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## **STUDIES OF THERMAL PROPERTIES AND EFFECTS OF MICROBIAL STRAINS ON MALEIMIDE-METAL COMPOSITES WITH PENDANT SUBSTITUTED AZO-LIGAND**

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**ABSTRACT:** The present studies were focused on the analysis of thermal and biological properties of various metal composites of [4-N-Phenylethanamide azo-3-N-(4-chlorophenyl) maleimide-co-Acrylic acid] [CPAChMI-AA], [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl) maleimide-co-Acrylic acid] [CPABMI-AA]. The monomers [4-N-Phenylethan amide azo-3-N-(4-chlorophenyl)Maleimide] [PAChMI], [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)Maleimide] [PABMI] and copolymers [CPAChMI-AA] and [CPABMI-AA] were synthesized. The monomers were made by reaction with maleic anhydride and substituted amino-derivative as 4-N-Phenyl ethanamide via dehydration-cum-cycloaddition reaction process and copolymerized with acrylic acid at 60-70°C in tetrahydrofuran (THF) solution using initiator as azoisobutyronitrile (AIBN). Metal composites of synthesized copolymers were prepared with some metals such as  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ . All compounds were characterized by means of FT-IR,  $^1\text{H-NMR}$ , elemental analysis and DSC and TGA evaluated thermal properties of polymers and their metal composites. Molecular weight and polydispersity were determined by gel permeation chromatography (GPC). Biological performances were examined in the form of microbial activities of the polymers and composites with various bacteria / fungi.

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**KEYWORDS:** Thermal and biological activity, Copolymers, Metal composite, TGA, DSC.

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## 1. INTRODUCTION

The construction of metal-polymers with d-block transition metals have been focused rapidly in recent years. Owing to their interesting higher thermal performances and variety of biological activities shows various potential applications [1], [2]. The blending of metals with thermal resist polymers effectively increases their thermal stability. Metal-polymer complexes namely metal-composites have many applications such as in waste water treatment for metal recovery, in hard water treatment via metal-ion exchange, protective coatings, thermally stable and reinforced materials, manufacturing of antimicrobial and surgical materials, gels and ointments for medical uses and other biological activity [3], [4]. According to the literature protocols, it has been found that different typed polymers used as ligand to formed variety of metal-polymer materials [5], [6], [7]. The chemical properties of nitrogen containing functional groups such as azo group, thiazole group and cyanide and thiocyanate groups have been intensively researched in various fields and especially in polymers areas for achieved required and high quality materials [8], [9]. In coordination chemistry, transition metal complexes with nitrogen containing ligands are revealed an important and interesting role. The metal composites including azo ligands are showed significant importance and played a pivotal role in many industries [10], [11]. The azo compound possesses special bonding properties due to the existence of -N=N- group [12] and have alone pair on nitrogen atom and when linked to an aromatic ring carrying an additional donor sites is well suitable for chelation and formed various metal complexes with transition metal ion with unusual structural, magnetic and biological properties. The thiazole functional group played significantly to generate the diversity of certain biological properties such as antibacterial, antiviral and antitubercular activities [13], [15]. The one pot synthesis of some novel derivatives of thiazolo [2, 3-dihydropyrimidinone] possessing [4-methylthiophenyl] moiety and examined their antibacterial and antifungal activities [16]. A series of 4-isopropylthiazole-2-carbohydrazide prepared from oxadiazole-thiazole and triazole-thiazole derivatives [17] synthesized compounds were evaluated for their preliminary in vitro antibacterial, antifungal and antitubercular activity against mycobacterium tuberculosis H<sub>37</sub>Rv strain. Metal-polyurea complex synthesized [18] and that showed excellent antimicrobial activity against *S. aureus*, *E. coli*, *B. subtilis* and *S. typhi*. The Cu<sup>2+</sup> chelated polyurea showed higher zone of inhibition against microbes and used in biomedical applications. They have exhibited moderate to excellent inhibited growth against the chosen bacteria and fungi due to the presence of N and S donor atoms present in the ligand molecule and there are several research reports, investigated various and newly synthesized nitrogen containing ligands to form metal-ligand complexes and examined on various thermal and significantly

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biological applications [19], [20], [21]. The present report aims to introduce the [4-N-Phenylethanamideazo-3-N-(4-chlorophenyl)maleimide] [PACHMI-AA] and [4-N-Phenylethanamide azo-3-N-(4-bromophenyl) maleimide] [PABMI-AA] copolymers act as azo-functional group based ligands and formed metal-composites and detail description on the synthesis, characterization, thermal properties and micro-biological activities of the copolymers and their metal-composites. The physicochemical properties and spectral characterization of all compounds were conducted by FTIR, <sup>1</sup>HNMR UV-Visible spectroscopies. Physical appearances and thermal degradation were analyzed from XRD and TGA. The antimicrobial activities of the polymers and composites were also reported against various bacterial and fungal strains.

## 2. MATERIALS AND METHODS

Maleic anhydride (merck), 4-N-Phenylethanamide, 4-aminochlorobenzene (sigma), Diphosphorus pentoxide (sigma), Tetra hydro furan (THF) (sigma), DMF (sigma), Sodium nitrate, Hydrochloric acid (Loba chemicals), 4-Bromo aniline (AR), Sodium nitrate, Hydrochloric acid, AIBN (Loba chemicals). Other reagents and solvent were used as received.

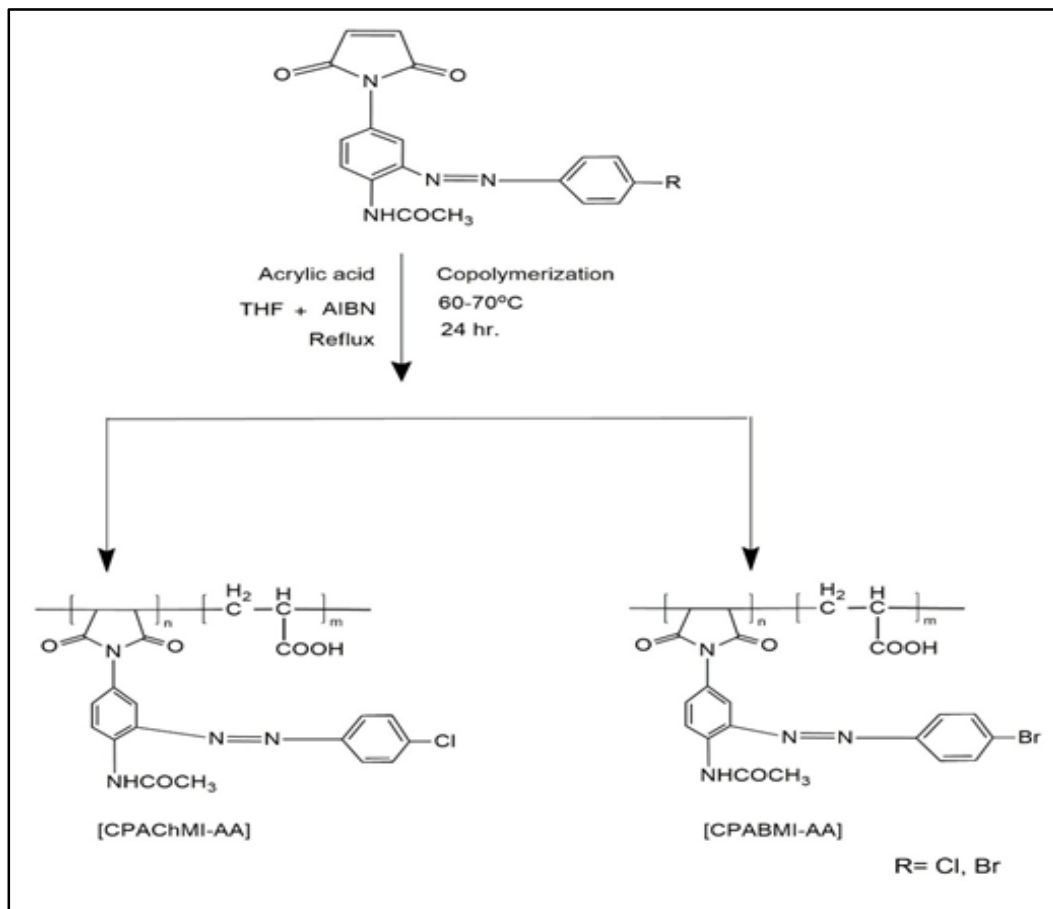
### 2.1 Experiments

#### Synthesis of [4-N-Phenylethanamide azo-3-N-(4-chlorophenyl) maleimide] [PACHMI] and [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)maleimide] [PABMI]-

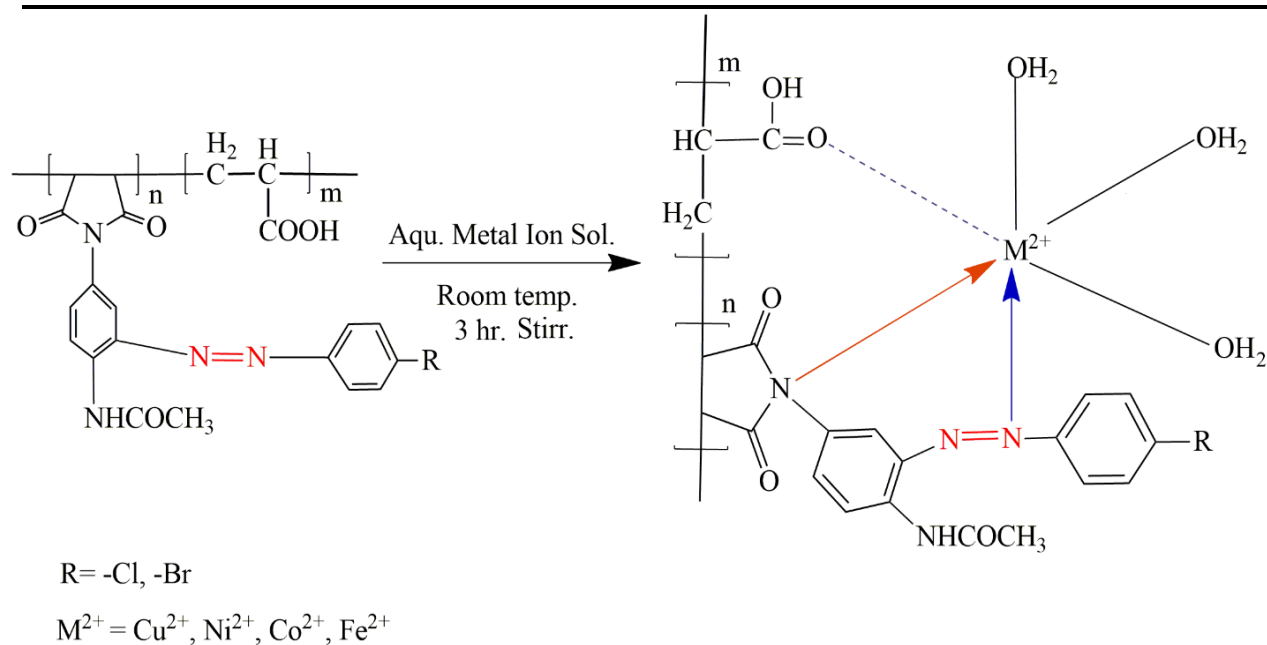
The [4-N-Phenylethanamide azo-3-N-(4-chlorophenyl)maleimide] [PACHMI], [4-N-Phenylethanamide azo-3-N-(4-bromophenyl)maleimide] [PABMI] were prepared by the reaction of P-amino acetanilide (0.1 mol) and maleic anhydride (0.1 mol) according to reported method [22]. Resulting monomers were synthesized by diazotization reaction in two steps according to literature protocol [23]. After this step, final solution was turned into pale yellow [PACHMI] and brownish yellow [PABMI] solids. After stirring for 30 min., it was filtered and washed with double distilled water and then dried at 60 °C under vacuum oven to give dried product of [PACHMI] and [PABMI] compounds. Synthesis of copolymers of [PACHMI] and [PABMI] with acrylic acid were synthesized in THF solution using initiator as AIBN according reported literature [24] [scheme 1].

### 2.2 Synthesis of metal composites

A methanolic solution (5 ml) [CPACHMI-AA]/[CPABMI-AA] (0.01 mol) (used as ligand) was added drop wise to a solution (5 ml) of 0.01 mol CuSO<sub>4</sub>.5H<sub>2</sub>O, FeSO<sub>4</sub>.7H<sub>2</sub>O, NiSO<sub>4</sub>.6H<sub>2</sub>O, CoSO<sub>4</sub>.6H<sub>2</sub>O in the same solution. The resulting solution was stirred for 3h at room temperature. The solid complexes precipitated were collected by filtration, washed several times with ethanol: water (1:1) mixture and dried under vacuum over CaCl<sub>2</sub> [scheme 2].



**Scheme 1: Synthesis of copolymers [CPAChMI-AA] and [CPABMI-AA]**



**Scheme 2: Synthesis of metal composites with copolymers [CPAChMI-AA] and [CPABMI-AA]**

### 3. RESULTS AND DISCUSSION

#### 3.1 Spectral Characterization

Fourier Transform Infrared (FTIR) spectra was recorded on a FTIR Perkin-Elmer spectrophotometer model RX-I. The compounds were analyzed using the KBr pellets. The spectra were obtained in bandwidth 250-4000  $\text{cm}^{-1}$ . Nuclear Magnetic Resonance ( $^1\text{H}$ NMR) spectra of monomer and cured compounds were analyzed on Bruker Advance II 400 MHz  $^1\text{H}$ NMR Spectrometer. All structures of synthesized were confirmed by these spectral techniques and polymerization reaction were proceed by unsaturated double bonds of both co-monomers units, which was confirmed by FT-IR and  $^1\text{H}$ -NMR spectral data. [Figure 1-4].

#### 1. [4-N-Phenylethanamideazo-3-N-(4-Chlorophenyl) Maleimide] [PACHMI]

Yield 85%, melting point 156.3°C; color yellow-brown, FT-IR (KBr): 1702  $\text{cm}^{-1}$  (C=O), 3300  $\text{cm}^{-1}$  (N-H), 3095  $\text{cm}^{-1}$  (CH=CH, C-H Stre.), 1603  $\text{cm}^{-1}$  (C=O, amide), 1666  $\text{cm}^{-1}$  (CH=CH, C-C Stre.), 1372  $\text{cm}^{-1}$  (C-N-C), 1534  $\text{cm}^{-1}$  (N=N), 836  $\text{cm}^{-1}$  (Ar-Cl, para) and 730  $\text{cm}^{-1}$  (Ortho subst.);  $^1\text{H}$ -NMR(ppm): 7.07-7.69 (Aromatic), 4.43-5.67 (HC=CH of Maleimide), 10.05 (CO-NH).

#### 2. [4-N-Phenylethanamideazo-3-N-(4-Chlorophenyl) maleimide-co-Acrylicacid] [CPACHMI-AA]

Yield 87 %, melting point 192.8°C; color dark brown, FT-IR (KBr): 1714  $\text{cm}^{-1}$  (C=O), 3360  $\text{cm}^{-1}$  (-OH of -COOH), 3281  $\text{cm}^{-1}$  (N-H), 3073  $\text{cm}^{-1}$  (CH=CH, C-H Stre.), 1601  $\text{cm}^{-1}$  (C=O, amide), 1315.1  $\text{cm}^{-1}$  (-C-O) 1447  $\text{cm}^{-1}$  (C-N-C), 1397, 964  $\text{cm}^{-1}$  (-OH bending) 1515.14  $\text{cm}^{-1}$  (N=N), 838.27  $\text{cm}^{-1}$  (Ar-Cl, para) and 711  $\text{cm}^{-1}$  (Ortho subst.);  $^1\text{H}$ -NMR(ppm): 6.59-7.92 (Aromatic), 1.37-1.78 (-HC-CH of Maleimide), 8.07 (Ortho-H of N=N-Ar), 2.07 (methyl proton of  $\text{CH}_3\text{CONH}_2$ ), 3.69 (aromatic amine), 10.06 (CO-NH).

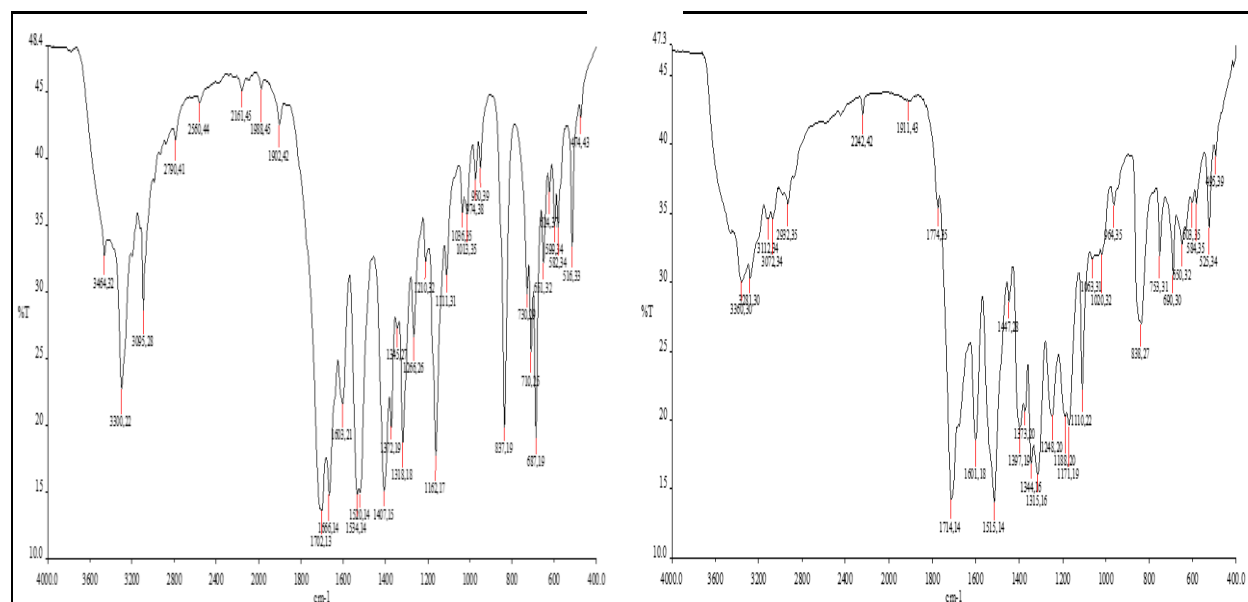
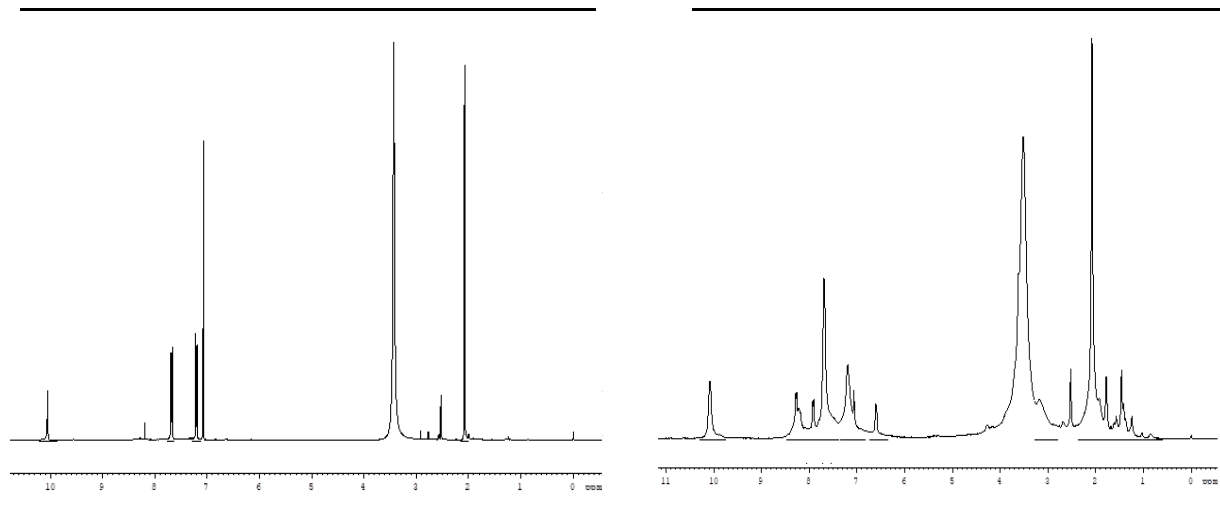


Figure 1: FTIR spectra of monomer [PACHMI] and copolymer [CPACHMI-AA]



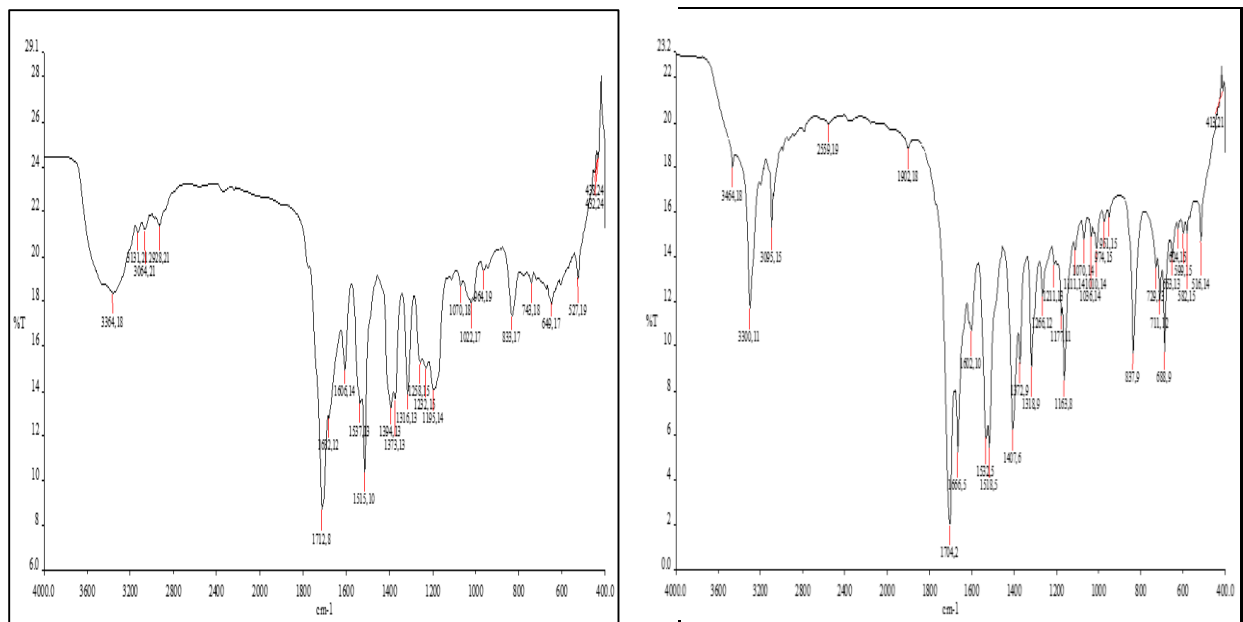
**Figure 2: <sup>1</sup>H NMR spectra of monomer [PACHMI] and copolymer [CPACHMI-AA]**

### 3. 4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)maleimide [PABMI]-

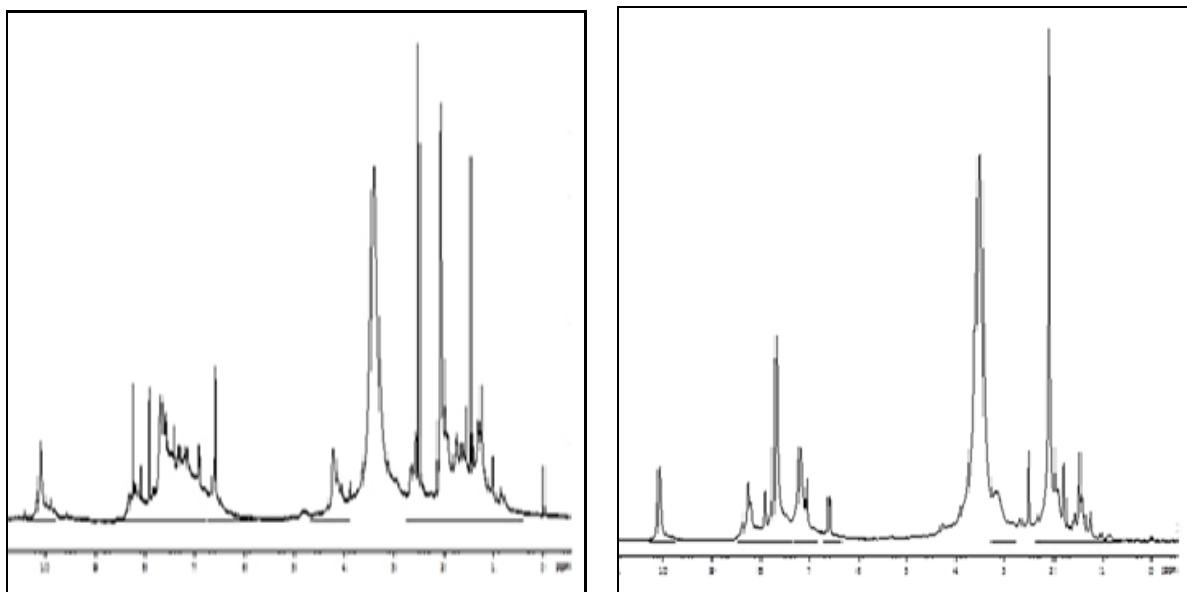
Yield 87%, melting point 148-50 °C; color dark brown, FT-IR (KBr): 1704 cm<sup>-1</sup>(C=O), 3300 cm<sup>-1</sup>(N-H), 3095 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1602 cm<sup>-1</sup>(C=O, amide), 1666 cm<sup>-1</sup>(CH=CH, C-C Stre.), 1372 cm<sup>-1</sup>(C-N-C), 1532 cm<sup>-1</sup>(N=N), 516 cm<sup>-1</sup>(Ar-Br), 837 cm<sup>-1</sup> and 711 cm<sup>-1</sup>(Para, Ortho); <sup>1</sup>H-NMR(ppm): 7.22-7.69 (Aromatic), 6.96-7.20 (HC=CH of Maleimide), 7.68 (Ortho-H of N=N-Ar), 7.67 (Meta -H of N=N-Ar), 10.06 (CO-NH).

### 4. [4-N-Phenylethanamide azo-3-N-(4-Bromophenyl)maleimide-co-Acrylic acid][CPABMI-AA]-

Yield 80 %, melting point 193-95 °C; color dark brown, FT-IR (KBr): 1712 cm<sup>-1</sup>, 1632 cm<sup>-1</sup>(-C=O, imide; -C=O, carboxylate), 3364 cm<sup>-1</sup>(-OH stre. of COOH), 3353 cm<sup>-1</sup>(N-H), 3069 cm<sup>-1</sup> (CH=CH, C-H Stre.), 1605 cm<sup>-1</sup>(C=O, amide), 1394 cm<sup>-1</sup>(C-N-C), 1316 cm<sup>-1</sup>(C-O stre. of carboxylic), 1373 cm<sup>-1</sup>, 954 cm<sup>-1</sup>(-OH bending) 1515.1 cm<sup>-1</sup>(N=N), 527.1 cm<sup>-1</sup>(Ar-Br); <sup>1</sup>H-NMR (ppm): 7.15-7.66 (aromatic), 6.65-7.14 (HC=CH of Maleimide), 8.19 (Meta -H of N=N-Ar), 3.69-1.22 {(CH-CH)-n}, 10.43 (CO-NH).



**Figure 3: FTIR spectra of monomer [PABMI] and copolymer [CPABMI-AA]**



**Figure 4: 1H NMR spectra of monomer [PABMI] and copolymer [CPABMI-AA]**

## 3.2 Spectral analysis of metal complexes

### 3.2.1 FT-IR Spectral analysis

Metal composites were prepared by using synthesized copolymers [CPAChMI-AA] and [CPABMI-AA]. All metal salts were used in hydrous state. In formation of metal composites, copolymer units utilized as ligand and nitrogen of maleimide ring and nitrogen of azo group were reacted electron donating sites and actively formed coordinated bonds with concern metal ions. -COOH functional group of acrylic acid was also formed bond with metal ion on the site of -C=O. The formations of metal composites were confirmed by FT-IR spectra. In spectral information, there have not major changes occurred in structures of metal composites. The band of -C=O of carboxylic acid showed weak intensity band due to the involvement metal and showed metal-chelation.

### 3.2.2 Electronic spectra and magnetic moments

Electronic spectra of metal composites with transition metals enhanced into broad bands due to availability of metal orbital because the transitions of electrons are spread over the range of energy levels. In electronic spectroscopy, various factors such as vibrational frequency of atoms, symmetry distortion, spin orbit coupling and John-Teller distortion are affected the electronic absorption spectra and these factors responsible to cause broadening of the absorption band. In this analysis, it was found that the spectral bands were broadened after irradiation of the composites. When the metal- ligand bond vibrates, electronic transition will occur over a range of energy levels and resultant, the broad band appears. The electronic spectrum of copper metal composites exhibited bands at 14527, 16758 and 24630  $\text{cm}^{-1}$  [CPAChMI-AA-Cu] and bands at 15027, 16721 and 24420  $\text{cm}^{-1}$  [CPABMI-AA-Cu] and the charge transfer spectra revealed to a distorted octahedral geometry with the magnetic moment of 2.06 B.M, 2.56 B.M. The electronic spectrum of Ni-metal composites exhibited three bands at 12524, 14745, and 24570  $\text{cm}^{-1}$  [CPAChMI-AA-Ni] and bands at 12124, 14995, and 24970  $\text{cm}^{-1}$  [CPABMI-AA-Ni] were assigned to the spin allowed transitions and assumed as octahedral geometry with a magnetic moment of 3.05 B.M, 3.24 B.M. The electronic spectrum of Cobalt metal composites also exhibited three bands at 12869, 12348, 14235, 15127 and 24870 , 24547  $\text{cm}^{-1}$  [CPAChMI-AA-Co] and [CPABMI-AA-Co] were assigned to the spin allowed transitions and showed octahedral geometry with a magnetic moment of 3.85 B.M, 4.09 B.M. The electronic spectrum of Fe-metal composites observed at 12321, 11988, 14835, 14479 and 24140, 24589  $\text{cm}^{-1}$  [CPAChMI-AA-Fe] and [CPABMI-AA-Fe] assigned to allowed spin transitions. Moreover, it has showed octahedral geometry with a magnetic moment of 4.15 B.M, 4.08 B.M. Attribute the electronic spectral absorption band range 3200-3600  $\text{cm}^{-1}$  can to the presence of water molecules in all metal-composites, either as a crystal water or in the coordinate-sphere. The electronic transition spectra of metal composites are described in Table 1.



**Table 1: Electronic transition spectra of metal composites**

Metal-composites	Band assignment
[CPAChMI-AA-Cu <sup>2+</sup> ] / [CPABMI-AA-Cu <sup>2+</sup> ]	Charge Transfer $2E_g \rightarrow 2T_{1g}$
[CPAChMI-AA-Ni <sup>2+</sup> ] / [CPABMI-AA-Ni <sup>2+</sup> ]	$3A_{2g} \rightarrow 3T_{2g}(F)$ $3A_{2g} \rightarrow 3T_{1g}(P)$
[CPAChMI-AA-Co <sup>2+</sup> ] / [CPABMI-AA-Co <sup>2+</sup> ]	$4T_{1g}(F) \rightarrow 4T_{1g}(P)$ $4T_{1g}(F) \rightarrow 4A_{2g}(F)$ $4T_{1g}(F) \rightarrow 4T_{2g}(F)$
[CPAChMI-AA-Fe <sup>2+</sup> ] / [CPABMI-AA-Fe <sup>2+</sup> ]	$5T_{2g} \rightarrow 5E_g$

### 3.3 Physical properties

Solubility of copolymers were examined by using solvents of varying parameters and it was seems that these were perfectly soluble in THF, DMF, DMSO, methanol, ethanol and partially soluble in acetone, 1, 4-dioxane and ethyl acetate. Viscosity and density also determined. Molecular weights of the synthesized copolymers were determined by GPC using Turbo matrix-40 Perkin Elmer instrument. In this process, polymers were dissolved in THF-solvent. The molecular weight and polydispersity index of copolymers [CPAChMI-AA] and [CPABMIAA] were determined. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) are furnished in Table 2.

**Table 2: Physical properties of monomers and copolymers [PAChMI] and [PABMI]**

Polymer Code	$\rho(g/cm^3)$	$\eta(dl/g)$	$M_n$	$M_w$	PDI(Poly Dispersity Index)
PAChMI	0.5873	0.119	-	-	-
CPAChMI-AA	0.9765	0.294	1146.2	1324.2	1.155
PABMI	0.8542	0.158	-	-	-
CPABMI-AA	0.9899	0.673	994.4	1385.5	1.393

### 3.4 XRD Analysis of metal composites

X-ray diffraction (XRD) patterns of maleimide copolymer-metal composites were examined. It provides comparative details of the behavior of copolymer and its metal composites. The pattern of metal-ligand crosslinking showed the relative half value width, it might be concluded that the copolymer is partially crystalline and the broad characteristic peak indicates the amorphous behavior of the copolymers and its metal complexes were showed crystalline nature. Therefore, the enhanced crystalline behavior of the metal-composites may be occurs due to the incorporation of metal ions with copolymer ligands.

### 3.5 Thermal Analysis

TGA for copolymers and metal composites have been carried out using Perkin Elmer-Purix-TGA Thermal Analyzer. The analysis was accumulated as the function of weight changes in taken compound with respect of time and temperature. The analysis was typically carried out in milligrams with a heating rate of 10 °C/min. from 50°C to 700°C in atmospheric air conditions. Thermal stability of copolymers and metal composites were analyzed by TG-curves. Almost all thermograms of copolymers were showed a one-step mass loss process with as low decomposition process in the range of 200-700°C.

TGA data shows that metal composites are revealed more thermal stable than their copolymers due to the interaction is effectively increases between metal ion and copolymer unit (ligand) and formed metal-ligand complex. The order of thermal stability of the metal composites is CPACHMI-AA-Cu<sup>2+</sup> > CPABMI-AA-Cu<sup>2+</sup> > CPACHMI-AA > CPACHMI-AA-Ni<sup>2+</sup> > CPACHMI-AA-Co<sup>2+</sup> > CPABMI-AA-Ni<sup>2+</sup> > CPABMI-AA-Co<sup>2+</sup> > CPACHMI-AA-Fe<sup>2+</sup> > CPABMI-AA > CPABMI-AA-Fe<sup>2+</sup>.

The greater stability of the metal composites may be due to the coordination network between metal ion and copolymer as ligand and the enhanced crosslinking, hence the rotation in polymer unit is completely hindered and i.e. responsible for rigid networking / crosslinking in entire structures. Resultant, thermal stabilities are increased highly in all metal composites. The thermal analysis results are collected in [table 3], indicated that the relative thermal stability by % weight loss v/s temperature.

**Table 3: Thermal analysis from TGA Thermograms of copolymers and their metal composites of [PACHMI] and [PABMI]**

Compound Code	% Weight Loss against Temperature					
	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C
[CPACHMI-AA]	7.34	19.87	38.1	54.34	73.93	92.36
[CPACHMI-AA-Cu]	4.13	12.54	31.20	45.27	67.12	86.02
[CPACHMI-AA-Ni]	6.25	18.14	42.21	55.15	77.24	88.31
[CPACHMI-AA-Co]	6.83	17.44	40.24	65.22	85.40	90.03
[CPACHMI-AA-Fe]	7.42	19.31	42.52	63.23	87.12	92.34
[CPABMI-AA]	6.75	23.53	37.68	47.15	67.25	95.47
[CPABMI-AA-Cu]	3.43	15.24	25.11	33.20	54.26	86.24
[CPABMI-AA-Ni]	7.45	18.47	35.21	57.05	69.04	87.01
[CPABMI-AA-Co]	8.63	17.42	40.14	68.42	73.55	90.73
[CPABMI-AA-Fe]	10.13	22.12	55.04	72.42	88.15	93.82

### 3.6 Microbial Evaluation

Maleimide compounds were contained some molecules as nitrogen, chlorine, oxygen shows great features against microb's growth. In this sequence to explore the experiment, the biological utilities of synthesized polymers and metal composites were tested in some pathogenic bacterial and fungal surroundings. Imide functional groups are itself shows antimicrobial features due to the presence of nitrogen molecule. For identify their antimicrobial qualities, antibacterial activities were performed against bacteria *Esherichia coil*, *P.aerogenosa*, *Esherichiaaerogenes*, *Staphylocous aureus* with 500 micrograms in concentration for 24 hours durations. Resultant, all synthesized polymers and composites were showed good resistance towardsbacterial growth. Antifungal activities were also examined with *Aspergillus nizer*, *Aspergillus flavus*, *Alternariasolani*, *Candida albicans*. Experimentally, old fungal culture (48 hours) inoculated into nutrient broth then incubated for 48 hours at  $37 \pm 2^{\circ}\text{C}$  in an incubator. Potatodextrose agar (PDA) media (25%) was used as diffusion medium. Different concentrations of standard drug and synthesized compounds along with control DMSO -solvent introduced in petri-dishes and placed in a refrigerator at  $10^{\circ}\text{C}$  for 2 hour for proper diffusion then petri dishes were referred into incubator and performed at  $37 \pm 2^{\circ}\text{C}$  for 24-36 hours. Concentration of all compounds were used in 500 micrograms. The results of microbe's growth of synthesized polymers and composites were evaluated with *streptomycin* antibacterial standard drug and *Griseofulvinas* antifungal standard drug. Among the copolymers, chlorine containing maleimide-copolymer showed good antimicrobial properties due to the presence of chlorine and nitrogen functional groups and another factor, the acrylic acid group used as co-monomer, existing with oxygen atoms to favour the microbial growth but the overall results are dominant for antimicrobial performances. From the antimicrobial results, the metal complexes of copolymers showed higher activity than their copolymer (ligand) it may be strongly dependent on the central metal ions and their coordination numbers. Due to the metal ions, the higher antimicrobial activity shared with the donor atoms (N and Cl) and which is responsible for  $\pi$ -electron delocalization over the chelate ring. This effect increases the lipophilic character of the metal ions, which favors to restrict the growth of microbes. From the results of the experiment, at 500 ppm concentration of the composites established better antimicrobial activity. Hence this is an interesting result that a very low concentration of the compounds are performed better to bring out an effective inhibition against the chosen microbe-strains. According to all scenario, the copolymer [CPAChMI-AA] was showed higher antibacterial and antifungal performances than CPABMI-AA. And all metal composites were also showed excellent antimicrobial properties. The toxicity of these polymers and composites for all microbes are revealed according to sequence as-

(i) CPAChMI-AA > CPABMI-AA

(ii) CPAChMI-AA-Cu > CPAChMI-AA-Co > CPAChMI-AA-Ni > CPABMI-AA-CU > CPABMI-AA-Ni > CPAChMI-AA-Fe > CPABMI-AA-Co > CPABMI-Fe

**Table 4: Screening of antibacterial activity against copolymers [CPAChMI-AA] and [CPABMI-AA]**

Compounds	Zone of Inhibition (in mm)			
Microb's species	<i>Esherichia coil</i>	<i>P. aerogenosa</i>	<i>Esherichia aerogenes</i>	<i>Staphylocous aureus</i>
Streptomycin (SD)	27	24	22	25
[CPAChMI-AA]	21.8	18.2	17.7	20.8
[CPABMI-AA]	19.4	16.6	14.5	19.4

**Table 5: Screening of antibacterial activity against metal composites of copolymers [CPAChMI-AA] and [CPABMI-AA]**

Compounds	Zone of Inhibition (in mm)			
Microb's species	<i>Esherichia coil</i>	<i>P. aerogenosa</i>	<i>Esherichiaaerogenes</i>	<i>Staphylocous aureus</i>
[CPAChMI-AA-Cu]	25.2	23.2	20.4	22.3
[CPAChMI-AA-Ni]	23.7	22.8	19.9	21.5
[CPAChMI-AA-Co]	22.9	22.1	19.3	21.2
[CPAChMI-AA-Fe]	20.2	20.6	16.5	19.5
[CPABMI-AA-Cu]	24.3	21.3	19.6	21.8
[CPABMI-AA-Ni]	22.4	20.7	18.2	18.9
[CPABMI-AA-Co]	21.9	19.6	17.8	17.6
[CPABMI-AA-Fe]	21.3	17.7	15.8	16.2

**Table 6: Screening of antifungal activity against copolymers [CPAChMI-AA] and [CPABMI-AA]**

Compounds	Zone of Inhibition (in mm)			
Microb's species	<i>Aspergillus nizer</i>	<i>Aspergillus flavus</i>	<i>Alternariasolani</i>	<i>Candida albicans</i>
Griseofulvin (SD)	26	23	20	22
[CPAChMI-AA]	19.9	16.7	17.9	20.1
[CPABMI-AA]	18.2	15.2	17.5	17.8

**Table 7: Screening of antifungal activity against metal composites of copolymers [CPAChMI-AA] and [CPABMI-AA]**

Compounds	Zone of Inhibition (in mm)			
	<i>Aspergillus nizer</i>	<i>Aspergillus flavus</i>	<i>Alternariasolani</i>	<i>Candida albicans</i>
[CPAChMI-AA-Cu]	23.2	20.5	20.4	19.5
[CPAChMI-AA-Ni]	21.8	19.3	19.6	18.2
[CPAChMI-AA-Co]	21.2	18.5	19.1	17.4
[CPAChMI-AA-Fe]	19.4	16.8	17.9	17.1
[CPABMI-AA-Cu]	20.7	19.7	19.5	19.3
[CPABMI-AA-Ni]	19.6	18.1	18.2	18.2
[CPABMI-AA-Co]	18.5	17.4	17.6	16.8
[CPABMI-AA-Fe]	17.2	16.2	16.5	15.9

#### 4. CONCLUSION

[4-N-Phenylethanamide azo-3-N-(4-chlorophenyl) maleimide-co-Acrylic acid] [PAChMI], [4-N-Phenylethanamide azo-3-N-(4-bromophenyl) maleimide-co-Acrylic acid] [PABMI] monomers and their copolymers with acrylic acid were synthesized. Transition metals of d-block such as  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$  were successfully incorporated into copolymers units and formed metal-complexes / metal composites through metal-ligand bonding. In metal chelation process nitrogen atom of imide group and azo group of copolymer unit played as a ligand electron donor site. These metal composites and polymers were characterized from FTIR,  $^1\text{H}$ NMR, UV-visible spectroscopies. XRD and TGA analysis were conducted to find out their thermal and geometric nature and some physical analysis was also evaluated. According to thermal analytical results, all metal composites were exhibited excellent thermal stability then their copolymers. Antimicrobial performances of metal composites were performed greatly then copolymers and results of these activities are favored to use in various biomedical applications. Synthesized maleimide-metal composites and their chemical structure / reactions and molecular weight are reinforcing to subject of further research work.

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#### CONFLICT OF INTEREST

The authors have no conflict of interest.

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