



## ORIGINAL ARTICLE

# Thermal degradation kinetics and antimicrobial studies of terpolymer resins



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**Abstract** The terpolymer (ASF) was synthesized by condensation of anthranilic acid and salicylic acid with formaldehyde in the presence of glacial acetic acid as a catalyst at  $140 \pm 2$  °C for 6 h with varying proportions of reactants. The terpolymer ASF-I was characterized by elemental analysis, FTIR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. The thermal decomposition behavior of ASF-I, II and III terpolymers was studied using thermogravimetric analysis (TGA) in a static nitrogen atmosphere at a heating rate of 20 °C/min. Freeman–Carroll, Sharp–Wentworth and Phadnis–Deshpande methods were used to calculate the thermal activation energy ( $E_a$ ) the order of reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ) and frequency factor ( $Z$ ). Phadnis–Deshpande method was used to propose the thermal degradation model for the decomposition pattern of ASF-I terpolymer resin. The order of the decomposition reaction was found to be 0.901. The thermal activation energy determined with the help of these methods was in good agreement with each other. The ASF-I, II and III resins were tested for their inhibitory action against pathogenic bacteria and fungi. The resins show potent inhibitory action against bacteria, such as *Escherichia*

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*coli*, *Klebsiella*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* and fungi viz. *Aspergillus flavus*, *Aspergillus niger*, *Penicillium* sp., *Candida albicans*, *Cryptococcus neoformans* and *Mucor* sp.

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## 1. Introduction

Thermal analyses play a vital role in studying the structure and properties of any material (Donia, 1998). Thermogravimetric analysis has been widely used to investigate the decomposition characteristics of polymeric materials (Wilkie et al., 1991; Al Shawabkeh et al., 2007). Aromatic terpolymers have excellent thermal stability, good mechanical properties, high chemical resistance and low dielectric constant hence they are widely used in semiconductor devices, printed circuit boards and shape memory alloys. Terpolymer materials are used for the synthesis of functional nanostructures because of their excellent thermal characteristics. Thus, thermal stability and thermal degradation kinetics may be significant for the production and application of terpolymer based materials. TGA data have been used to determine the thermal degradation kinetics and thermal stability of terpolymer (Gupta and Singh, 2005; Riswan Ahamed et al., 2010a, b). The study of thermal behaviors of terpolymers in different environment and temperature provides useful information about the nature of the species produced at various temperatures due to degradation (Tarase et al., 2010). Equally, the incidence of fungal and bacterial infections has increased dramatically in recent years. The widespread use of antifungal and antibacterial drugs and their resistance against fungal and bacterial infections have led to serious health hazards. The resistance of wide spectrum antifungal and antibacterial agents has initiated the discovery and modification of the new antifungal and antibacterial drugs (Peara and Patterson, 2002). The study reported that the TGA technique can be applied to acrylonitrile-butadiene-styrene terpolymer to evaluate the activation energy by isothermal and dynamic thermogravimetric methods (Yang, 2000). The relative thermal stabilities of some new terpolymers derived from *p*-cresol, melamine and formaldehyde were determined using Freeman–Carroll method (Singru et al., 2008). 8-Hydroxyquinoline and guanidine with formaldehyde terpolymer have been synthesized and their thermal degradation kinetics was evaluated. From the results, the decomposition reaction of terpolymer has been classified as a slow reaction, which is evident from the low frequency factor values (Michael et al., 2007). Thermal stabilities of copoly(maleimide-methyl methacrylate), terpoly (maleimide-methylmethacrylate-acrylic acid) and terpoly(maleimide-methylmethacrylate-methacrylic acid) have been investigated (Oswal et al., 2004). Terpolymer based on the condensation reaction of 8-hydroxyquinoline 5-sulfonic acid and melamine with formaldehyde was synthesized in the presence of an acid catalyst and its thermal stability has been reported. The high initial decomposition temperature of terpolymer indicates that terpolymer was thermally stable at high temperatures (Singru and Gurnule, 2010). Thermal degradation parameters of terpolymers involving 2,2-dihydroxybiphenyl, urea and formaldehyde were calculated by the Freeman–Carroll and Sharp–Wentworth methods. From the results, it was reported that terpolymers have good thermal stability and the decomposition reaction follows the first order

kinetics (Jadhao et al., 2006). Resin derived from salicylaldehyde, ethylene diamine and formaldehyde indicates that the terpolymer has more ordered structure and involves slow decomposition reaction which was supported by the low frequency factor values (Masram et al., 2010). An ecofriendly technique was adopted to synthesize a terpolymer involving anthranilic acid, thiourea and formaldehyde monomers and the TGA data show that the terpolymer was found to be thermally stable and the order of the decomposition reaction was nearly one (Azarudeen et al., 2009). The study reported the influence of various manufacturing parameters including reaction content, reaction time and reaction temperature to optimize the process variables of poly( $\epsilon$ -caprolactone-co-1,2-butylene carbonate) terpolymer. DSC and TGA were used to investigate the thermal properties and degradation parameters of terpolymer (Liu et al., 2010). Owing to the serious health hazards of pathogenic bacteria and fungi, more research efforts have been devoted for the development of new antimicrobial agents. In the recent years, low molecular weight polymers have been synthesized to use as antimicrobial agents. Further compared to the conventional low-molecular-weight biocides, polymers have enhanced antimicrobial activity, reduced residual toxicity, prolonged stability, efficiency and selectivity. Antimicrobial polymers have been used as coatings in food processing, filters and biomedical devices. (Ahmad et al., 2007). A series of cyano derivatives of N-alkyl and N-aryl piperazine were synthesized and their antimicrobial activities were evaluated against Gram-positive and Gram-negative strains *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *S. epidermidis*, *Escherichia coli* and antifungal activities against *Aspergillus fumigatus*, *Aspergillus flavus* and *Aspergillus niger*. Few of the synthesized derivatives possess potent antibacterial activity and some of the compounds were reported for its cytotoxic activity (Chaudhary et al., 2007). Biological evaluation of novel nitrogen containing aniline-formaldehyde resin has been studied and the compounds were reported as a potent antifungal and antibacterial agent (Parveen et al., 2008). Long chain aliphatic esters as well as organic and ferrocene containing Schiff bases were synthesized and reported to have good antitumor, anticancer and antioxidant agents (Nawaz et al., 2009). Poly[(2-hydroxy-4-methoxybenzophenone) ethylene] resin and its polychelates with lanthanides(III) were screened for antibacterial activity and the metal chelated compounds maintain better activity compared to the ligand (Patel et al., 2007).

This article deals with the synthesis and the characterization of the terpolymer resins derived from anthranilic acid and salicylic acid with formaldehyde. The decomposition pattern of the terpolymer resins was evaluated by TGA and the kinetic parameters, such as activation energy ( $E_a$ ), order of the reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ) and frequency factor ( $Z$ ) determined by Freeman–Carroll (FC) and Sharp–Wentworth (SW) methods (Freeman and Carroll, 1958; Sharp and Wentworth, 1969). The thermal degradation model for the terpolymer was also

proposed by Phadnis–Deshpande method (Phadnis and Deshpande, 1983). Further, the terpolymer resin was also screened for pathogenic microbes, such as *E. coli*, *Klebsiella*, *S. aureus* and *P. aeruginosa* and fungi viz. *A. flavus*, *A. niger*, *Penicillium* sp., *Candida albicans*, *Cryptococcus neoformans* and *Mucor* sp.

## 2. Experimental

### 2.1. Materials

Anthranilic acid and salicylic acid were procured from Merck, India and purified by rectified spirit. Formaldehyde (37%) was of AR grade, Merck and used as received. Double distilled water was used for all the experiments. All other chemicals were of analytical grade and used without further purification.

### 2.2. Terpolymer synthesis

The terpolymer ASF-I was synthesized by the polycondensation of anthranilic acid (0.1 mol) and salicylic acid (0.1 mol) with formaldehyde (0.2 mol) in glacial acetic acid medium at  $140 \pm 2^\circ\text{C}$  in an oil bath for 6 h. The resulting mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The terpolymer obtained was washed with warm water and ether and then filtered off. Finally, the terpolymer resin was air dried and the dried resin was further purified by dissolving in 8% NaOH and regenerated in 1:1 (v/v) HCl/water. The resin was then filtered off and dried at  $75^\circ\text{C}$  for 24 h in an air oven. The yield of the terpolymer

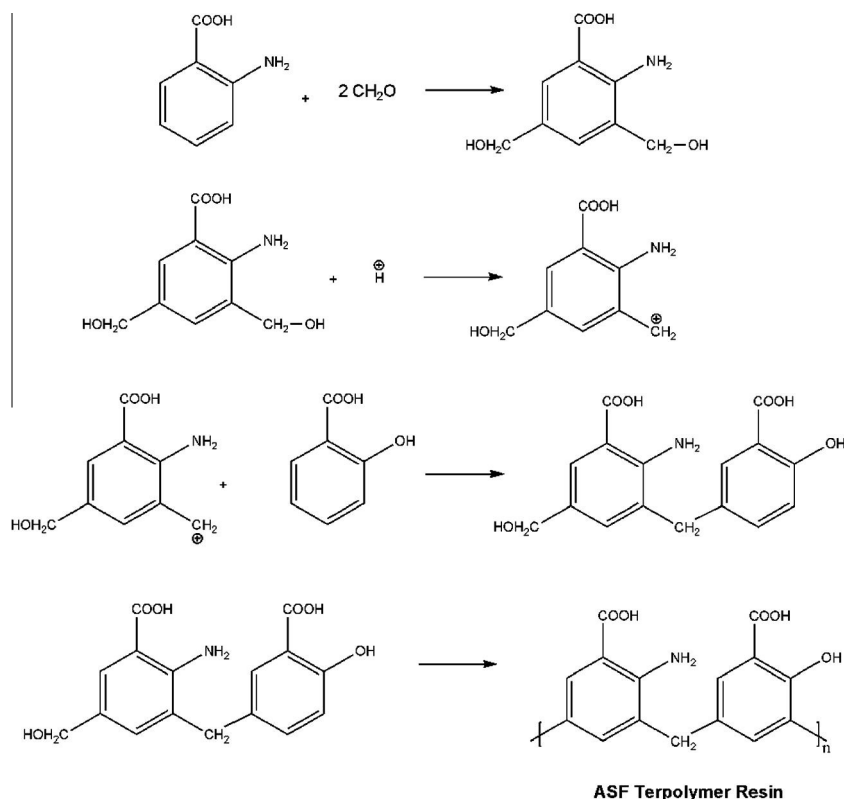
was found to be 78%. The reaction mechanism for the synthesis of ASF terpolymer resin is shown in Scheme 1. The same procedure was adopted for the synthesis of ASF-II and ASF-III terpolymer resins involving 1:1:3 and 2:3:5 molar proportions of the monomers chosen for the preparation of terpolymer.

### 2.3. Spectral and elemental analyses

Bruker (Model Tensor 27) spectrophotometer was used for recording FTIR spectrum of the terpolymer resin to identify the linkages and functional groups. The proton NMR spectrum of the ASF-I terpolymer resin was recorded in  $\text{DMSO-}d_6$  solvent using Bruker 400 MHz.  $^{13}\text{C}$  NMR spectrum was recorded using Bruker 100 MHz. The elements such as C, H and N present in the ASF-I were determined using Elementar instrument (Model Vario EL III).

### 2.4. Thermogravimetric analysis

The modes of thermal degradation of the terpolymers ASF-I, II and III were analyzed using thermogravimetric analyzer (TA Instruments Model SDT Q600) at a heating rate of  $20^\circ\text{C}/\text{min}$  in a static nitrogen atmosphere. Based on the results obtained, the degradation pattern, activation energy ( $E_a$ ), order of the reaction ( $n$ ), entropy change ( $\Delta S$ ), free energy change ( $\Delta F$ ), apparent entropy ( $S^*$ ), frequency factor ( $Z$ ) were calculated by Freeman–Carroll and Sharp–Wentworth methods. The thermal degradation model for the decomposition reaction was proposed using Phadnis–Deshpande method.



**Scheme 1** Reaction mechanism for the synthesis of ASF terpolymer.

## 2.5. Antimicrobial studies

### 2.5.1. Disc diffusion technique

Antimicrobial activity was tested by the filter paper disc diffusion technique involving the cultures of the selected organisms for 24 h (Devi et al., 2009). The test solutions of ASF-I, II and III terpolymers were prepared in sterile dimethyl sulfoxide solvent for the study. The compounds were tested at different concentrations ranging from 50 to 1000 ppm to find out the minimum concentration of the terpolymer required to inhibit the microbial growth. Ciprofloxacin (100 µg/mL) was taken as the standard for antibacterial activity. The organisms were seeded into sterile nutrient agar medium by mixing 1 mL of inoculum with 20 mL sterile melted nutrient agar kept at 48–50 °C in a sterile petri dish. The medium was allowed to solidify first. Then the test solutions, the standard drugs as well as the blank were impregnated in whatmann filter paper discs and placed on the solidified medium in the petri dish and left undisturbed for 2 h at room temperature. The petri dishes were then incubated at 37 °C for 24 h and the zone of inhibition for the test samples, standard and the control (DMSO) was measured.

Sterile yeast nitrogen base (HI Media) with 2% agar was inoculated by a rotating swab (soaked in standard inoculum suspension) over the surface of the media. Fluconazole (100 mg/ml) was taken as the standard for antifungal activity. The test solution impregnated discs were placed on the agar and incubated at 37 °C for 18 h. The zone of inhibition was measured by measuring the minimum dimension of the zone of fungal growth around the filter paper disc.

### 2.6. Scanning electron microscope studies

The morphology of the ASF-I, II and III terpolymers was analyzed by scanning electron microscope using HITACHI instrument (Model S-3000 H). The ASF terpolymers were scanned at different magnifications such as 4400×, 1500× and 6000× magnifications.

## 3. Results and discussion

The anthranilic acid and salicylic acid with formaldehyde terpolymer resins were soluble in solvents like *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), dimethylsulfoxide (DMSO) and aqueous NaOH and KOH solutions, whereas the resins were insoluble in benzene, xylene, toluene and water. The elements, such as carbon (%C), hydrogen (%H) and nitrogen (%N) content were analyzed for the ASF-I resin and presented in Table 1. Based on the analytical data, the empirical formula of the repeating unit for the ASF-I terpolymer resin is found to be C<sub>15</sub>H<sub>11</sub>NO<sub>5</sub>.

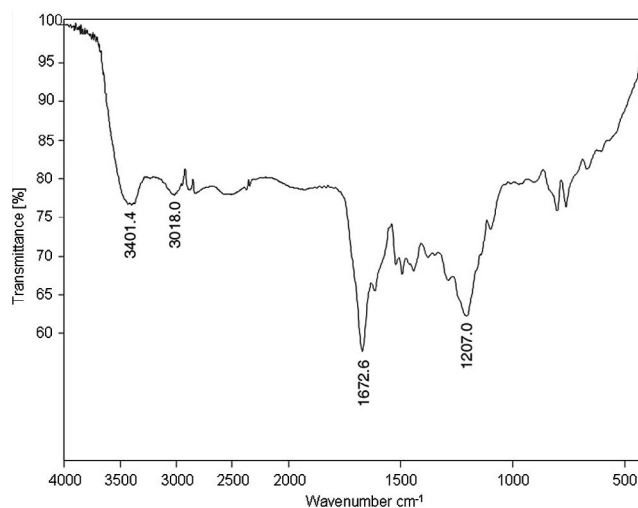
### 3.1. Spectral analysis

#### 3.1.1. FTIR spectra

The recorded FTIR spectrum of the ASF-I terpolymer resin is shown in Fig. 1. The spectrum shows a broad band at 3401 cm<sup>-1</sup> due to the ν (O–H) stretching of Ar-OH involved in the intramolecular hydrogen bonding with Ar-COOH. The strong band that appeared at 1207 cm<sup>-1</sup> is due to ν (C–N) stretching of Ar-NH<sub>2</sub> (Shah et al., 2006). The strong

**Table 1** Elemental analysis of ASF-I terpolymer resin.

Compound	Analysis (%)		
	Calculated (experimentally found)		
	C	H	N
ASF-I resin	64.75 (64.61)	5.64 (5.55)	4.68 (4.50)



**Figure 1** FTIR of ASF-I terpolymer.

band at 1672 cm<sup>-1</sup> may be assigned to ν (C=O) stretching of ketonic group of acid (Riswan Ahamed et al., 2010a, b). The band that appeared at 3401 cm<sup>-1</sup> is due to ν NH-stretching of amino group (Raj et al., 2010). This band seems to be merged with a broad band of –OH group of –COOH present in the resin. The tetra substitution in the benzene ring is established by the presence of medium bands at 1100 and 803 cm<sup>-1</sup> that are assigned to ν (C–H) bending vibration (Raj et al., 2010). The weak band at 3018 cm<sup>-1</sup> is due to the ν (C–H) stretching vibration of methylene group (Shah et al., 2006).

#### 3.1.2. <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR spectrum of ASF-I terpolymer resin is shown in Fig. 2. The NMR spectrum reveals that the signals around 2.7–4.4 δ (ppm) are due to the methylenic protons of the Ar-CH<sub>2</sub>-Ar linkage (Pretsch et al., 2000; Riswan Ahamed et al., 2011). The multiplet signals observed in the range at 6.6–7.4 δ (ppm) indicates the presence of aromatic protons (Pretsch et al., 2000; Burkanudeen et al., 2010a, b). The signal displayed at 8.35 δ (ppm) may be due to the carboxylic proton of Ar-COOH (Silverstein and Webster, 1998; Azarudeen et al., 2010). The signal in the region at 9.8 δ (ppm) is assigned to the –OH group of Ar-COOH involved in the intramolecular hydrogen bonding with proton of –OH in Ar-OH (Morrison and Boyd, 1996; Azarudeen et al., 2011). An intense signal that appeared in the region at 5.7 δ (ppm) is assigned to the –NH<sub>2</sub> protons of Ar-NH<sub>2</sub> in the terpolymer resin (Riswan Ahamed et al., 2010a, b).

#### 3.1.3. <sup>13</sup>C NMR spectra

<sup>13</sup>C NMR spectrum of ASF-I resin is depicted in Fig. 3 and the peaks are assigned based on the literature values (Pretsch et al., 2000; Silverstein and Webster, 1998; Burkanudeen et al.,

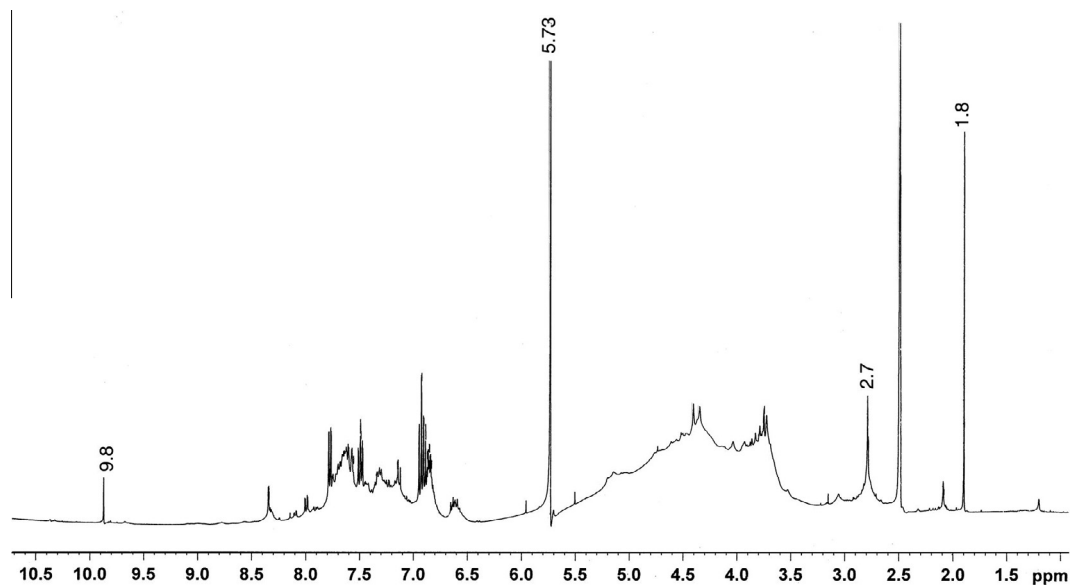


Figure 2  $^1\text{H}$  NMR of ASF-I terpolymer.

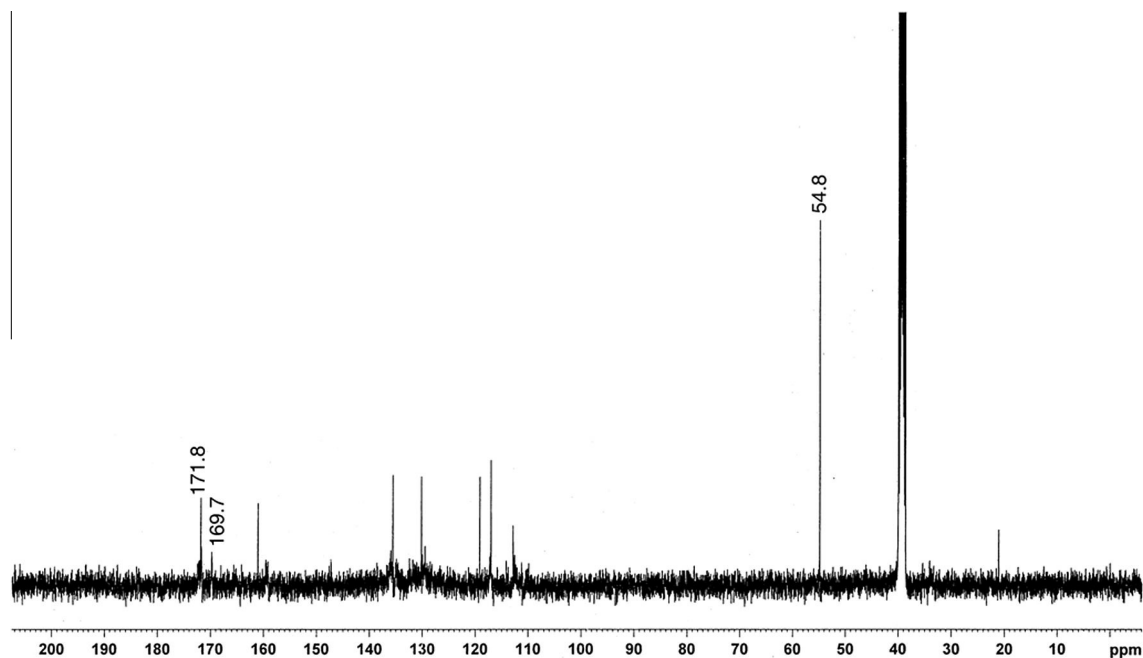


Figure 3  $^{13}\text{C}$  NMR of ASF-I terpolymer.

2010a, b). The  $^{13}\text{C}$  NMR spectrum shows the corresponding peaks at 112.8, 149.1, 129.5, 136.0, 130.2 and 119.1 ppm with respect to  $\text{C}_1\text{--C}_6$  of the aromatic ring of anthranilic acid. The intense signals that appeared at 111.6, 161.0, 129.5, 135.6, 130.2 and 117.0 ppm may be attributed to  $\text{C}_1\text{--C}_6$  of the aromatic ring of salicylic acid. Peaks around 169.7 and 171.8 ppm are due to the  $\text{--C=O}$  group of carboxylic acid present in both the aromatic rings of the terpolymer. The peak that appeared at 54.86 ppm may be assigned to the  $\text{--CH}_2$  bridge between the aromatic rings in the terpolymer resin. Based on the spectral data obtained from FTIR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ), the structure of the ASF-I terpolymer resin is proposed.

### 3.2. Thermogravimetric analysis

The thermogravimetric analysis is an effective and useful technique to appraise the thermal stability of the terpolymers. The thermogram of the ASF-I resin is shown in Fig. 4. The initial weight loss observed up to 180 °C is due to the elimination of water molecules from the terpolymer resin. Thermogram reveals that the decomposition of the ASF-I resin has three stages of degradation. The first degradation stage begins at 180 °C, which extends up to 260 °C with the weight loss of 15.5% (calcd 16.21%) which corresponds to the loss of carboxylic group as  $\text{CO}_2$ . The second degradation takes place at

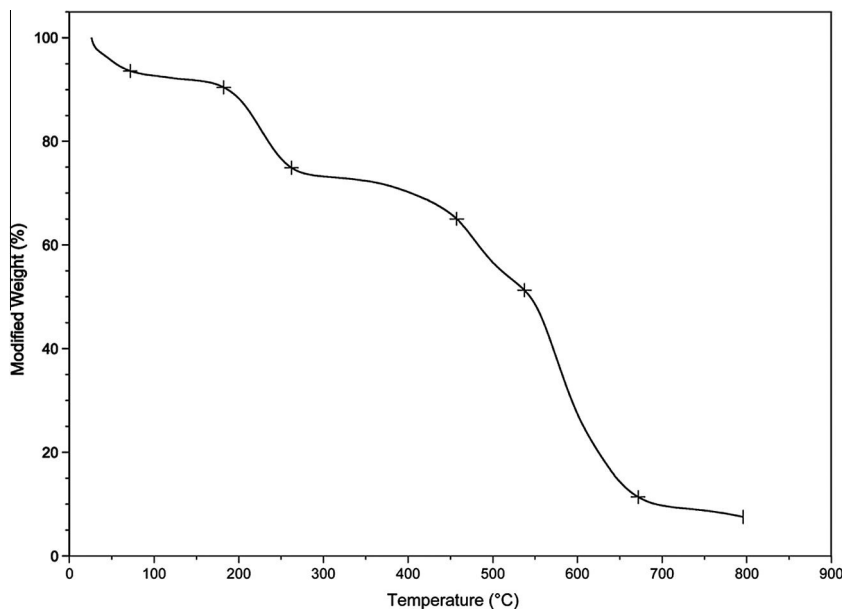


Figure 4 Thermogram of ASF-I terpolymer.

260 °C and end up at 540 °C with the weight loss of 23.1% (calcd 23.21%) and this may be due to the elimination of –NH<sub>2</sub>, –OH and –CH<sub>2</sub> attached to the aromatic ring. Finally the third degradation stage starts at 540 °C and the complete degradation takes place at 670 °C with the weight loss of 39.91% (calcd 40.05%). The half degradation temperature of the terpolymer resin is 571 °C.

- (i) [ASF]*n* → [ASF]*n* + *n*H<sub>2</sub>O
- (ii) [ASF]*n*  $\xrightarrow{180^{\circ}\text{C}}$  [ASF]*n* + loss of COOH as CO<sub>2</sub>
- (iii) [ASF]*n*  $\xrightarrow{180-260^{\circ}\text{C}}$  aromatic ring + loss of side chains
- (iv) Aromatic ring  $\xrightarrow{260-540^{\circ}\text{C}}$  complete degradation

From the TG data of the terpolymer resins, the following methods have been used to calculate the kinetic parameters and to propose the thermal degradation model.

3.2.1. Freeman–Carroll method

The activation energy (*E<sub>a</sub>*) and the order of reaction (*n*) for the terpolymer degradation were calculated using the following expression proposed by Freeman–Carroll.

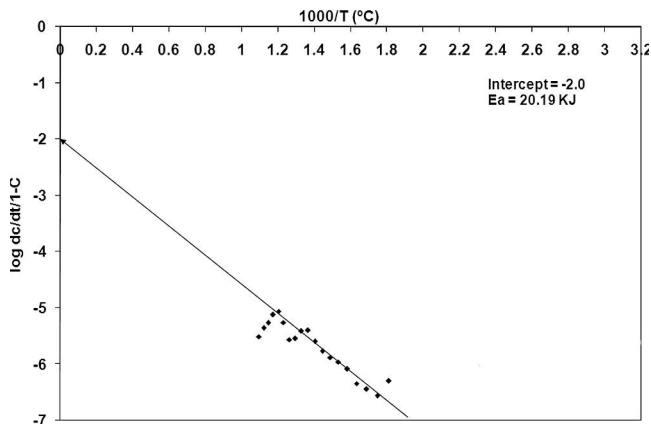


Figure 5 Sharp–Wentworth plot of ASF-I terpolymer.

$$\frac{\Delta \log(dw/dt)}{\Delta \log W_r} = \frac{-E_a}{2.303R} \left\langle \frac{\Delta(1/T)}{\Delta \log W_r} \right\rangle + n$$

where, *dw/dt* is the rate of change of weight with time; *W<sub>r</sub>* = *W<sub>c</sub>* – *W*, where *W<sub>c</sub>* is the weight loss at the completion of reaction or at definite time and *W* is the total weight loss up to time *t*; *n* is the order of the reaction, *T* and *R* are the temperature and the gas constant, respectively.

Hence, a plot of Δlog(dw/dt)/Δlog*W<sub>r</sub>* versus Δ(1/*T*)/Δlog*W<sub>r</sub>* gives a slope of –*E<sub>a</sub>*/2.303*R* with an intercept equal to *n* on the *y*-axis where *x* = 0.

3.2.2. Sharp–Wentworth method

The following expression given by Sharp–Wentworth was used to determine the activation energy (*E<sub>a</sub>*), entropy change (Δ*S*) and free energy change (Δ*F*).

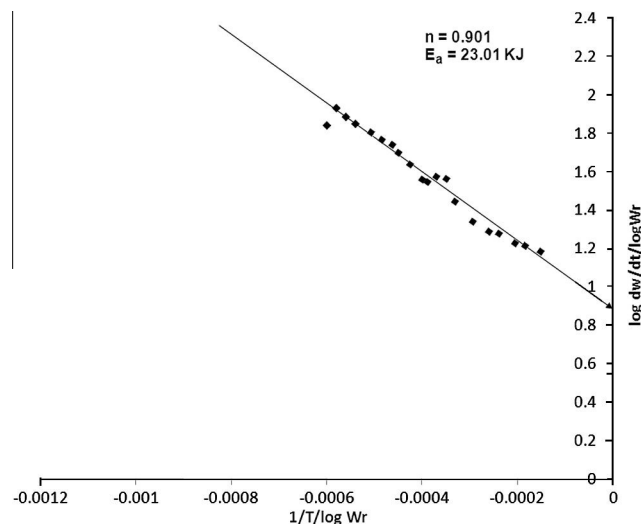


Figure 6 Freeman–Carroll plot of ASF-I terpolymer.

$$\frac{\log(dc/dt)}{(1-C)} = \frac{\log \alpha'}{\beta} = \frac{E_a}{2.303RT}$$

where,  $\beta$  is the linear heating rate. The graph of  $\log dc/dt/(1-C)$  versus  $1000/T$  gives a slope of  $-E_a/2.303R$  with an intercept on the  $y$  axis where  $x = 0$ .

A representative thermal activation energy plot of Sharp–Wentworth and Freeman–Carroll method for the ASF-I terpolymer resin is shown in Figs. 5 and 6, respectively. Kinetic parameters such as entropy change ( $\Delta S$ ), free energy change

**Table 2** Formulae for calculating thermodynamic parameters using Freeman–Carroll method.

(i) Entropy change ( $\Delta S$ )

$$\text{Intercept} = \log \frac{KR}{h\Phi E_a} + \frac{\Delta S}{2.303R} \quad (1)$$

where,  $K = 1.3806 \times 10^{-16}$  erg/deg/mol  
 $R = 1.987$  cal/deg/mol (8.314 J/K/Mol)  
 $h = 6.625 \times 10^{-27}$  erg s  
 $\Phi = 0.166$   
 $\Delta S$  = change in entropy  
 $E_a$  = activation energy from graph

(ii) Free energy change ( $\Delta F$ )

$$\Delta F = \Delta H - T\Delta S \quad (2)$$

where,  $\Delta H$  = enthalpy change = activation energy  
 $T$  = Temperature in K  
 $\Delta S$  = from Eq. (1)

(iii) Frequency factor ( $Z$ )

$$B_{2/3} = \frac{\log ZE_a}{R\Phi} \quad (3)$$

$$B_{2/3} = \log 3 + \log[1 - 3\sqrt{1 - \alpha}] - \log p(x) \quad (4)$$

where,  $Z$  = frequency factor  
 $B$  = calculated from Eq. (4)  
 $-\log p(x)$  = calculated from Doyle's table corresponding to activation energy  
 $\alpha$  = degree of transformation ( $\alpha = W/W_c$ )

(iv) Apparent entropy ( $S^*$ )

$$S^* = 2.303R \log \frac{Zh}{RT^*} \quad (5)$$

$Z$  = from Eq. (3)  
 $T^*$  = half decomposition temperature

( $\Delta F$ ), apparent entropy ( $S^*$ ) and frequency factor ( $Z$ ) were calculated based on the thermal activation energy ( $E_a$ ) using the expressions shown in Table 2. The thermal stabilities of the terpolymer resins were predicted to be high due to the low activation energy of the degradation process. The linear structure of the resin further proves the higher thermal stability of the resin.

Using the Freeman–Carroll and Sharp–Wentworth methods, the kinetic parameters were calculated and presented in Table 3. The values obtained for all the terpolymer resins suggest that the degradation takes place in the same mode for ASF-I, II and III. From the results, it is obvious that the activation energy values calculated from FC and SW are in good agreement with each other for all terpolymers. The low frequency factor value obtained predicts that the degradation reaction is slow (Singru and Gurnule, 2010; Masram et al., 2010). This is further supported by the negative value of the entropy change. However, a few points do not fall on the straight line in the graphs (Figs. 5 and 6) which show that the reaction does not obey the exact first kinetics.

### 3.2.3. Phadnis–Deshpande method

Phadnis–Deshpande method is a mathematical tool for the confirmation of the mechanism of a solid state reaction from thermo-analytical curves obtained isothermally or non-isothermally. In general, the correlation coefficient of the plot for different mechanism functions was regarded as a standard procedure for determining the reaction mechanism (Liu et al., 2010). One of the expressions is,

$$g'(\alpha) = -\frac{E_a}{RT}$$

where,  $g'(\alpha)$  is the integral function of conversion  $\alpha$ . The functions of  $g'(\alpha)$  frequently used are listed in Table 4. The activation energies calculated for ASF terpolymers according to Phadnis–Deshpande method are presented in Table 5. It is identify that the value of activation energy (22.59 kJ/mol) of ASF-I calculated by the above expression suits very well the value of reaction mechanism 5 proposed by Phadnis–Deshpande (Phadnis and Deshpande, 1983). This is comparable to  $E_a$  calculated by FC and SW methods. Hence, the ASF-I terpolymer degradation kinetic model follows a nucleation and nuclei growth (Avrami-Erofeev nuclei growth) mechanism.

### 3.3. Antimicrobial testing

The results of microbial screening of the ASF-I, II and III terpolymer resins are presented in Table 6 for antibacterial and Table 7 for antifungal studies.

#### 3.3.1. Antibacterial activity

An admirable result was obtained for ASF terpolymer resins against *E. coli* bacterium which is markedly higher than the

**Table 3** Kinetic and thermodynamic parameters of ASF terpolymer resins.

Compound	Half decomposition temperature $T_h$ (K)	Activation energy, $E_a$ (kJ mol <sup>-1</sup> )		Entropy change, $\Delta S$ (J)	Free energy, $\Delta F$ (kJ)	Frequency factor, $Z$ (s <sup>-1</sup> )	Apparent entropy, $S^*$ (J)	Order of reaction $n$
		FC	SW					
ASF-I	544.1	23.01	20.19	-154.01	93.92	505.25	-23.44	0.901
ASF-II	573.2	24.45	19.14	-156.92	94.61	493.21	-22.96	0.954
ASF-III	564.9	24.91	19.23	-155.79	94.36	482.36	-23.04	0.909

**Table 4** Phadnis–Deshpande model for solid state reaction mechanism.

Symbol	$g'(\alpha)$	Reaction mechanism
1	$\ln \alpha$	Power law
2	$2\ln \alpha$	Power law
3	$\ln [1 - (1 - \alpha)^{1/3}]$	Phase boundary (contracting sphere)
4	$\ln [1 - (1 - \alpha)^{1/2}]$	Phase boundary (contracting cylinder)
5	$1/2\ln [-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami-Erofeev nuclei growth)
6	$1/3\ln [-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami-Erofeev nuclei growth)
7	$1/4\ln [-\ln(1 - \alpha)]$	Nucleation and nuclei growth (Avrami-Erofeev nuclei growth)
8	$\ln [(1 - \alpha)\ln(1 - \alpha) + \alpha]$	Valensi, 2-dimensional diffusion
9	$2\ln [1 - (1 - \alpha)^{1/3}]$	Jander, 3-dimensional diffusion
10	$\ln [1 - 2/3\alpha - (1 - \alpha)^{2/3}]$	Brounshtein-Ginstling, 3-dimensional diffusion

standard. *E. coli*, a gram negative rod-shaped bacterium affects the urinary tracts in humans. *Klebsiella* is a genus of non-motile, gram-negative bacterium that causes a wide range of disease states, notably pneumonia, septicemia and soft tissue infections. The results showed a good activity against

*Klebsiella*. *S. aureus*, a gram-positive and spherical bacterium leads to life-threatening diseases like pneumonia, osteomyelitis, endocarditis and toxic shock syndrome. From the experiment, the resins were found to have moderate activity against *S. aureus* species. *P. aeruginosa* is a common bacterium which can cause diseases like pulmonary tract and urinary tract burns and wounds in animals and human beings for which the ASF resins had moderate activity.

**Table 5** Activation energies of ASF resins based on Phadnis–Deshpande method.

Reaction mechanism	$E_a$ (kJ/mol)		
	ASF-I	ASF-II	ASF-III
1	55.66	58.96	60.01
2	123.96	118.12	115.98
3	88.36	91.28	90.01
4	91.25	94.35	90.25
5	<b>22.59</b>	<b>20.12</b>	<b>19.65</b>
6	33.89	35.69	32.12
7	50.02	51.44	49.58
8	181.27	189.35	191.02
9	187.85	191.28	197.55
10	190.20	195.85	194.28

The values indicated in bold is closest to the  $E_a$  value estimated by FC and SW methods.

**Table 6** Antibacterial activity of the ASF terpolymer resins.

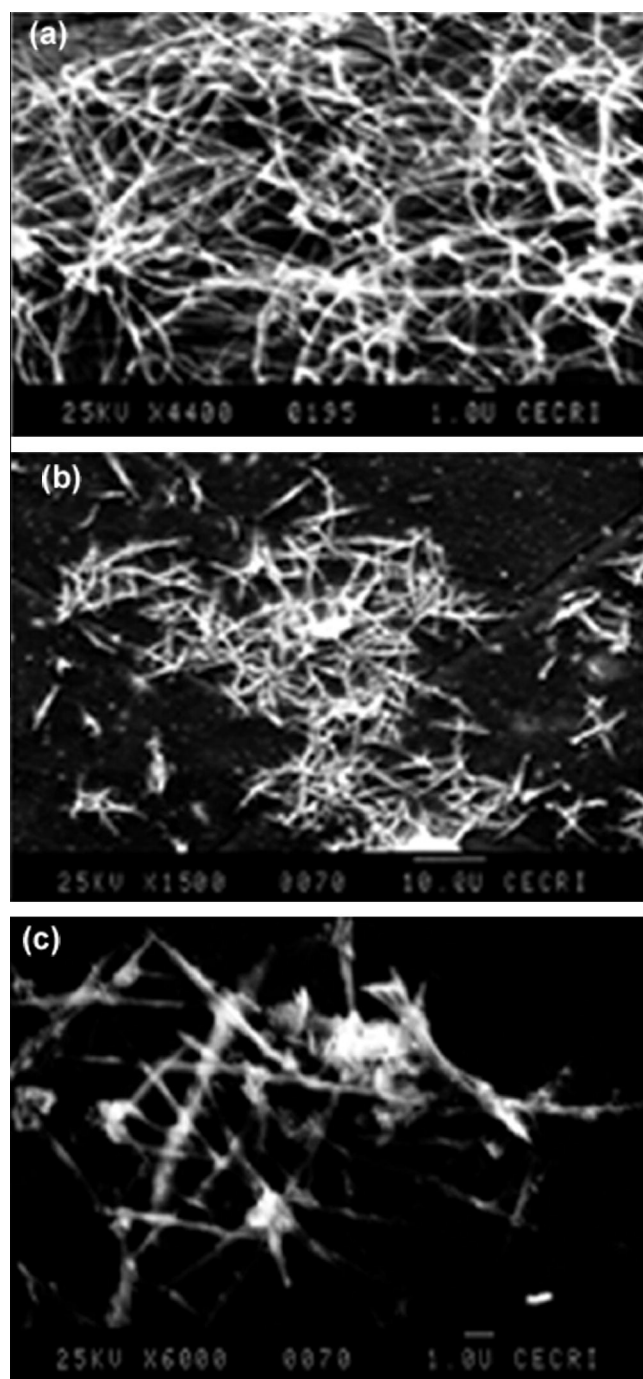
Compound	Zone of inhibition (mm)			
	<i>E. coli</i>	<i>Klebsiella</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>
ASF-I	16	19	10	06
ASF-II	15	17	09	05
ASF-III	16	18	09	06
Standard (Ciprofloxacin)	15	20	15	12
Control (DMSO)	–	–	–	–

**Table 7** Antifungal activity of the ASF terpolymer resins.

Compound	Zone of inhibition (mm)					
	<i>Aspergillus flavus</i>	<i>Aspergillus niger</i>	<i>Penicillium species</i>	<i>Candida albicans</i>	<i>Cryptococcus neoformans</i>	<i>Mucor sp.</i>
ASF-I	11	14	12	22	14	19
ASF-II	10	12	09	20	12	17
ASF-III	11	13	09	19	15	16
Standard (Fluconazole)	20	21	19	21	18	22
Control (DMSO)	–	–	–	–	–	–

### 3.3.2. Antifungal activity

The antifungal activities of the ASF terpolymer resins also provide appealing results against the chosen fungal strains. The terpolymers possess a moderate activity against *A. flavus*, a mold type fungal strain which may invade arteries of the lung or brain to cause infections and also produces a toxin. *A. niger* is one of the most common causes for otomycosis. The resins found to have moderate activity for *A. niger*. *Penicillium* sp. cause infection in humans and the resulting disease is known generically as penicilliosis. The resins had moderate activity against *Penicillium* sp. *C. albicans* is a diploid fungus and a causal agent of opportunistic oral and genital infections in humans and also emerged as an important cause of morbidity and mortality in immuno compromised patients. The ASF-I terpolymer resin exhibits a very good activity against *C. albicans* over the standard. *C. neoformans* is an encapsulated yeast-like fungus that can live in both plants and animals cause lung infection. The resins had good activity against this fungal strain. The resins showed good activity against *Mucor species*, a filamentous fungus which causes septic arthritis, renal infections and pulmonary infections. The antimicrobial activity of the terpolymer resins may be due to the presence of  $-\text{NH}_2$  and  $-\text{OH}$  groups. It is perceived that the factors, such as solubility, conductivity, dipole moment and cell permeability may also contribute to the increased antimicrobial activity against the chosen microbes (Bagihalli et al., 2009; Azarudeen et al., in press).



**Figure 7** SEM images of (a) ASF-I, (b) ASF-II, and (c) ASF-III terpolymers.

### 3.4. Morphology

The SEM images of the ASF-I, II and III terpolymers are shown in Fig. 7 at 4400 $\times$ , 1500 $\times$  and 6000 $\times$  magnifications, respectively. The surface morphology of terpolymers that exhibit the development of crystals from polymer solution corresponding to the most prominent organization in polymer on a large scale such as in size of sharp edged particles dispersed in amorphous domains indicates the presence of a crystalline structure. The photographs of terpolymer resins that also show a fringed micelle model having dips and

shallow pits on the surface of the polymers indicate the presence of amorphous structure. Thus the ASF terpolymers show crystalline-amorphous structures which are the characteristics of polymers. The extent of crystalline character depends on the acidic nature of the monomers (Singru et al., 2010).

### 4. Conclusion

- Terpolymer involving anthranilic acid, salicylic acid and formaldehyde were synthesized in the presence of glacial acetic acid as a catalyst at  $140 \pm 2$  °C for 6 h with the varying proportions of reactants.
- The spectral characterizations of the terpolymer confirm the linear structure.
- TGA curve shows that the terpolymer resin had good thermal stability. The activation energy calculated for the resins by different methods was found to be in good agreement with each other.
- The low frequency factor and the negative entropy values calculated from Freeman–Carroll method suggested that the thermal decomposition would be a slow reaction.
- The thermal degradation kinetics indicate that ASF-I terpolymer shows three step degradation profile which follows the nucleation and nuclei growth (Avrami-Erofeev nuclei growth) thermal decomposition model.
- The ASF-I, II and III terpolymer resins were found to have excellent antimicrobial activity against the chosen bacteria and fungi. Further, in the case of *C. albicans* and *E. coli*, the terpolymer resin showed enhanced activity than the standard drug.

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### References

- Ahamad, T., Kumar, V., Parveen, S., Nishat, N., 2007. Applied Organometallic Chemistry 21, 1013.
- Al Shawabkeh, A.F., Al Wahab, H.A., Shahab, Y.A., 2007. Journal of Optoelectronics and Advanced Materials 9, 2075.
- Azarudeen, R.S., Riswan Ahamed, M.A., Jeyakumar, D., Burkanudeen, A.R., 2009. Iranian Polymer Journal 18, 821.
- Azarudeen, R.S., Riswan Ahamed, M.A., Arunkumar, P., Prabu, N., Jeyakumar, D., Burkanudeen, A., 2010. International Journal of Chemical and Environmental Engineering 1, 23.
- Azarudeen, R.S., Riswan Ahamed, M.A., Burkanudeen, A.R., 2011. Desalination 268, 90.
- Azarudeen, R.S., Riswan Ahamed, M.A., Burkanudeen, A.R. Journal of Polymer Research, doi:10.1007/s10965-010-9536-8, in press.
- Bagihalli, G.B., Patil, S.A., Badami, P.S., 2009. Journal of the Iranian Chemical Society 6, 259.
- Burkanudeen, A., Azarudeen, R., Riswan Ahamed, M., Ramesh, P., Vijayan, N., 2010a. International Journal of Chemical and Environmental Engineering 1, 29.
- Burkanudeen, A.R., Azarudeen, R.S., Riswan Ahamed, M.A., 2010. International Conference on Chemical Engineering and Applications, Proceedings, Singapore, Feb 26–28, pp. 282–286.

- Chaudhary, P., Nimesh, S., Yadav, V., Verma, A.K., Kumar, R., 2007. *European Journal of Medicinal Chemistry* 42, 471.
- Devi, G.S., Muthu, A.K., Kumar, D.S., Rekha, S., Indhumathi, Nandhini, R., 2009. *International Journal of Drug Development and Research* 1, 105.
- Donia, A.M., 1998. *Thermochimica Acta* 320, 187.
- Freeman, E.S., Carroll, B., 1958. *The Journal of Physical Chemistry* 62, 394.
- Gupta, R.K., Singh, R.A., 2005. *Journal of Polymer Research* 12, 189.
- Jadhao, M.M., Paliwal, L.J., Bhavne, N.S., 2006. *Journal of Applied Polymer Science* 101, 227.
- Liu, Y., Peng, D., Huang, K., Liu, S., Liu, Z., 2010. *Polymer Degradation and Stability* 95, 2453.
- Masram, D.T., Bhavne, N.S., Kariya, K.P., 2010. *European Journal of Chemistry* 7, 564.
- Michael, P.E.P., Barbe, J.M., Juneja, H.D., Paliwal, L.J., 2007. *European Polymer Journal* 43, 4995.
- Morrison, R.T., Boyd, R.N., 1996. *Organic Chemistry*. Prentice Hall of India Pvt. Ltd., New Delhi.
- Nawaz, H., Akhter, Z., Yameen, S., Siddiqi, H.M., Mirza, B., Rifat, A., 2009. *Journal of Organometallic Chemistry* 604, 2198.
- Oswal, S.L., Sarkar, N.S., Bhandari, V.K., Oza, H.B., Patel, C.B., 2004. *Iranian Polymer Journal* 13, 297.
- Parveen, S., Ahamad, T., Malik, A., Nishat, N., 2008. *Polymers for Advanced Technologies* 19, 1779.
- Patel, M.M., Kapadia, M.M., Patel, G.P., Joshi, J.D., 2007. *Reactive and Functional Polymers* 67, 746.
- Peara, S., Patterson, T.F., 2002. *Clinical Infectious Diseases* 35, 1073.
- Phadnis, A.B., Deshpande, W., 1983. *Thermochimica Acta* 62, 361.
- Pretsch, E., Buhlmann, P., Affolter, C., 2000. *Structure Determination of Organic Compounds*. Springer, New York.
- Raj, J.A., Vedhi, C., Burkanudeen, A., Arumugam, P., Manisankar, P., 2010. *Ionics* 16, 171.
- Riswan Ahamed, M.A., Azarudeen, R.S., Karunakaran, M., Burkanudeen, A.R., 2010a. *Iranian Polymer Journal* 19, 635.
- Riswan Ahamed, M.A., Azarudeen, R.S., Karunakaran, M., Karikalan, T., Manikandan, R., Burkanudeen, A., 2010b. *International Journal of Chemical and Environmental Engineering* 1, 7.
- Riswan Ahamed, M.A., Azarudeen, R.S., Jeyakumar, D., Burkanudeen, A.R., 2011. *International Journal of Polymeric Materials* 60, 124.
- Shah, B.A., Shah, A.V., Shah, P.M., 2006. *Iranian Polymer Journal* 15, 809.
- Sharp, J.B., Wentworth, S.A., 1969. *Analytical Chemistry* 41, 2060.
- Silverstein, R.M., Webster, F.X., 1998. *Spectrometric Identification of Organic Compounds*, sixth ed. Wiley, New York.
- Singru, R.N., Gurnule, W.B., 2010. *Journal of Thermal Analysis and Calorimetry* 100, 1027.
- Singru, R.N., Zade, A.B., Gurnule, W.B., 2008. *Journal of Applied Polymer Science* 109, 859.
- Singru, R.N., Gurnule, W.B., Khati, V.A., Zade, A.B., Dontulwar, J.R., 2010. *Desalination* 263, 200.
- Tarase, M.V., Zade, A.B., Gurnule, W.B., 2010. *Journal of Applied Polymer Science* 116, 619.
- Wilkie, C.A., Thomson, J.R., Mittleman, M.L., 1991. *Journal of Applied Polymer Science* 42, 901.
- Yang, M.H., 2000. *Polymer Testing* 19, 105.