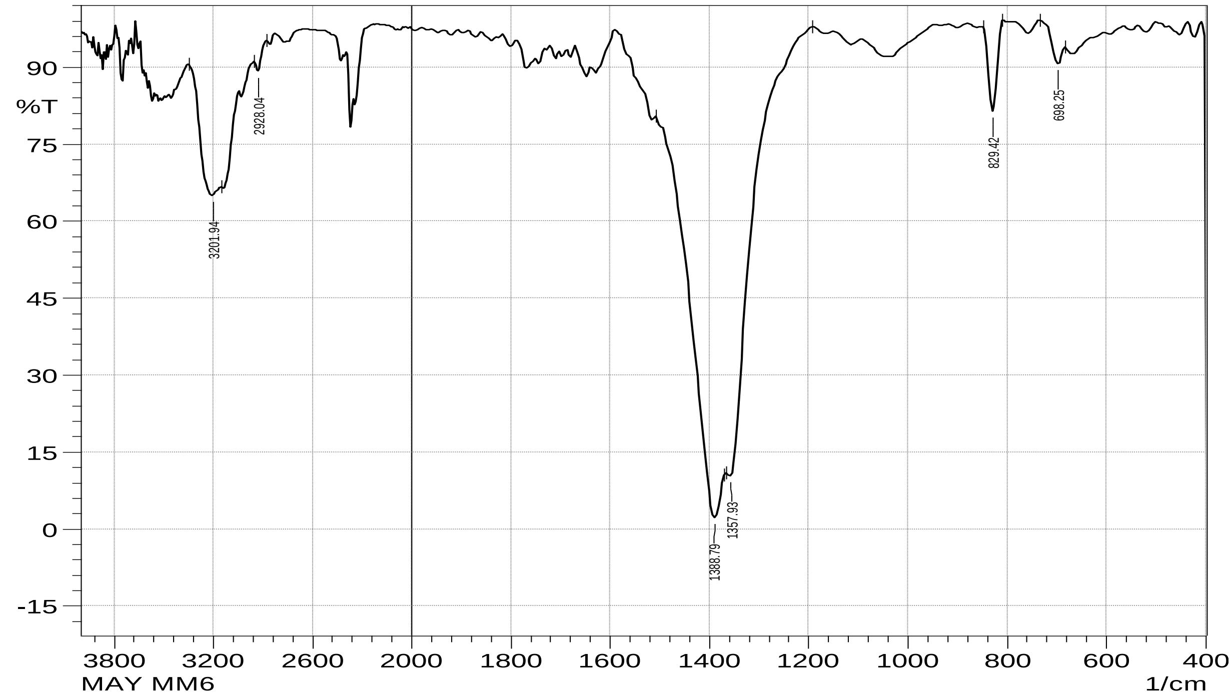


Figure 7: FTIR spectrum of SAA[Zn]

4.2 Scanning Electron Microscopy (SEM)

Analysis of scanning electron microscopy (SEM) of the polymeric complexes typically showed in Figure 8 the morphology of PVA99 and PVA75 and no considerable differences have been observed. The regular crystalline nature and the particle size of the PVA99 and PVA75 nickel and zinc complexes remains unchanged, indicating the complex formation into the polymers matrix. In addition, SAA metal ions (Ni^{+2} and Zn^{+2}) complexes showed spherical micro particles in shape and well-formed rough surface may be due to the strong interaction in between metal ions and ligands through the complex formation [20].

4.3 Energy-dispersive X-ray spectroscopy analysis (EDX)

The nickel and zinc content of the polymeric complexes was confirmed with EDX analysis. Figure 9 shows the EDX spectra of Ni & Zn modified PVA and SSA complexes. The EDX spectrum clearly showed the presence of Ni^{+2} and Zn^{+2} ions on the modified polymer complexes. The peak corresponding to the elemental nickel and zinc for modified PVA and SAA was confirmed by EDX spectra.

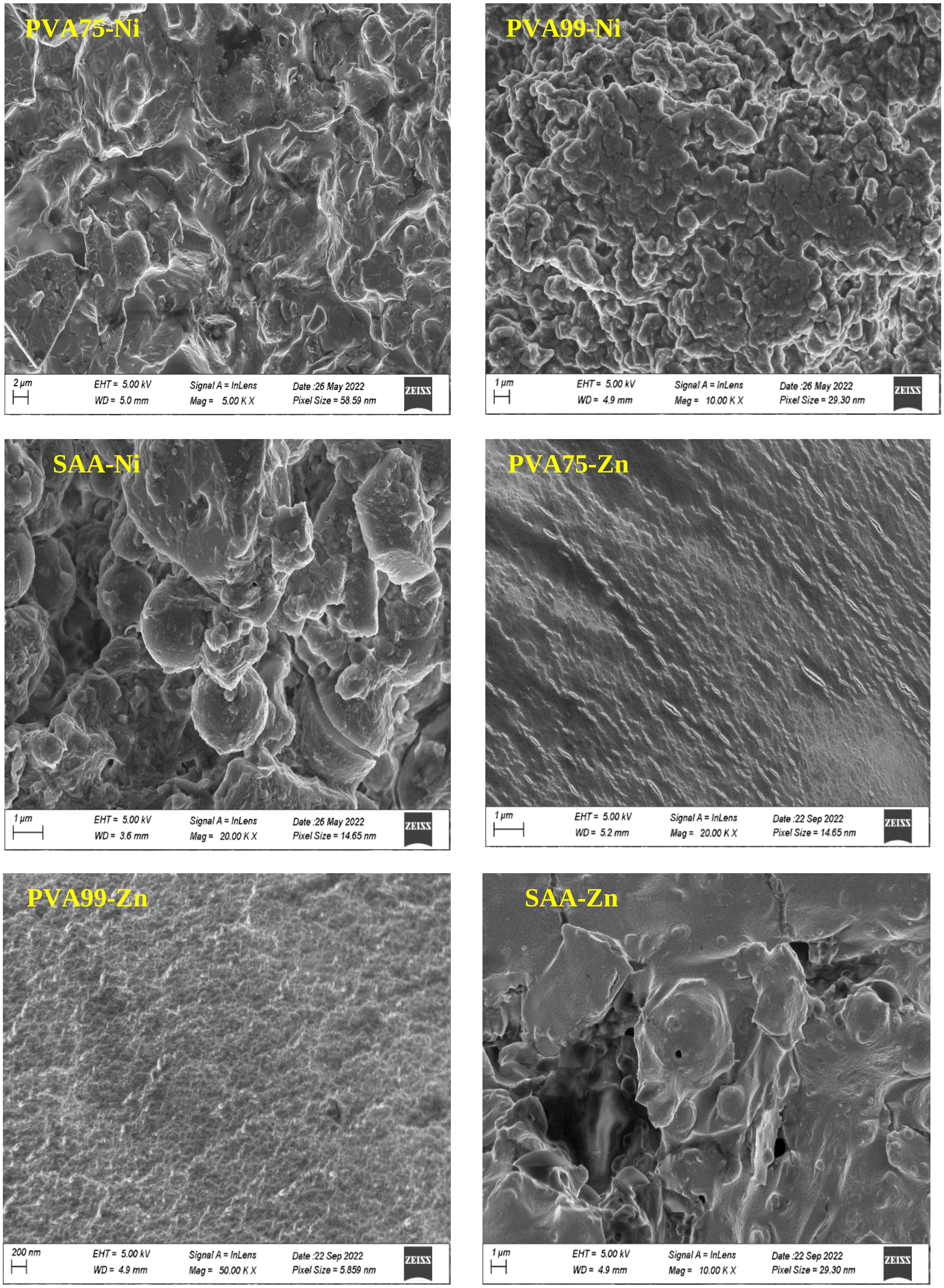
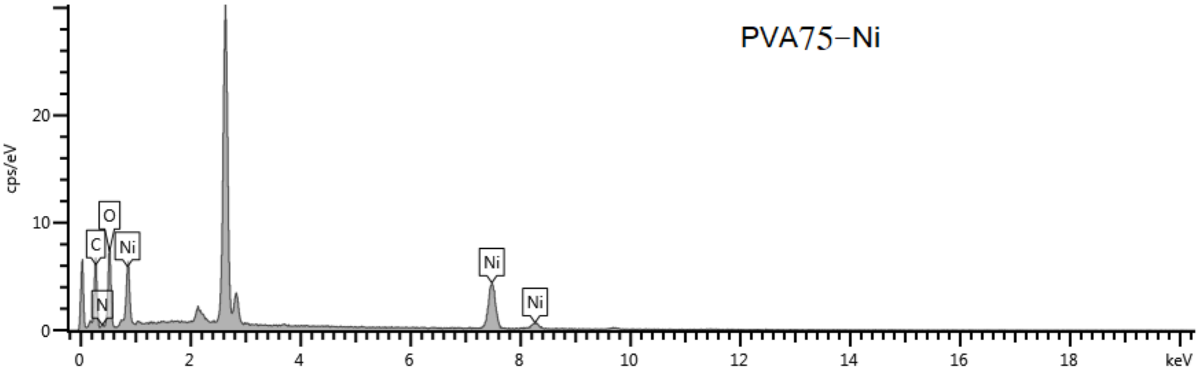
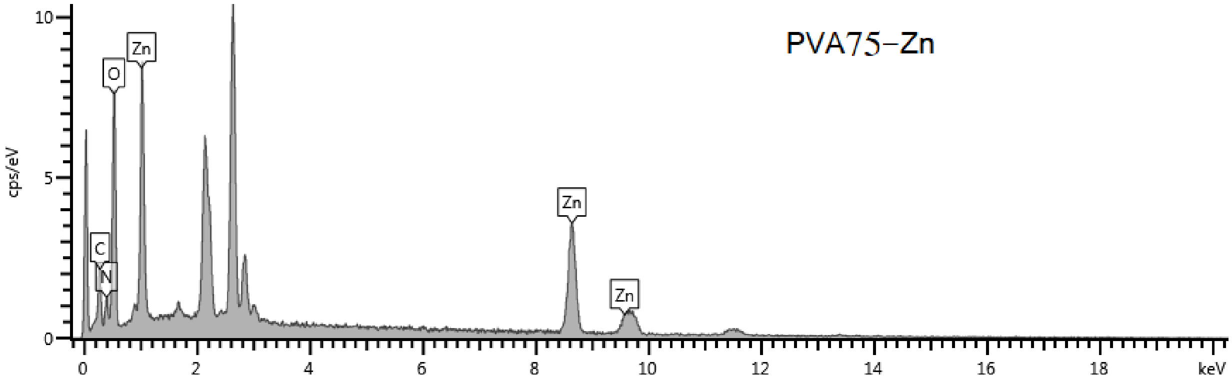


Figure 8: SEM of PVA75, PVA99 and SAA complexes


PVA75–Ni
cps/eV
0
10
20
C
O
N
Ni
Ni
Ni
0
2
4
6
8
10
12
14
16
18
keV


PVA75–Zn
cps/eV
0
5
10
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Zn
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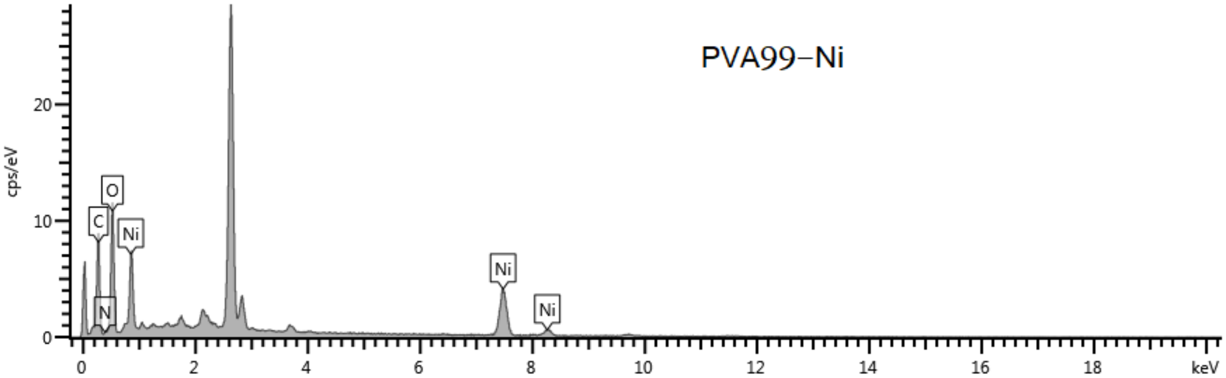
PVA99–Ni
cps/eV
0
10
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C
Ni
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Ni
Ni
0
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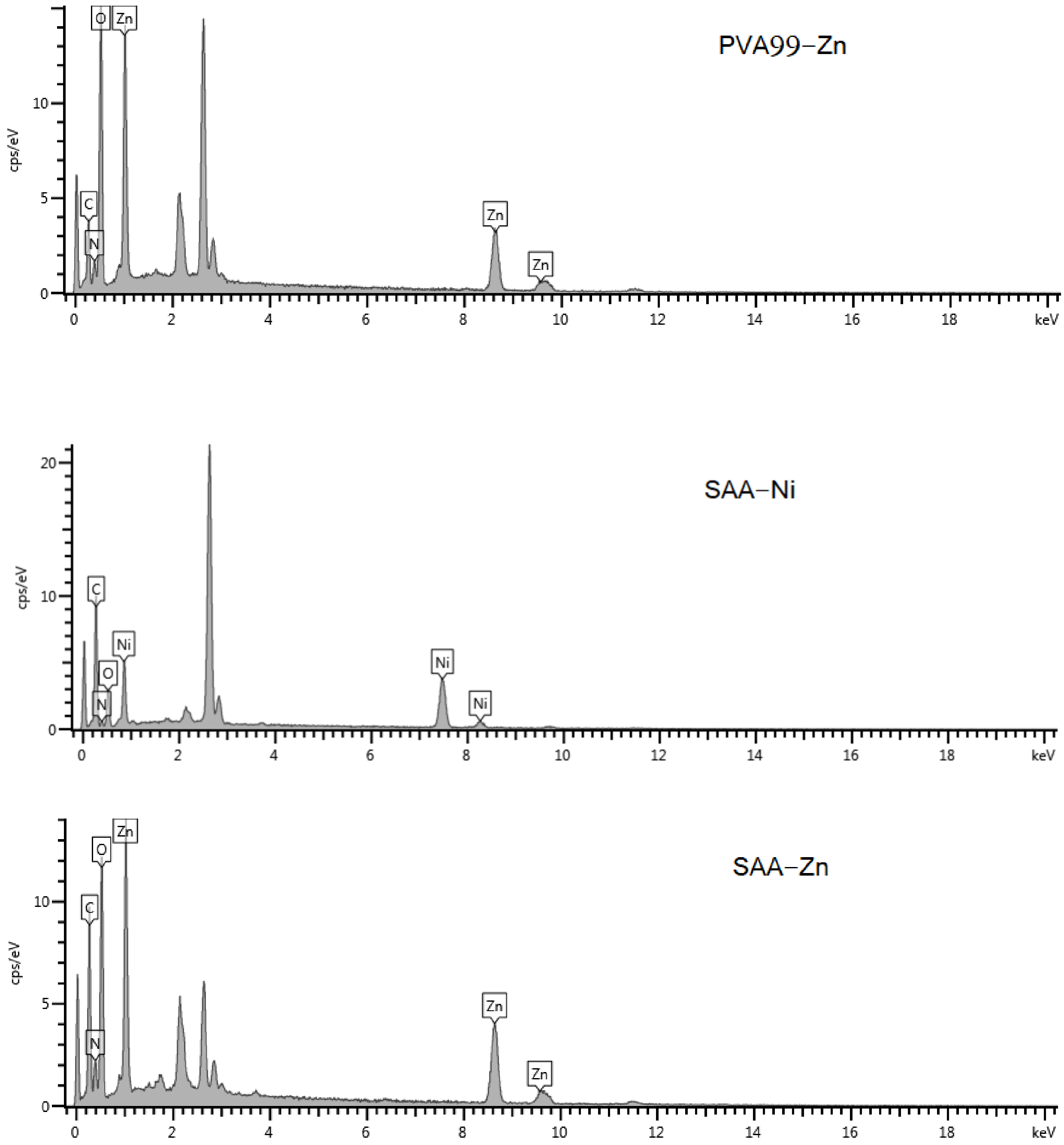

Figure 9: EDX Analysis of polymeric complexes

4.3 Thermal Stability studies

The thermal stability of polymeric complexes 4 was studied by thermogravimetric analysis TGA. The results of TGA analysis of polymeric Schiff base complex 4 was shown in Table 2. Low weight loss in the beginning (less than 100 ^{o}C) of the spectra showed escaping of humidity and solvent trapped. Three main weight loss stages was observed in PVA spectra represented: in polymeric complex. First at 180-220 °C corresponds to 15 % weight loss, which was related to decomposition of ligand from polymers, second at 290 °C that showed decomposition of PVA (PVA99 and PVA75) while for SAA was at the range 416-418 ^{o}C. Third and final stage, which lasting to 600 °C for all polymers complexes, could be due to oxidation of metals and formation of M-O and carbonization of SAA and PVA. Comparison of TGA spectral data of the polymeric complexes and the neat polymers (Table 2). The data of polymeric complexes exhibits high stability.

Table 2: Results from TGA analysis

Polymer	Transition Metal	Decomposition Temperature ^{o}C	Weight Loss%	Temperature of Weight Loss ^{o}C	Rate of Decomposition % / min.	Char Content % at 800 ^{o}C
PVA99	-	236	25	258	1.48	6.46
			50	275		
		416	75	381		
	Ni	163	25	201	1.17	20.7
			50	373		
		370	75	649		
	Zn	118	25	105	0.95	8.28
			50	133		
		-	75	460		
PVA75	-	276	25	306	1.62	4.38
		418	50	330		
			75	420		
	Ni	163	25	187	1.31	14.82

			50	303		
		230	75	506		
	Zn	141	25	115	0.94	12.4
			50	150		
		-	75	420		
SAA	-	292	25	340	1.82	1.81
			50	374		
		-	75	385		
	Ni	187	25	209	1.5	10.27
			50	326		
		267	75	506		
	Zn	134	25	167	0.94	28.28
			50	244		
		198	75	-		

5. Conclusions

Three new polymeric polyvinyl alcohol (two types) and styrene-allyl alcohol copolymer Schiff base of nickel (II) and zinc (II) complexes which were prepared by the formationof Schiff base ligands on polymeric framework are investigated. The Polymeric-Schiff bases and their metal complexes were confirmed by FTIR spectroscopy, scanning electronic microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Thermogravimetric analysis (TGA) results revealed that the polymer–metal complexes showed high thermal stability.

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تحضير وتشخيص قواعد شيف البوليمرية الجديدة ومعقداتها

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المستخلص

تم تحضير معقدات العناصرانتقالية النيكل والزنك (Ni و Zn) لليكاندات قواعد شيف البوليمرية لثلاثة من البوليمرات الجديدة ستايرين-الليل الكحول (SAA) ونوعين من البولي فنيل الكحول (PVA). كانت هذه البوليمرات عوامل داعمه لتحضير ليكاند قاعدة شيف وتحميلها عليها بتكوين معقدات للعناصر الانتقالية النيكل والزنك (Ni و Zn). تم تشخيص المعقدات البوليمرية المحضرة بواسطة التحليل الطيفي FTIR و التحليل الحراري الوزني (TGA) على التوالي. تم تقدير محتوى المعادن الانتقالية (Ni و Zn) باستخدام تحليل SEM-EDX.