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Synthesis and Characterization of Copolymer Derived from Sulphanilic acid, Melamine and Formaldehyde.

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ABSTRACT

Copolymer sulphanilic acid-melamine-formaldehyde (SAMF) has been synthesized by the condensation polymerization of sulphanilic acid (SA), melamine (M) and formaldehyde (F) as monomers in the presence of 1M HCl as a catalyst in 1:1:4 molar ratios of reacting monomers. The copolymer was characterized by various spectral technique such as elemental analysis, fourier transform infrared (FTIR), ^{1}H NMR and XRD techniques. The number average molecular weight of copolymer was determined by non-aqueous conductometric titration method. The morphological feature of the SAMF copolymer was recognized by Scanning electron microscopy (SEM).

Keywords: Copolymer, Characterization, Sulphanilic acid, Synthesis, Polycondenstion.

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INTRODUCTION

In recent years, a special courtesy has been focused to explore the possibility of using polymer materials as potent biomaterials and thermally stable materials due to their versatile application in various field such as adhesives, coating material, packaging, electroluminescent devices, hardener for epoxy resins, fire resistant materials [1-4]. Consequently, many polymers are now being synthesized, tested, and used not only for their bulk properties of the polymers but also for the properties of thermal stability and antimicrobial ability because of their high efficiency and superior utility [5–7].These improved properties, associated with organic moiety of the coordination polymers, can be used as heat-resistant surface coatings in the field of space research to prevent from the atmosphere and can also be used as biocidal coatings to prevent from the several microorganisms [8-10].

The thermal analysis research embraces a collection of techniques where the physical property of the substances is measured as a function of temperature when exposed to a controlled substance temperature. Thermally stable copolymers have been windfall for polymer chemist because of their high efficiency. They find applications as lubricants, adhesives, coating materials, catalysts, semiconductors, ion exchangers, fire resistant materials. Anbarasan R. et al extensively studied the thermal property of NIR fluorescent probe based on Poly (anthranilicacid)/and nanocomposite [11]. Gurnule et.al. synthesized copolymer resin derived from 2, 4-dihydroxypropiophenone, 1, 5-diaminonaphthalene and formaldehyde and studied its thermal kinetics [12]. Many studies have been carried out on heavy metal removal by various methods such as precipitation, reduction, reverse osmosis, flocculation, ion-exchange, adsorption and solvent extraction. The ion-exchange method plays an important role in the extraction of tracking metals, the separation of impurities, industrial segments and the process of cleaning and concentrating. Mandavgade et. al. synthesized and comments on ion exchange properties of copolymer resin derived from 8-hydroxyquinoline-5-sulphonic acid-catechol-formaldehyde [13].

Effective antimicrobial properties possessing copolymer has been synthesized by Burkanudeen AR, et al using monomers anthranilic acid, urea and formaldehyde [14]. Gurnule et al blended polymeric resin and it's composite for Selective removal of toxic metal ions from waste water [15]. Photoluminescence properties of copolymer derived from 8-hydroxyquinoline-5-sulfonic acid, hexamethylenediamine and formaldehyde has been synthesized and studied by Chetana Kohad and W. B. Gurnule and suggest the cooperative help amongst design and photoluminescence via new and essential commitments from dynamic specialists within the area.[16-17].

Emulsion polymerization technique was used to prepare Copolymer SBR- nano tin oxide composite and significantly focused on thermal and mechanical properties of composite by Rani Mankar and coworker [18]. Double layered hydroxide/graphene oxide composites modified using 7-octenyltrimethoxysilane was prepared by co-precipitation method [19].

Numerous scientists work on synthesis of polymeric materials with improved properties [20-21] and their flexible utility in our everyday life and the copolymer resin shape an extraordinary class of polymers, are generally known for their huge application such as electrical conductivity, thermal resistance properties, incredible abrasives [22-23].

Present study aimed to synthesize new copolymer using specified monomers sulphanilic acid, melamine and formaldehyde. This synthesized copolymer was then characterized by various analytical and spectral techniques.

EXPERIMENTAL METHODS

Materials

All the chemicals used for the synthesis were purchased from Central Scientific Company Nagpur. Sulphanilic acid and Melamine belong to Loba Chemie Pvt. Ltd. in Extra pure form and Formaldehyde from Qualigens Thermo Fisher Scientific India Pvt. Ltd. All the chemicals were used as received without any further purification.

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Synthesis of SAMF Co-polymer

The copolymer SAMF was synthesized by polycondenstion technique involving monomersulphanilic acid, melamine and formaldehyde in 1:1:4 molar ratios using 1M HCl as catalyst for about 5hinan oil bath at the temperature range 120^{0}C.After completion of the reaction creamish hard solid material was formed. This solid product was then transferred into ice cold water and left overnight. It is then wash with warm water, methanol and acetone followed by filtration to remove unreacted monomers and impurities. Finally, the copolymers were dried in air or in oven at 75^{0}C for 24 hours. The reaction sequence has been depicted in the following figure 1.

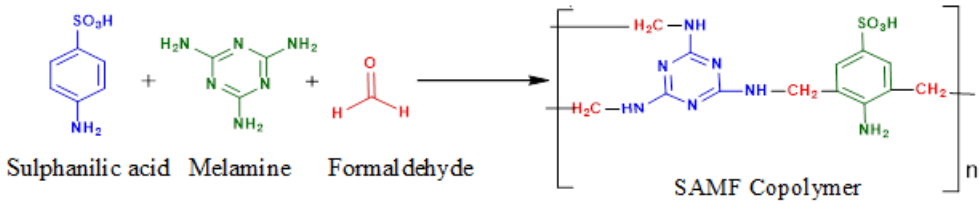

Figure 1: Synthesis of SAMF copolymer

Physicochemical and Analytical Studies

The elemental analysis was carried out by using elementary Vario EL III instrument. X-ray diffraction (XRD) measurement of synthesized sample was carried out using Bruker Model D8 Advance A25X.Fourier transform infrared (FT-IR) spectrum of prepared sample was recorded on a Thermo Nicolet iS50 FTIR spectrophotometer with range from of 4000cm^{-1} to 400 cm^{-1}.Proton NMR spectra were recorded in Dimethyl Sulfoxide-d_6 (DMSO) solvent using Bruker Avance III 400 MHz spectrometer. The morphology of synthesized sample was examined using scanning electron microscopy (SEM) JEOL, JSM—6390LV, Tokyo, Japan). The SEM measurements were performed at 15 kV accelerating voltage. All the analytical and spectral studies for newly synthesizes copolymer was carried out at sophisticated test and instruments centre (STIC) Kochi, Kerala India.

RESULTS AND DISCUSSION

The newly synthesized copolymer was found to be light creamiest in colour and soluble in dimethyl sulphoxide (DMSO) solvent whereas insoluble in the most of common organic solvent. The yield of SAMF copolymer was found to be 85%.

Elemental Analysis

Newly synthesized copolymer SAMF was analyzed for elements carbon, hydrogen, nitrogen and sulphur content. On the basis of result obtained, empirical formula and empirical weight of single repeating unit of copolymer was found to be $C_{13}H_{14}N_7SO_3$ and 348 which is in good agreement with calculated values.

The number average molecular weight (M_n) of newly synthesized copolymer SAMF was dogged by non-aqueous conductometric titration in DMF expending 0.1 M KOH in absolute alcohol as titrant. When graph is plotted with specific conductance against miliequivalents of base,from the first and last break which is utilized to calculate degree of polymerization (DP) and from which number average molecular weight was estimated for copolymer resin as per following equation.

$$DP = \frac{Total\ miliequivalent\ of\ the\ base\ required\ for\ last\ break}{Miliequivalent\ of\ the\ base\ required\ for\ last\ break}$$

Mn = DP x Molecular weight of the repeating unit

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Table 1: Elemental analysis and molecular weight determination of SAMF copolymer.

Copolymer	% of C Obs. (Cal.)	% of H Observed (Calculated)	%N Observed (Cal.)	%S Observed (Cal,)	DP	Mol. Wt. (Mn)	M.F. of repeating unit	Mol. Wt. of repeating Unit
SAMF	37.95 (42.62)	2.79 (3.82)	23.30 (26.77)	4.05 (4.96)	26	8738	$C_{13}H_{14}N_7SO_3$	348

Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectra of synthesized copolymer were recorded at Sophisticated Test and Instrumentation Centre (STIC), Kochi Kerala, India using Thermo Nicolet iS50 FTIR spectrophotometer. The broad bond at 3201 cm^{-1} may be attributed to stretching vibration of hydroxyl group (O-H) of sulphonic acid group (SO_3H) present in aromatic ring of sulphanilic acid moiety as well as phenyl –NH stretching vibration of melamine moiety [24]. Stretching vibration in the range of 1745-1494 cm^{-1}may cause due to aromatic ring with sulphanilic acid group [25]. A peak at 1327 cm^{-1}indicate triazine ring of melamine unit. Stretching vibration at 1007,886, and 812 cm^{-1} is attributed to the presence of triazine ring [26]. Characteristic peak observed at 1494 and 1650 cm-1 is attributed to C=N stretching frequency belonging to melamine moiety. The sharp and strong band appears at 1327 cm-1 shows presence of –CH2- Methylene Bridge in copolymer chain [27]. The FTIR spectrum of SAMF copolymer is depicted in figure 2.

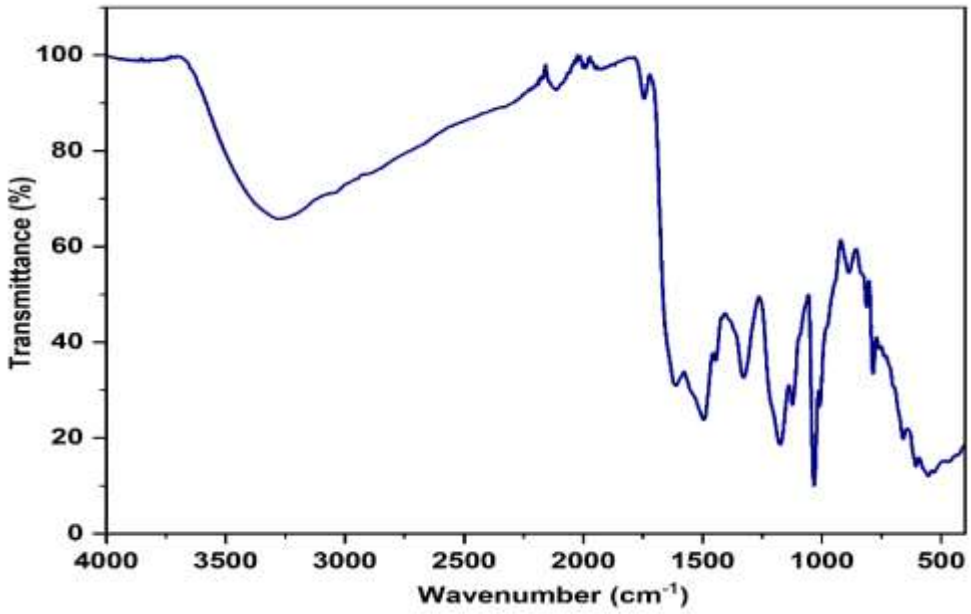

Figure 2: Fourier Transform Infrared spectra of SAMF copolymer

X-ray diffraction Studies (XRD)

X-ray diffraction pattern observed for SAMF copolymer showed transition between amorphous and crystalline nature of polymer. XRD pattern of synthesized copolymer designate broad shoulder, which may due to amorphous nature of polymer whereas high intensity with narrow band shows crystalline nature. Fig. 3 XRD graph shows both features high intensity with narrow band and small broadness [28-29]. But, in view of the relative half value width, it may be concluded that the polymer is partially crystalline and the broad characteristic peak indicates the amorphous nature of the copolymer.

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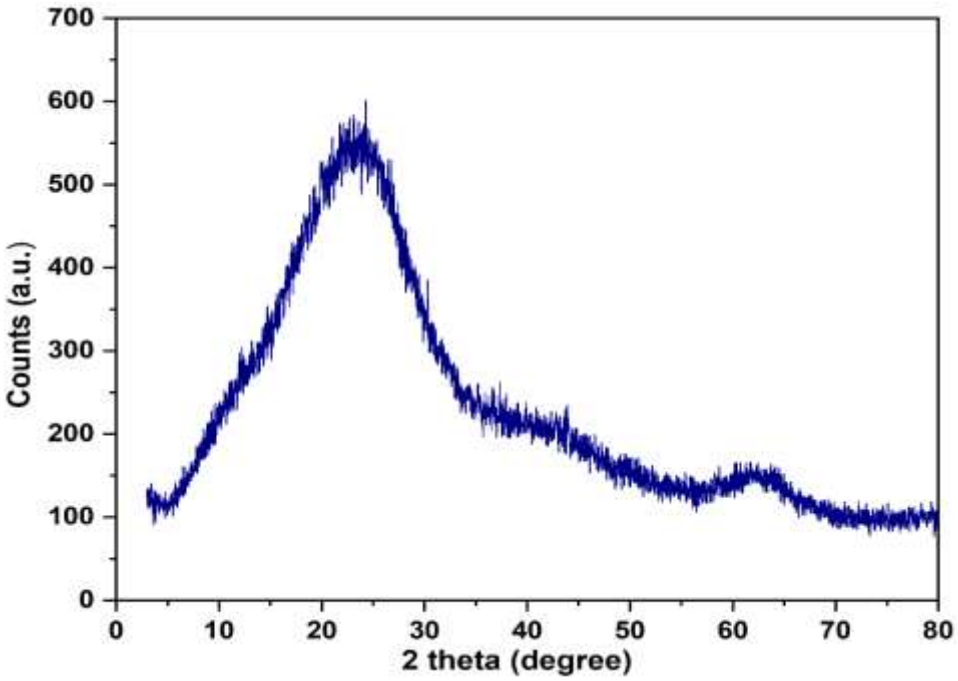

Figure 3: X-ray diffraction (XRD) outline of SAMF copolymer

Scanning Electron Microscopy (SEM)

The SEM photographs obtained in ×500 and ×1000, ×3000 and x6000, magnifications for SAMF copolymer are shown in Figure 4. It indicates that the SAMF copolymer has a spherulites and fringed structure and the surface features of the copolymer shows a fringed, scattered, and miscellaneous model of the crystalline–amorphous structure [30]. It is clear from SEM picture that scatted and bordered with small pits that stand in for the transition between crystalline and amorphous. The morphology of the polymer shows a fringed model of the semi crystalline nature. The fringes represent the transition between the crystalline and the amorphous phases. The copolymer exhibits a more amorphous character with a close-packed surface having deep pits.

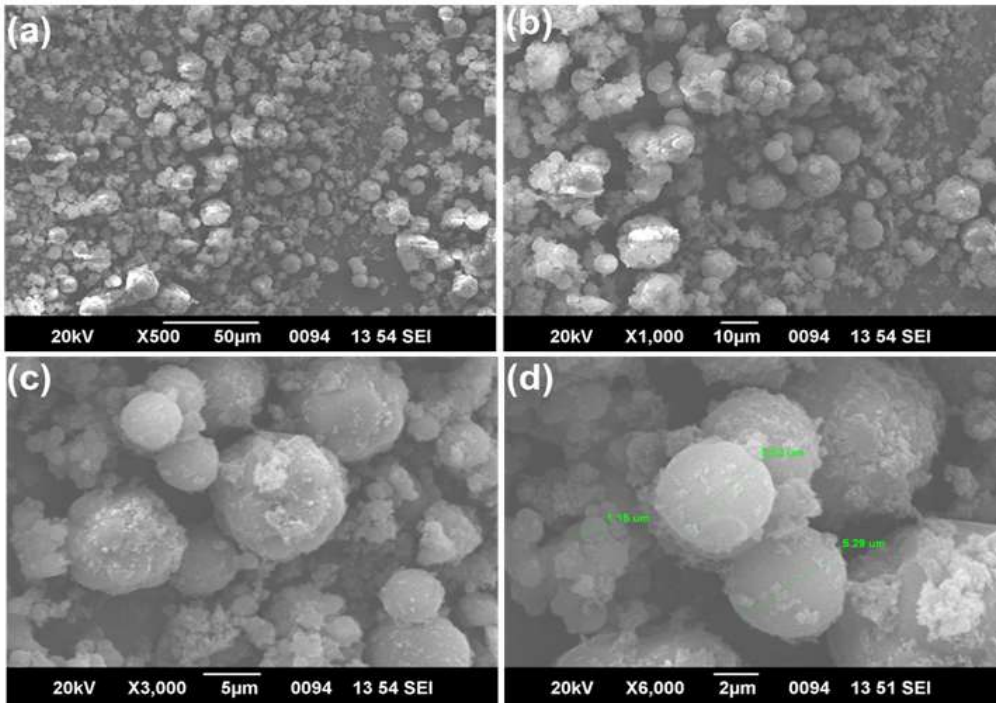

Figure 4: Scanning Electron Microscopy image of synthesized Copolymer

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^{1}H NMR Study of Synthesized Copolymer

^{1}H NMR spectra of synthesized copolymer were interpreted on the basis of literature [31-32] and shown in the figure 5.NMR signal appear in the range of 7.11 to 7.75ppm are assigned for all aromatic proton of benzene ring. A weak singlet at 9.2(δ) ppm suggests the presence of the –SO3H group [33-34]. Methylene proton that triggers signal at 1.96(δ) ppm possibly assigned to Ar-CH2-N [35]. Proton NMR spectra was recorded in Dimethyl Sulfoxide-d_6 (DMSO) solvent using Bruker Avance III 400 MHz spectrometer at sophisticated test and instrument centre (STIC) Kochi, Kerala (India).

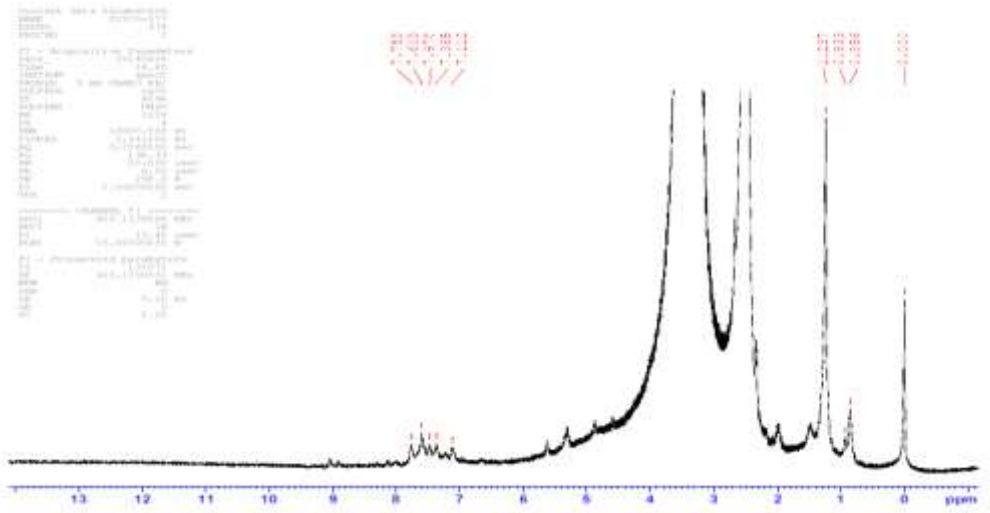

Figure 5: ^{1}HMR spectra of SAMF Copolymer

CONCLUSION

SAMF copolymer was amalgamated by Polycondenstion technique using monomers sulphanilic acid, melamine and formaldehyde in 1M HCl acid catalyst at 120^{0}C for about 5h. On the basis of various analytical and spectral studies synthesized copolymer structure was confirmed using elemental, Fourier Transform infrared (FTIR), nuclear magnetic resonance (^{1}HNMR) studies. Surface morphology of copolymer was confirmed by scanning electron microscope (SEM) as well as x ray diffraction (XRD) which elucidates transition between crystalline and amorphous nature. This widespread approach enriches our understanding of copolymer structure and properties in polymer era.

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