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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 ± 2 °C for 6 h with varying proportions of reactants. The terpolymer ASF-I was characterized by elemental analysis, FTIR, ^{1}H NMR and ^{13}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 (ΔS), free energy change (ΔF), 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

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bacteria and fungi. The resins show potent inhibitory action against bacteria, such as *Escherichia coli*, *Klebsiella*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* and fungi *viz*. *Aspergillus flavus*, *Aspergillus niger*, *Penicillium* sp., *Candida albicans*, *Cryptococcus neoformans* and *Mucor* sp.

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 (ε-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. (Ahamad 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 (ΔS), free energy change (ΔF), 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