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RESEARCH ARTICLE

Thermal Stability of Some New Metal Containing Polymers Based on Resol-Bisphenol A Formaldehyde Resin

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ABSTRACT:
Polymers containing vanadium, molybdenum, nickel, copper and zinc ions have been synthesized by reaction of resol- bisphenol A formaldehyde resin (RBF) with the schiff base complexes of these metal ions. The incorporation of metal ions, especially the molybdenum ion, into the polymer matrices produced polymers with good thermal stability. The resulting metal containing polymers showed higher thermal stability. The thermal analysis of the obtained polymers were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

KEY WORDS: bisphenol-A, formaldehyde, metal containing polymers, thermal stability, schiff base

INTRODUCTION:
Metal containing polymers have been gaining more attention because of their potential important applications(1,2). The incorporation of metals can be modify the essential bulk properties of these polymer such as thermal stability, dielectric, conductivity and other physicochemical characteristics. In general, the thermal stability of metal-containing polymer systems is relatively enhanced compared to that of the bulk polymer(3). Moreover, the coordinating ability of the metal within the polymer backbone permits these materials to act as sensors, and as building blocks for supramolecular structures(4). Also, the metal moiety can be incorporated into the polymer back-bone by either covalently bonding directly to the main chain or coordinating to ligands within the backbone. The metal moiety could also be pendant or attached to the side chain of the polymer(5,6).

Two approaches are generally used for the attachment of metal complexes with polymers. The first approach involves the introduction of the bifunctional metal complexes as a monomer, followed by their polymerization(7). The second approach involves the linking of metal complexes directly onto preformed functional polymers(8). Some metal complexes commonly used in the synthesis of metal containing polymers are Schiff base, ferrocene, imidazole, secondary and tertiary amine metal complexes, and so forth(9-12). Among these metal complexes Schiff base metal complexes have been widely used due to their corrosive resistant, microbial as well as thermal resistant properties(13-15). In this work, Schiff base metal complexes were reacted with RBF in 1:3 molar ratios to produced metal containing polymers. The hydroxyl functional groups in the metal complexes are expected to undergo a reaction with RBF to yield thermally stable polymers and thermal behavior of the obtained polymers have been investigated.

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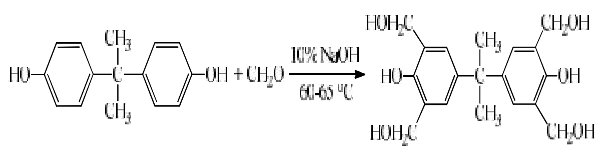
EXPERIMENTAL:

Materials:
All chemicals were obtained from Merck, BDH, RDH, Aldrich, Fluka, H&W, Thomas and Tedia, and were provided in pure grade.

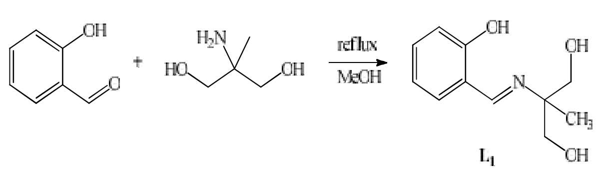
Analytical Methods:
The FTIR spectra were recorded on a FTIR-8400S spectrophotometer in 4000-400 cm^{-1} region by using KBr discs. Elemental analyses were carried out using a Perkine-Elmer 2400 Series II CHN analyser. The thermal properties of the cured metal containing polymers were investigated with Perkin-Elmer differential scanning calorimeters (DSC-7), and thermogravimetric analysis (TGA-7 and TGA-Q50) Perkin-Elmer at a heating rate of 5 C min^{-1} and 10 C min^{-1} respectively under a nitrogen atmosphere.

Synthesis:
Synthesis of Resol- Bisphenol A Formaldehyde Resin (RBF):
The resin was syntheses by condensation reaction between BPA and formaldehyde with sodium hydroxide as catalyst(16) (scheme 1).

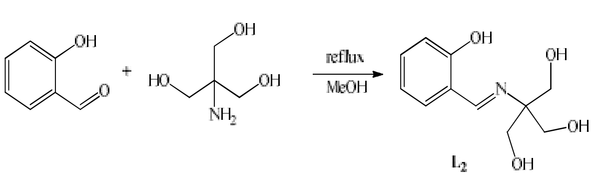


Scheme 1: Synthesis of RBF

Synthesis of Schiff Base Complexes (ML):
The Schiff bases were synthesis by condensation of salicylaldehyde with 2-amino-2-methyl-1,3-propane-diol and 2-amino-2-(hydroxymethyl)-1,3-propanediol in 1:3 molar ratios, respectively(17,18) (scheme 2-3). Then these ligands were reacted with transition metal ions: V(V), Mo(VI), Ni, Cu and Zn(II)(19-24)

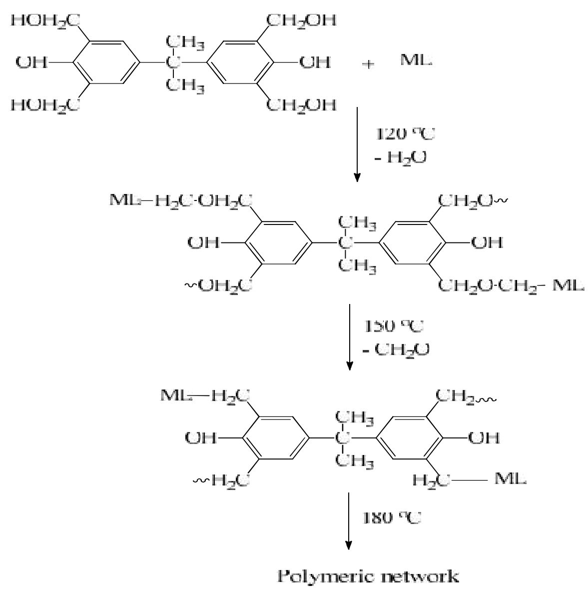


Scheme 2: Synthesis of L_1



Scheme 3: Synthesis of L_2

Synthesis of Metal-Containing Polymers (RBF-ML):
All polymer-metal complexes were blended by mixing (0.75 g) resol of bisphenol-A (RBF) and (0.25 g) of the Schiff base complexes (ML) at room temperature, according to scheme 4. Then placed in an oven at (120 C) for 3 hours to complete the process of hardening and subsequent hardening process at (150˚C) for 2 hours and at (180˚C) for 2 hours for post curing.



Scheme 3: Synthesis of RBF-ML (ML=V(V)L_1, V(V)L_2, Mo(VI)L_1, Mo(VI)L_2, Ni(II)L_1, Ni(II)L_2, Cu(II)L_1, Cu(II)L_2, Zn(II)L_1, Zn(II)L_2)

RESULTS AND DISCUSSION:
RBF resin was obtained via the reaction of BPA with formaldehyde in a basic medium leads to formation of the resol-type resin. The FTIR spectra of RBF exhibited absorption band of group OH at 3409 cm^{-1}, CH_3 at 1369 and 1288 cm^{-1}, CH aromatic at 2931 cm^{-1}, 900 and 850 cm^{-1} due to three- or tetra- substituted aromatics.
The Schiff base 1,3-dihydroxy-2-methyl-(salicylideneamino) propane (L_1) and 1,3-dihydroxy-2-hydroxymethyl-(salicylideneamino) propane (L_2) were synthesized by condensation of carbonyl compounds with primary amine and these ligands reacted with transition metal ions. The FTIR spectra and CHN analysis data are summarized in Table 1 and. Table 2.

Table 1: FTIR data of Schiff base and its complexes (cm^{-1})

Compounds	ν(O-H)	ν (C=N)	ν(C-O)	ν(M−O)	ν(M−N)	ν(M=O)
L_1	3328	1629	1278	-	-	-
L_2	3300	1639	1307	-	-	-
$V(V)L_1$	3400	1623	1299	563	462	956
$V(V)L_2$	3375	1627	1296	576	466	958
$Mo(VI)L_1$	3321	1620	1296	572	453	929,891
$Mo(VI)L_2$	3311	1622	1292	576	457	929,896
$Ni(II)L_1$	3396	1637	1284	582	457	-
$Ni(II)L_2$	3319	1629	1321	584	447	-
$Cu(II)L_1$	3294	1634	1305	591	474	-
$Cu(II)L_2$	3323	1625	1307	549	460	-
$Zn(II)L_1$	3311	1637	1286	584	455	-
$Zn(II)L_2$	3294	1631	1288	578	453	-

Table 2: Elemental analysis data of Schiff base and its complexes

Compound	Formula	Elemental analysis data calculated (found) (%)		
		C	H	N
L_1	$C_{11.5}H_{17}NO_{3.5}$	61.32 (61.74)	7.61 (7.19	6.22(6.56)
L_2	$C_{11}H_{15}NO_4$	58.66 (58.53)	6.71 (6.55)	6.22 (5.97)
$V(V)L_1$	$C_{20}H_{26}N_2O_8V_2$	48.19 (47.77)	4.78 (4.19)	5.11 (4.87)
$V(V)L_2$	$C_{11}H_{14}NO_6V$	43.01 (42.77)	4.59 (4.11)	4.56 (4.59)
$Mo(VI)L_1$	$C_{11}H_{15}NO_6Mo$	37.41 (37.16)	4.28 (3.97)	3.97 (3.84)
$Mo(VI)L_2$	$C_{11}H_{15}NO_7Mo$	35.78 (35.28	4.10 (3.63)	3.79 (3.61)
$Ni(II)L_1$	$C_{28}H_{46}N_2O_{14}Ni_2$	45.36 (45.04)	6.09 (5.19)	4.23 (4.08)
$Ni(II)L_2$	$C_{27}H_{42}N_2O_{15}Ni_2$	42.17 (42.00)	5.95 (5.27)	3.93 (3.75)
$Cu(II)L_1$	$C_{44}H_{60}N_4O_{16}Cu_4$	45.75 (46.23)	5.24 (4.71)	4.85 (4.56)
$Cu(II)L_2$	$C_{44}H_{60}N_4O_{20}Cu_4$	43.35 (43.05)	4.96 (4.62)	4.60 (4.03)
$Zn(II)L_1$	$C_{15}H_{21}NO_7Zn$	45.88 (46.54)	5.39 (4.73)	3.57 (4.08)
$Zn(II)L_2$	$C_{15}H_{21}NO_8Zn$	42.58 (42.03)	5.22 (4.88)	3.82 (3.75)

Polymer-metal complexes have been prepared by blending ML with RBF, the functional groups which undergo a reaction are the hydroxyl groups in ML and the methylol groups in RBF, they were mix well until the homogeneity of the mixture and the process of hardening at (120 C) for (15-30 min) to ensure interaction of methylol groups in phenolic resins with hydroxyl groups in the metal complexes, that leads to the formation of ether linkage (-COC), then the temperature was raised to (150 C) for two hours and the loss of formalin molecules (CH_2O) were occurred the ether groups were converted to methylene linkage (-CH2-). The subsequent hardening process occurred at (180 C) for 2 hours to ensure that the polymer network were frowned completely. The metal-containing polymers were characterized by FTIR spectroscopy, All Polymers had similar FTIR spectra (Table 3).. The important characteristic absorption bands are as follows: the high intense band due to phenolic-OH appeared in the region at (3413-3309) cm^{-1} and azomethine ν(C=N) at (1637-1620) cm^{-1}.The ν(M–O) and ν(M–N) bands have been assigned in the region (559-524) cm^{-1} and (474-433) cm^{-1}, respectively.

Table 3: FTIR data of metal-containing polymers (RBF-ML) (cm^{-1})

Resins	ν(O-H)	ν(C=N)	ν(C-O)	ν(M−O)	ν(M−N)	ν(M=O)
$RBF\text{-}V(V)L_1$	3413	1627	1087	559	462	952
$RBF\text{-}V(V)L_2$	3371	1608	1049	543	474	956
$RBF\text{-}Mo(VI)L_1$	3409	1647	1060	559	455	929,889
$RBF\text{-}Mo(VI)L_2$	3409	1650	1049	555	459	931,887
$RBF\text{-}Ni(II)L_1$	3379	1639	1051	543	457	-
$RBF\text{-}Ni(II)L_2$	3382	1620	1049	524	470	-
$RBF\text{-}Cu(II)L_1$	3379	1623	1053	536	451	-
$RBF\text{-}Cu(II)L_2$	3382	1620	1053	543	459	-
$RBF\text{-}Zn(II)L_1$	3371	1612	1054	551	433	-
$RBF\text{-}Zn(II)L_2$	3386	1620	1053	551	455	-

Thermal Analysis

The thermal properties of cured the metal-containing polymers have been carried on by DSC and TGA techniques. The DSC theromgrams of cured polymer containing vanadium, molybdenum, nickel, copper and zine ions are shown in Figures (1-11) and the Tg values

Table 4: Tg of metal-containing polymer

Resins	(Tg) C^0
RBF-V(V)L_1	46.59
RBF-V(V)L_2	81.46
RBF-Mo(VI)L_1	81.42
RBF-Mo(VI)L_2	-
RBF-Ni(II)L_1	55.76
RBF-Ni(II)L_2	59.46
RBF-Cu(II)L_1	-
RBF-Cu(II)L_2	67.39
RBF-Zn(II)L_1	82.50
RBF-Zn(II)L_2	82.31

Tg (C^0)- glass transition temperature

of are higher for the complexes V(V)L_2, Mo(VI)L_1, Cu(II)L_2, Zn(II)$L_{1,}$ Zn(II)L_2.It was noted a difference in the Tg values of polymer to another depending on the density of cross linking and the presence of aromatic structures in the repeating unit and the polymer chain length. The exothermic peck at higher than 200 C^0 was attributed to the dissociation of these polymers.

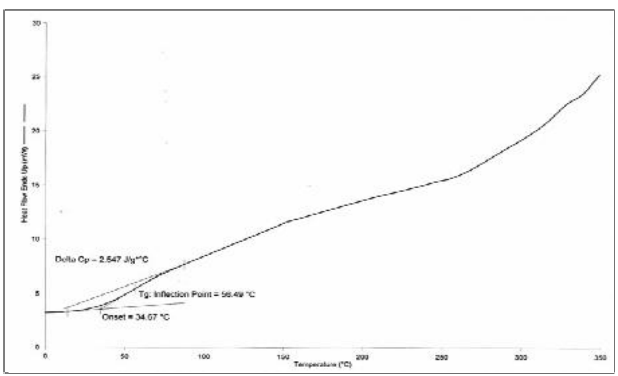


Fig. 1. DSC thermogramsof RBF

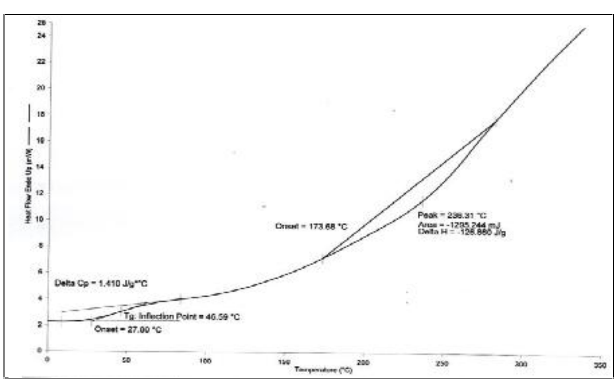


Fig. 2. DSC thermograms of RBF-V(V)L_1

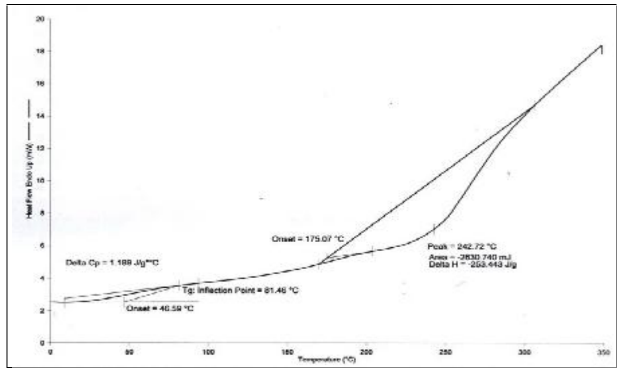


Fig. 3. DSC thermograms of RBF-V(V)L_2

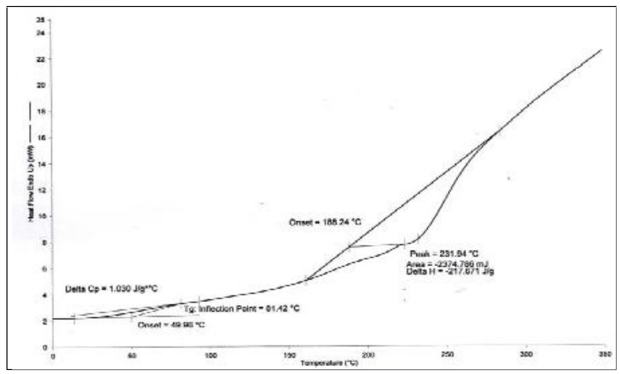
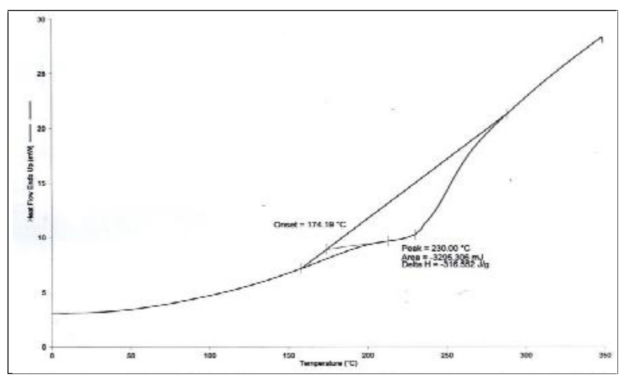


Fig. 4. DSC thermograms of RBF-Mo(VI)L_1



F Fig. 5. DSC thermograms of RBF-Mo(VI)L_2

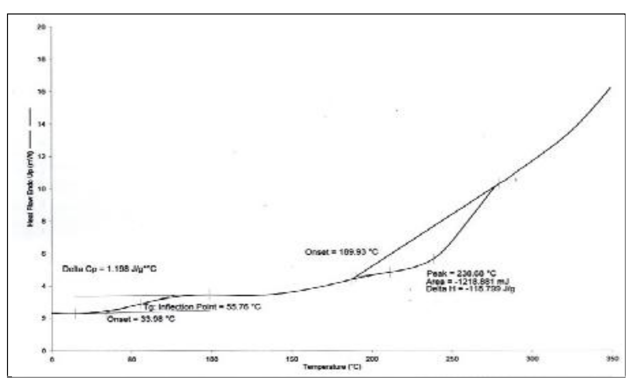


Fig. 6. DSC thermograms of RBF-Ni(II)L_1

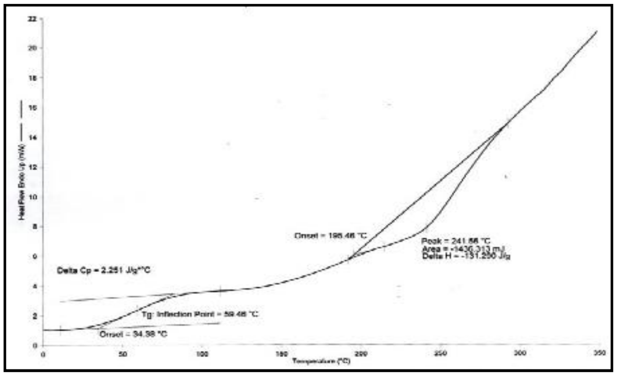


Fig. 7. DSC thermograms of RBF-Ni(II)L2

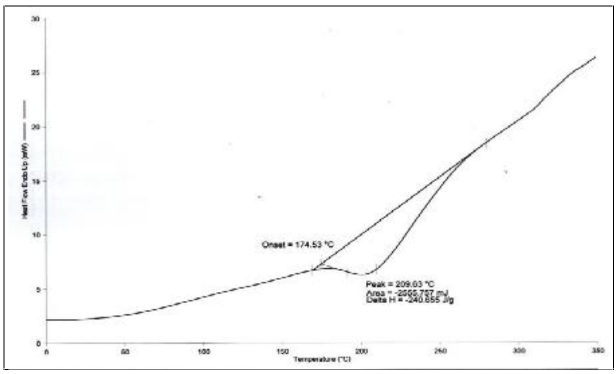


Fig. 8. DSC thermograms of RBF-Cu(II)L_1

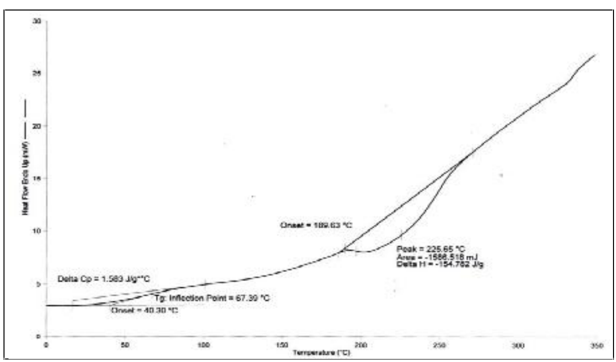


Fig. 9. DSC thermograms of RBF-Cu(II)L_2

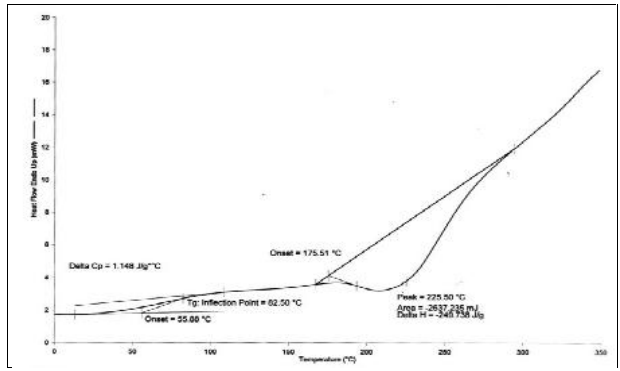


Fig. 10. DSC thermograms of RBF-Zn(II)L_1

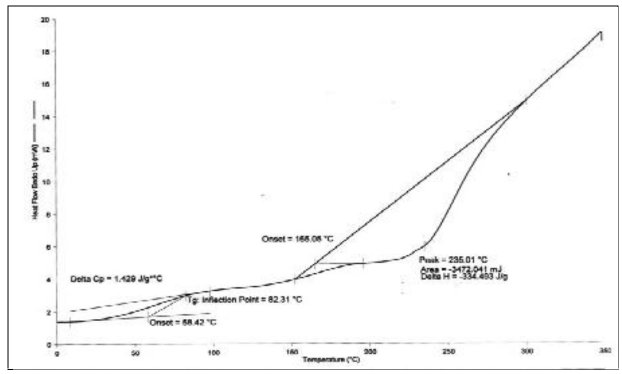


Fig. 11. DSC thermograms of RBF-Zn(II)L_2

The thermal stability of cured resol- bisphenol A formaldehyde containing metals ions were investigated by TGA and DTG thermograms (Figs. 12-22) and Table 5. For these polymers shows more than one thermal decomposition temperature. The enhancement of the thermal stability due to incorporation of metal ions into RBF. The thermograms of the cured resol- bisphenol A formaldehyde containing metal ions clearly indicate that the thermal stability of cured resins were improved with the incorporation of metal ions into the RBF resin. The results of thermogravimetric analysis were revealed that

Table 5: TGA / DTG thermograms data

Resin	DT (^oC)			$T_{50\%}$ (^oC)	T_s(^oC)	ΔE	Char (%)
	T_{op1}	T_{op2}	T_{op3}			(KJ/ mol)	at 700^{o}C
RBF	267	408	-	561	-	43.21	45.76
RBF-V(V)L_1	267	408	-	> 700	471	52.31	55.18
RBF-V(V)L_2	272	446	-	> 700	446	62.74	52.98
RBF-Mo(VI)L_1	252	417	500	> 700	471	83.27	59.14
RBF-Mo(VI)L_2	257	429	480	> 700	457	79.32	58.76
RBF-Ni(II)L_1	274	383	-	> 700	417	70.11	54.53
RBF-Ni(II)L_2	249	392	-	> 700	410	63.63	52.58
RBF-Cu(II)L_1	257	291	380	> 700	391	52.81	51.35
RBF-Cu(II)L_2	263	386	-	> 700	400	51.05	48.69
RBF-Zn(II)L_1	-	386	-	> 700	398	71.03	55.45
RBF-Zn(II)L_2	257	386	-	> 700	402	69.72	54.78

DT: decomposition temperature; Top: optimum decomposition temperature; $T_{50\%}$: Half Weight Loss Temperature (temperature for 50 % weight loss); Ts: half volatilization temperature; ΔE: activation energy of decomposition the RBF–Mo(VI)$L_1$are thermally more stable. The order of stability on the basis of thermal weight at 700 C can be given in thefollowing order RBF–Mo(VI)L_1> RBF–Mo(VI)L_2> RBF–Zn(II)L_1> RBF–Zn(II)L_2> RBF–Ni(II)L_1> RBF–V(V)L_2> RBF–Ni(II)L_2> RBF–V(V)L_1> RBF–Cu(II)L_1> RBF–Cu(II)L_1. All the polymers showed good thermal stability even at high temperature than the RBF due to the presence of the metal ions in the polymer networks. Activation energy for these polymers are higher in L_1 then L_2. On the other hand, it was observed that these polymers have a higher decomposition temperature, activation energy, $T_{50\%}$ and char % content compared with RBF. These were indicated that the chemical modification process of resolresin increasing the thermal stability. Therefore, these polymers can be used as thermal insulation.

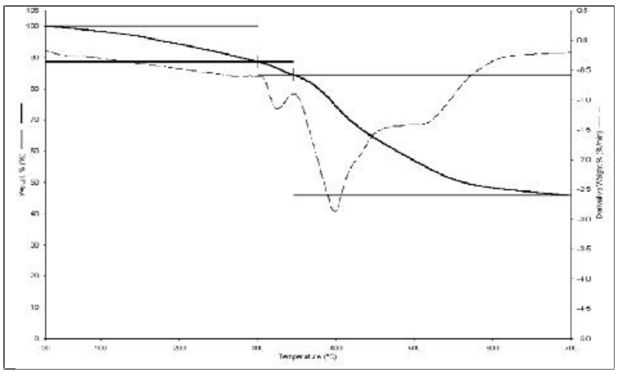


Fig. 12. TGA thermograms of RBF

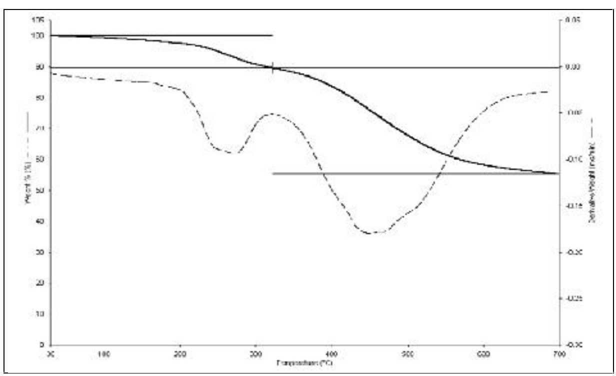


Fig. 13. TGA thermograms of RBF-V(V)L_1

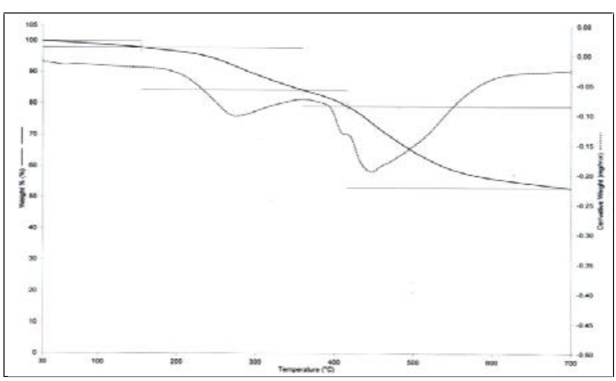


Fig. 14. TGA thermograms of RBF-V(V)L_2

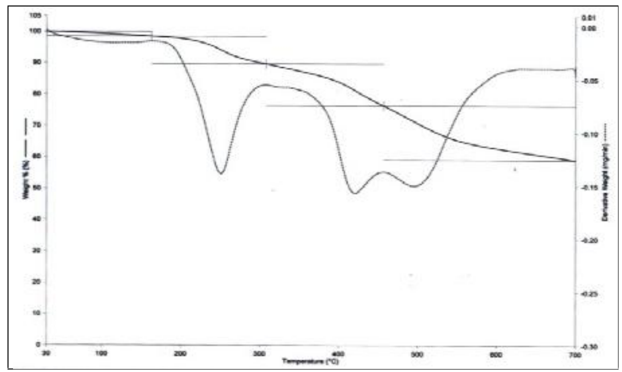


Fig. 15. TGA thermograms of RBF-Mo(VI)L_1

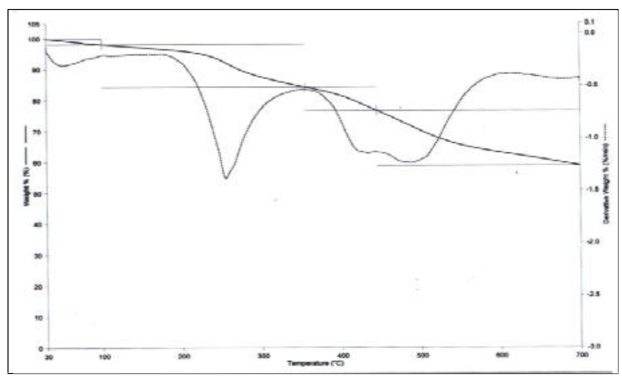


Fig. 16. TGA thermograms of RBF-Mo(VI)L_2

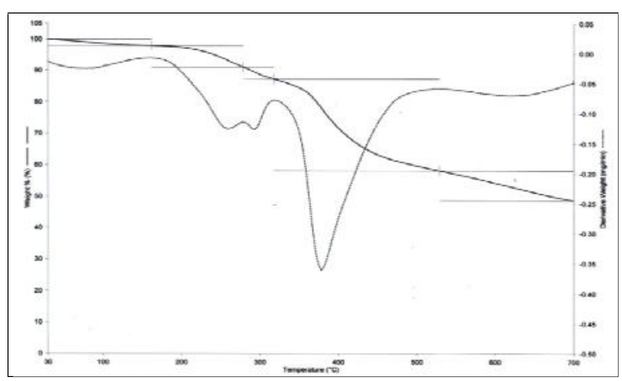


Fig. 17. TGA thermograms of RBF-Ni(II)L_1

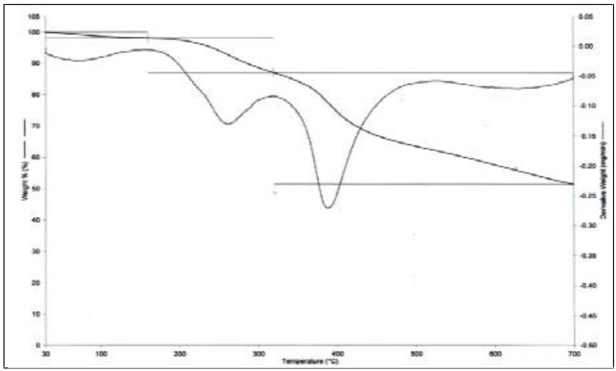


Fig. 18. TGA thermograms of RBF-Ni(II)L_2

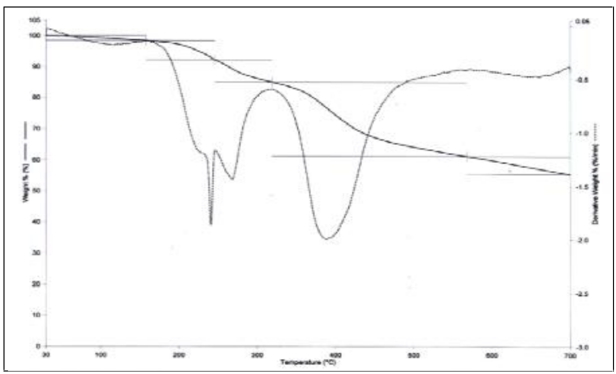


Fig. 19. TGA thermograms of RBF-Cu(II)L_1

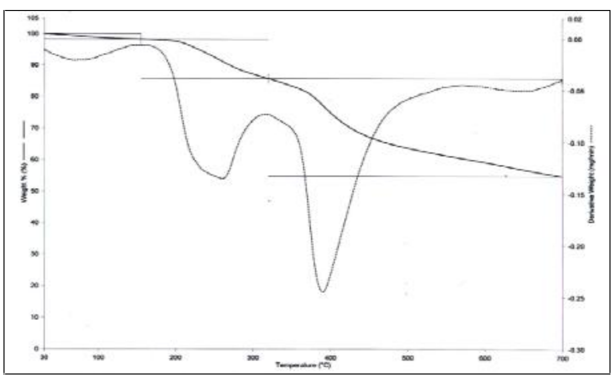


Fig. 20. TGA thermograms of RBF-Cu(II)L_2

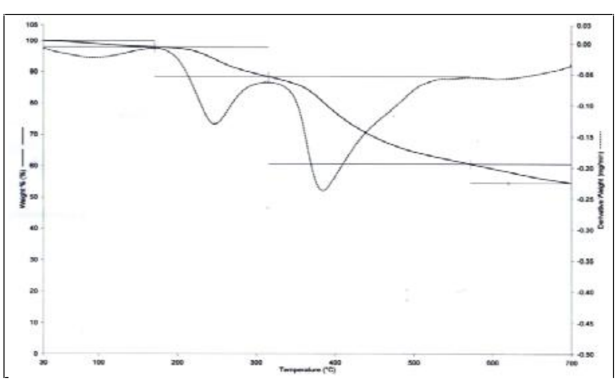


Fig. 21. TGA thermograms of RBF-Zn(II)L_1

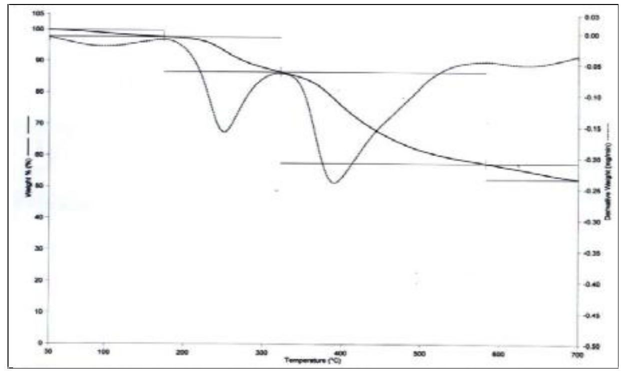


Fig. 22. TGA thermograms of RBF-Zn(II)L_2

CONCLUSIONS:

Polymers containing metal complexes were prepared by blending schiff base metal complexes with RBF. Introduction of schiff base metal complexes into the polymer matrix results in good thermal stability, especially in the case of the molybdenum-containing polymer, which is comparable to the resol resin. Also, the char % content reach more than 50 % which may allow these polymers to be used in different thermal purposes like, thermal insulate.

REFERENCES:

1- Chan WK. Metal Containing Polymers with Heterocyclic Rigid Main Chains: Review. Coordination Chemistry Reviews. 251(17–20); 2007: 2104–2118.

2- Abd-El-Aziz AS and Manners I. Frontiers in Transition Metal-Containing Polymers. John Wiley and Sons, Inc., Hoboken, New Jersey, USA. 2007.

3- Biswas M and Mukherjee A. Synthesis and Evaluation of Metal-Containing Polymers. Advances in Polymer Science. 115; 1994: 89-123.

4- Leung ACW and. MacLachlan MJ. Schiff Base Complexes in Macromolecules. Journal of Inorganic and Organometallic Polymers. 17(1); 2007: 57-89.

5- Abd-El-Aziz AS and Strohm EA. Transition metal- containing macromolecules: En route to new functional materials. Polymer. 53(22); 2012: 4879–4921.

6- Ciardelli F, Tsuchida E and Wohrle D (Eds.). Macromolecule–Metal Complexes. Springer-Verlag, Heidelberg. 1996.

7- Cazacu M, Marcu M, Vlad A, Rusu GI and Avadanei M. Chelate polymers. VI. New copolymers of the some siloxane containing bis(2,4-dihydroxybenzaldehyd-imine)Me^{2+} with bis(p-carboxy-phenyl) diphenylsilane," Journal of Organometallic Chemistry. 689(19); 2004: 3005-3011.

8- Sridaeng D and Chantarasiri N. Thermally stable polyureas and poly(urea-imide)s containing zinc and nickel napthtrien complexes. Journal of Applied Polymer Science. 114(6); 2009: 3945-3954.

9- Ahamad T and S.M. Alshehri. New Thermal and Microbial Resistant Metal-Containing Epoxy Polymers. Bioinorganic Chemistry and Applications. 2010: 1-7.

10- Senthilkumar N, Raghavan A and Sultan Nasar A. Novel Metal-containing Polyurethane Elastomers Prepared using Tetradentate Schiff Base Metal Complexes. Macromolecular Chemistry and Physics. 206(24): 2005: 2490–2500.

11- Hussein MA and Asiri AM. Organometallic Ferrocene and Phosphorus-Containing Polymers: Synthesis and Characterization. Designed Monomers and Polymers. 15(3); 2012: 207-251.
12- Lázaro Martínez JM, Chattah AK, Torres Sánchez RM, Buldain GY and Campo Dall' Orto V. Synthesis and characterization of novel polyampholyte and polyelectrolyte polymers containing imidazole, triazole or pyrazole. Polymer. 53(6); 2012: 1288-1297.
13- Chantarasiri N, Tuntulani T, Tongraung P, Seangprasertkit-Magee R and Wannarong W. New Metal-Containing Epoxy Polymers from Diglycidyl Ether of Bisphenol A and Tetradentate Schiff Base Metal Complexes. European Polymer Journal. 36(4); 2000: 695-702
14- Nishat N, Hasnain S, Ahmad T and Parveen A. Synthesis, Characterization, and Biological Evaluation of New Polyester Containing Schiff Base Metal Complexes. Journal of Thermal Analysis and Calorimetry. 105(3); 2011: 969-979.
15- Lakshmi B, Shivananda KN, Prakash GA, Isloor AM and Mahendra KN. Synthesis and Characterization of Schiff Base Metal Complexes and Reactivity Studies with Malemide Epoxy Resin. Bulletin of the Korean Chemical Society. 33(2); 2012: 473-482.
16- Motawie AM, Badr MM, Amer MS, Moustafa HY and Ali IM. Some Coating Studies on Phenolic Epoxy/ Poly (Vinyl Acetal), Resins. Journal of Applied Sciences Research. 4(9); 2008: 1043-1051.
17- Raptopouloub CP, Papadopoulosa AN, Malamataria DA, Ioannidisa E, Moisidisa G, Terzisb A and Kessissoglou DP. Ni(II) and Cu(II) schiff base complexes with an extended H-bond network. Inorganica Chimica Acta. 272(1–2); 1998: 283–290.
18- Dey M, Rao CP, Saarenketo PK, Rissanen K, Kolehmainen E and Guionneau P. Mn(IV) and Co(III)-Complexes of -OH-rich Ligands Possessing O2N, O3N and O4N Cores: Syntheses, Characterization and Crystal Structures. Polyhedron. 22(27); 2003: 3515-3521.
19- Asgedom G, Sreedhara A and Rao CP. Oxovanadium(V) Schiff Base Complexes of tris(hydroxymethyl)aminomethane with salicylaldehyde and its Derivatives: Synthesis, Characterization and Redox Reactivity. Polyhedron, 14(13-14); 1995: 1873-1879.
20- Chen GJ, McDonald JW and Newton WE. Synthesis of Molybdenum(IV) and Molybdenum(V) Complexes using Oxo Abstraction by Phosphines. Mechanistic Implications. Inorganic Chemistry. 15(11); 1976: 2612–2615.
21- Sandbhor U, Padhye S and Sinn E. Cis di-oxomolybdenum(VI) complexes with a tridentate ONO donor ligand; synthesis, X-ray crystal structure, spectroscopic properties and oxotransfer chemistry. Transition Metal Chemistry. 27(6); 2002: 681–685.
22- Dey M, Rao CP, Saarenketo PK and Rissanen K. Mono-, Di- and Tri-nuclear Ni(II) Complexes of N-, O-donorligands: Structural Diversity and Reactivity. Inorganic Chemistry Communications. 5(11); 2002: 924–928.
23- Dey M, Rao CP, Saarenketo PK and Rissanen K. Synthesis, Structural Diversity, Inter-conversion and Reactivity of Cu(II) Complexes of Hydroxy-rich Molecules. Inorganic Chemistry Communications. 5(11); 2002: 380–383.
24- Dey M, Rao CP, Saarenketo PK, Rissanen K and Kolehmainen E. Four-, Five- and Six-Coordinated Zn(II) Complexes of OH-Containing Ligands: Syntheses, Structure and Reactivity. European Journal of Inorganic Chemistry. 2002(8); 2002: 2207–2215.