MICROWAVE ASSISTED SYNTHESIS AND CHARACTERISATION OF TERPOLYMER DERIVED FROM O-AMINOPHENOL, MELAMINE AND FORMALDEHYDE

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ABSTRACT
This paper presents the microwave assisted synthesis of a terpolymer by using the o-aminophenol , melamine and formaldehyde. The o-APMF terpolymer have been synthesized from o-aminophenol (o-AP), melamine (M) and formaldehyde (F) in DMF media at 132±2 ºC for 110 sec. The synthesized terpolymer was purified and then characterized on the basis of spectral data generated from FTIR, H^1NMR, C^{13}NMR and SEM.

Keywords: *microwave irradiation, structure, spectral analysis, o-APMF.*

INTODUCTION

The terpolymers offered novelty and versatility; hence they occupy the pivotal position in the field of material science. The progress in the field of terpolymer has been extensively rapid, as they are useful in packaging, adhesive, coating in electrical sensors and organometalic semiconductors. [1-3]. Polymer additives improve manufacture process and product quality. It can form continuous phase of coating with no deleterious effects on coatings, and having better thermal stability [4-6].
In recent years, microwave techniques have been mainly applied for domestic, industrial and research purposes. Various synthetic reactions using microwave irradiation involve processes to prevent pollution and consume minimum amounts of materials as well as energy while producing little or no waste material. More recently, microwave-assisted organic synthesis, a new method, has been developed to obtain more efficient compounds in a short reaction time period [12, 13]. This method has been applied for many inorganic, organic and polymer syntheses. [14-18]. Various researchers have reported the application of microwave technology in terpolymer synthesis [19,20]. Microwave irradiation has been applied in recent years for step-growth polymerizations and ring-opening polymerizations as well as radical polymerizations [21].

In this article, we present the synthesis and characterization of terpolymer (o-APMF) derived o-aminophenol, melamine using the linkage of formaldehyde. The newly synthesized terpolymer has been characterized by elemental analysis and spectral methods.

MATERIAL AND METHODS:

SYNTHESIS OF o-APMF TERPOLYMER

o-APMF terpolymer was prepared from o-aminophenol (0.1 mol, 1.243 gm,) and melamine (0.1 mol, 1.26 gm,) with formaldehyde (11.1 ml of 37 %, 0.3mol) in the molar ratios of 1:1:3 in the presence of DMF medium at 130 ± 2^0C for 110 Second using a microwave system. The resinous brown solid mass obtained was immediately removed from the flash as soon as the reaction period was over and then it purified. Excellent yield of terpolymer be obtained by this reaction.

The resinous brown product so obtained was repeatedly washed with cold distilled water, dried in air and powdered with the help of mortar and pestle. The powdered sample was washed many times with boiling water and methanol to remove unreacted monomers. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water with constant and rapid stirring to avoid lump formation. The process of reprecipitation

was repeated thrice. The resulting terpolymer sample was filtered, washed several time with boiling water, dried in air, powdered and kept in vacuum over silica gel. The yield of the copolymer resin was found to be 89%.

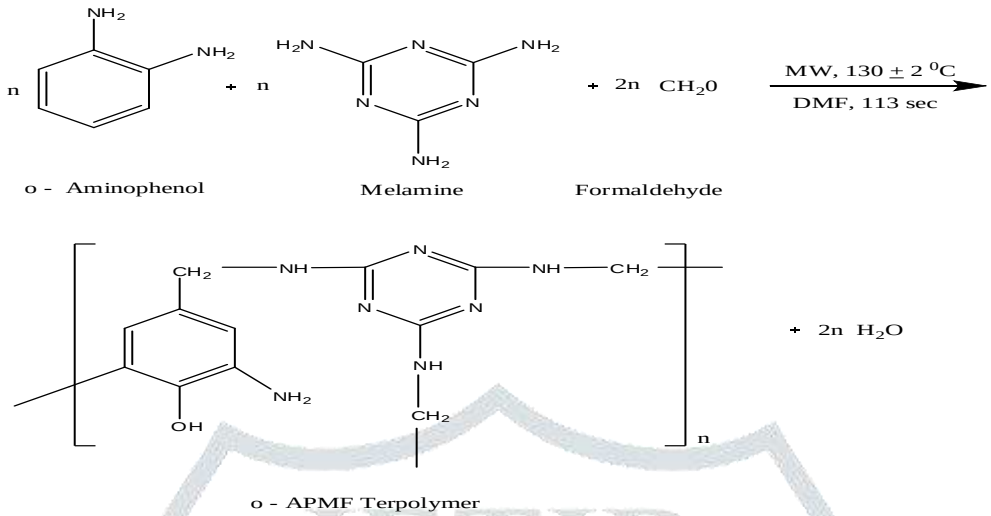


Fig. 1. Reaction and Suggested Structure of Representative o-APMF terpolymer

RESULTS AND DISCUSSION:

A) ^{1}H NMR SPECTROSCOPY

The NMR specta of o-APMFwere scanned in DMSO and have been shown (Fig. 2). The NMR spectral data are incorporated in (Table 1). All the o-APMF terpolymer show the weak multiplate signal (unsymmetrical pattern) in the region of 6.55 - 6.75(δ) ppm may be attributed to aromatic proton. The signal appeared in the range of 7.74 to 7.80 (δ) ppm can be assigned due to phenolic hydroxyl protons. The position of the signal of phenolic hydroxyl proton is slightly shifted to downfield, indicating clearly the intramolecular hydrogen bonding of -OH group [186-187]. The signal at 2.27 - 2.36 (δ) ppm may be due to methylene proton of Ar-CH_2 moiety.The intense weakly multiplate signals at 2.14 - 2.16 (δ) ppm may be attributed to methyl proton of Ar-CH_3 group. The signal at 3.26to 3.38 (δ) ppm may be due to the methylene proton of Ar-CH_2-N moiety. The signal in the region 5.18-5.22 (δ) ppm are attributed to protons of -NH bridge.

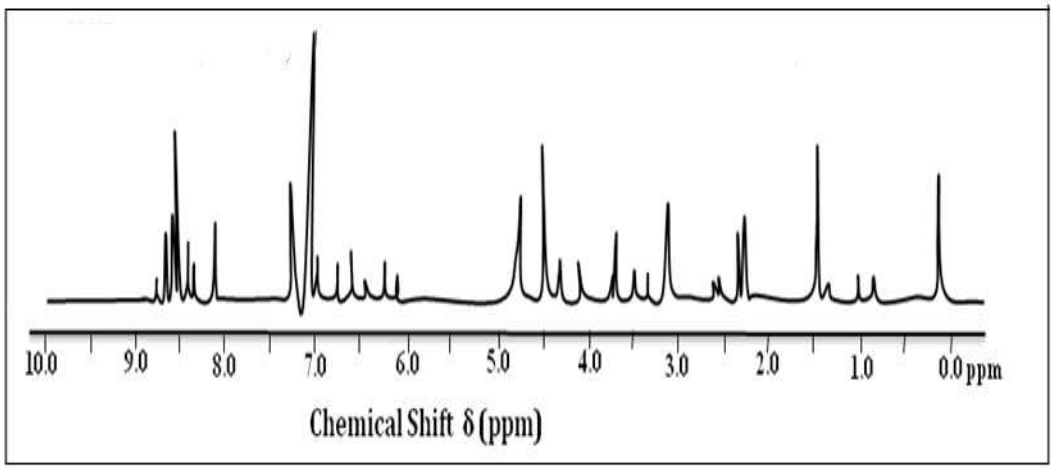


Fig. 2. ^{1}H NMR Spectra of o-APMF Terpolymer

Table-1 ^{1}H NMR Spectral Data of o-APMF Terpolymer

Observed Chemical Shift (δ) ppm				Nature of proton assigned	Expected chemical shift (d) ppm
o-APMF-I	o-APMF-II	o-APMF-III	o-APMF-IV		
2.15	2.14	2.16	2.17	Methyl proton Ar-CH_3 group	2.00 - 3.00
2.27	2.29	2.31	2.36	Methylene proton of Ar-CH_2 moiety	2.00 - 3.00
3.38	3.3	3.26	3.34	Methylenic proton of Ar-CH_2-N moiety	3.00 - 3.50
5.22	5.22	5.18	5.19	Proton of –NH bridge	5.00 - 8.00
6.8	6.55	6.7	6.7	Aromatic Proton (Ar-H)	6.2 - 8.5
7.74	7.76	7.77	7.8	Proton of phenolic-OH involved intramolecular hydrogen bonding	7.00 - 12.00

B) ^{13}C NMR SPECTROSCOPY

A ^{13}C NMR spectrum of o-APMF terpolmer is presented in Fig. 3. The ^{13}C NMR spectra of o-APMF terpolymer peak are assigned with reference to the literature value. The ^{13}C NMR spectra show the corresponding peaks appeared at 118.64, 119.92, 128.93, 133.90 and 136.90 ppm may be corresponded to carbons present in aromaticring of the benzophenone. The peak appeared at 164.77 ppm of may be corresponding to carbonyl group of biuret moiety. The medium peak appeared at 116.55 ppm may be confirmed the presence of –C-NH group of copolymer resin. The peak appeared at 80.48 ppm may be due to the presence of –C-OH group in aromatic benzophenone group. The peaks appeared at 43.46 ppm may be due to the –CH_2 – bridge in terpolymer. The ^{13}C NMR spectrum clearly established the linear structure of the terpolymer synthesized from o-aminophenol-melamine-formaldehyde.

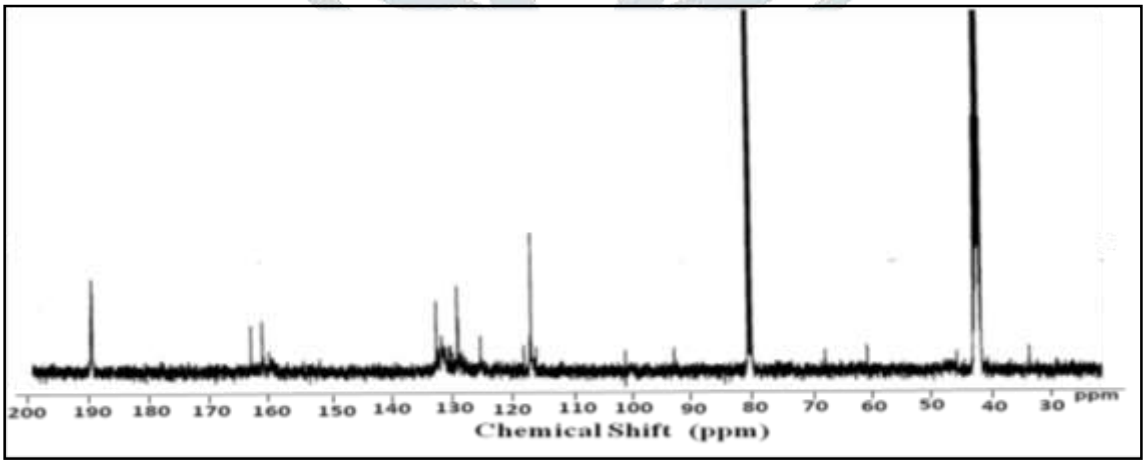


Fig. 3. ^{13}C NMR Spectra of o-APMF Terpolymer

C) INFRA-RED SPECTROSCOPY

The recorded FTIR spectra of o-APMF terpolymer are shown in (Fig. 4) and important IR band along with their assignments have appeared in the spectrum is tabulated in (Table 3). The FTIR spectra of

terpolymer are found to be similar pattern of various bands at the characteristics frequencies, which are described below.

The spectrum shows a very board absorption band appeared at 3331-3419cm^{-1} may be due to the stretching vibrations of phenolic hydroxyl (-OH) groups involved in intramolecular hydrogen bonding. A peak at 1570-1700 cm^{-1} may be ascribed to aromatic skeletal ring. The sharp, medium/ weak absorption bands appeared at 946-949 cm^{-1} and 1038-1040 cm^{-1} may be due to 1,2,3,5 substitution of aromatic benzene ring respectively. The sharp and strong band appeared at 3042-3094 cm^{-1} indicates the presence of -NH bridge or may be due to -CH_3 stretching. The bands appeared at 1478 to 1482 cm^{-1} may be due to -NH bending of secondary amide and the band at 1354-1360 cm^{-1} may be due to (-CH_2-) bridge[22].

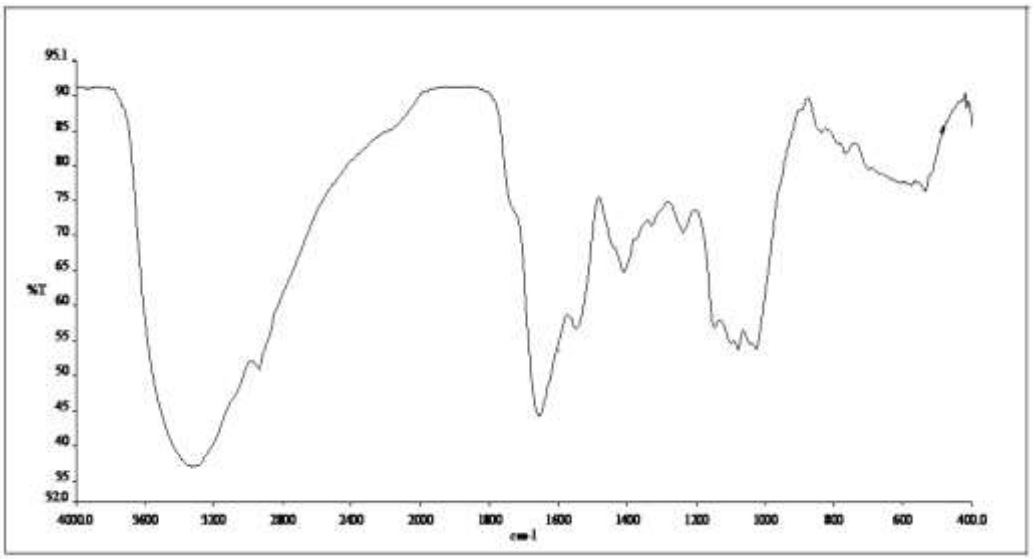


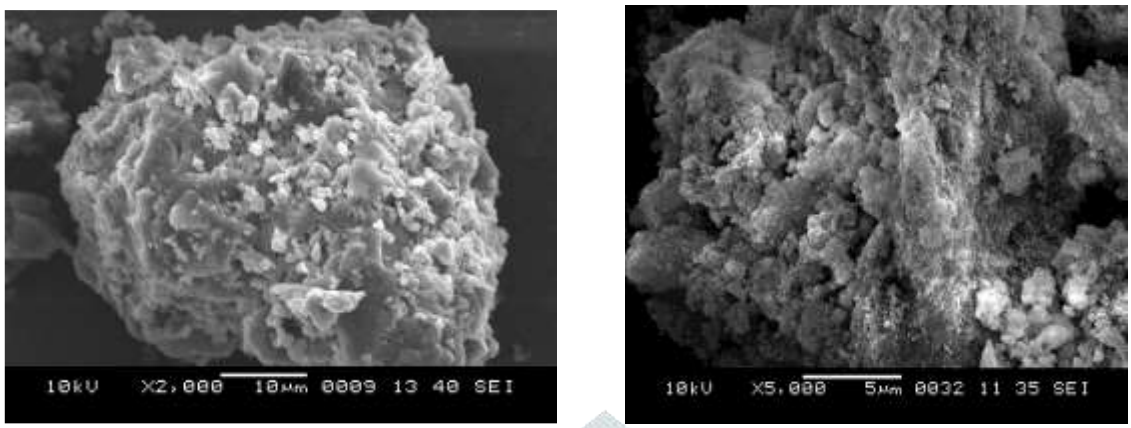
Fig. 4. Infra Red Spectra of o-APMF Terpolymer

Table 3
IR Frequencies of o-APMF Terpolymer

Observed band frequencies (cm^{-1})				Assignment	Expected band frequencies (cm-1)
o-APMF-I	o-APMF-II	o-APMF-III	o-APMF -IV		
3331 (b,st)	3381 (b,st)	3384 (b,st)	3382 (b,st)	-OH phenolic intermolecular hydrogen bonding	3450-3200
2912 (w, m)	2920 (w, m)	2942 (w, m)	2940 (w, m)	Aryl C-H stretching	3000-2910
3042 (b,st)	3066(b,st)	3086(b,st)	3094(b,st)	>CH_2, >NH, -CH3 stretching	~3000
1653 (sh,b)	1569 (sh,b)	1572 (sh,b)	1583 (sh,b)	Aromatic ring (substituted)	1700-1500
1482 (m)	1480 (m)	1478 (m)	1480 (m)	-NH bending of secondary amide	1500-1450
1354 (w)	1360 (w)	1357 (w)	1359 (w)	-CH_2- bridge	1390-1370
946 (w)	948 (w)	947 (w)	950(w)	1,2,3,5 substitution in benzene	~950
1038 (m)	1039 (m)	1040 (m)	1039 (m)		~1050

sh=sharp, b=broad, st= strong, m= medium, w=weak

D. SCANNING ELECTRON MICROSCOPY (SEM)



(a) **(b)**

Fig. 5. SEM Micrographs of o-APMF-I Terpolymer

The scanning electron morphology of o-APMF terpolymer sample was investigated by different magnification 2000X and 5000X, which are shown in Fig. 5 (a) and (b) respectively. The terpolymer appeared to be dark drawn in color. The scanning electron morphology of o-APMF terpolymer shown spherule and fringed model. The spherules are complex polycrystalline formation having as good as smooth surface. This indicates the crystalline nature of o-APMF terpolymer. The morphology of terpolymer shows also a fringes model of the crystalline amorphous structure. The extent of crystalline character depends on the acidic nature of the monomer. But the photograph shows the fringed and scatted nature having shallow pits represent the transition between crystalline and amorphous. The terpolmer exhibits more amorphous characters with closed packed surface having deep pits, which is shown Fig.5. Due to the deep pits, terpolmer exhibits higher exchange capacity for Pb (II) ions (as well as other many metal ions). This could be the reason of bigger nitrated Pd (II) ions, which can easily penetrate in to the deep pits. Thus by scanning electron morphology of the o-APMF terpolmer shows the transition between crystalline and amorphous nature. When compare to the other resin, the o-APMF terpolymer resin is more amorphous in nature, hence shows higher metal ion exchange capacity.

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