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MW-assisted synthesis of carboxymethyl tamarind kernel polysaccharide-*g*-polyacrylonitrile: Optimization and characterization

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ABSTRACT

Microwave-assisted synthesis of graft copolymer of carboxymethyl tamarind seed polysaccharide and polyacrylonitrile was carried out. The effect of formulation and process variables on grafting efficiency of carboxymethyl tamarind kernel polysaccharide-*g*-poly(acrylonitrile) was studied using response surface methodology. The results revealed that the significant factors affecting grafting efficiency were concentrations of ammonium persulphate, acrylonitrile and interaction effects of ammonium persulphate and acrylonitrile concentrations. The optimal calculated parameters were found to be microwave exposure time—99.48 s, microwave exposure power—160 W, concentration of acrylonitrile—0.10% (w/v), concentration of ammonium persulphate—40 mmol/l, which provided graft copolymer with grafting efficiency of 96%. The formation of graft copolymer was confirmed by FT-IR studies and validated by scanning electron micrographs. Thermogravimetric analysis indicated higher thermal stability of graft copolymer and X-ray diffraction study revealed increase in crystallinity on graft polymerization. Further, the graft copolymer showed pH dependant swelling.

1. Introduction

Polysaccharides are found abundantly in nature ranging from plant, animal and marine sources. Further due to their non-carcinogenicity, biocompatibility and easy availability, they serve as renewable reservoirs for synthesis of multifunctional materials (BeMiller & Whistler, 1992). Among the various modification approaches grafting is one of the most promising. In grafting monomer is covalently bonded on to the polymer backbone. It provides means of synthesizing hybrid polymers, having the advantages of two or more component polymers. A number of techniques such as chemical, radiation, photochemical, plasma induced and enzymatic grafting have been employed (Bhattacharya & Misra, 2004). Conventional grafting procedures are characterized by polysaccharide backbone degradation and formation of undesired homopolymer *via* concurrent competing reactions which lower the percentage grafting. These problems can be overcome by use of microwave assisted reactions, which provide graft copolymer with higher percentage grafting in a shorter duration of time. Moreover microwave assisted reactions can be carried out in a open reaction vessel with reduced solvent content unlike the conventional reactions which require inert atmosphere (Singh, Kumar, & Sanghi, 2012).

A number of vinyl monomers such as acrylamide (Singh, Tiwari, Tripathi, & Sanghi, 2004), acrylic acid, acrylonitrile, methyl acrylate etc. have been grafted on polysaccharides such as gum acacia, chitosan (Liu, Wang, & Wang, 2007), and tamarind seed polysaccharide (Ahuja, Kumar, & Kumar, 2013). Microwave assisted graft copolymer reactions are influenced by number of factors such as microwave exposure time, microwave exposure power (Kumar, Singh, & Ahuja, 2009), concentration of vinyl monomer, concentration of polysaccharide backbone, concentration of initiator etc.

During earlier study acrylonitrile grafted psyllium (Mishra, Srinivasan, & Gupta, 2003), okra (Mishra, & Pal, 2007), chitosan (Shankar, Gomathi, Vijyalakshmi, & Sudha, 2014) have been employed as flocculant and superabsorbing polymers. In the present study microwave assisted graft copolymerization of acrylonitrile on carboxymethyl tamarind kernel polysaccharide has been optimized using central composite experimental design. The optimized batch of graft copolymer was further characterized by FT-IR, X-ray diffraction, thermogravimetric analysis, scanning electron microscopy and swelling characteristics.

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2. Experimental

2.1. Materials

Carboxymethyl tamarind kernel polysaccharide (CMTKP) was procured from Hindustan Gums and Chemicals Pvt. Ltd. (Bhiwani, India). Acrylonitrile (AN) was obtained from S.D. Fine Chem Ltd. (Mumbai, India). Ammonium persulphate (APS) GR (99% pure) was procured from Sisco Research Laboratory (Mumbai, India). All other chemicals of reagent grade were used as such.

2.2. Synthesis of CMTKP-g-poly(acrylonitrile)

Microwave-assisted grafting of AN on CMTKP was done using previously reported method (Malik & Ahuja, 2011). Briefly, powdered CMTKP (1% w/v) was added to aqueous solution of acrylonitrile (0.1–0.4%, w/v) and mixed thoroughly in a reaction vessel. Desired amount of APS (10–40 mmol/l) was added to the above solution and the reaction vessel was placed on turntable of a domestic microwave oven (2300 ET-B, Bajaj Electricals Ltd., Mumbai, India). Microwave irradiation at power of 160–480 W, for time of 60–120 s was carried out. After required exposure to microwave irradiation, reaction mixture was cooled by placing it in cold water. The resultant graft copolymer was then precipitated with methanol and unreacted residues were removed by washing with methanol (80%). Precipitated graft copolymer was dried in hot air oven at 60 °C and pulverized. Grafting efficiency was calculated using the following formula.

$$\%GE = \frac{W_1 - W_0}{W_2} \times 100 \quad (1)$$

$\%GE$ is grafting efficiency, W_1 is weight of graft copolymer, W_0 is weight of polysaccharide and W_2 is weight of monomer.

2.3. Experimental design

Synthesis of CMTKP-g-PAN was optimized using 3-level, 4-factor central composite experimental design. Concentrations of AN (A), APS (X_2), microwave irradiation time (X_3) and microwave power (X_4) were used as independent variables on the basis of preliminary trials. Grafting efficiency was selected as dependent variable and the effect of independent variables on grafting efficiency was studied at 3 levels i.e., low (−1), middle (0), high (+1). The experimental design and statistical analysis of data were done using the Design Expert software (version 7.0.0 Stat-Ease-Inc. Minneapolis MN).

2.4. Characterization

2.4.1. FTIR spectra

IR spectra of CMTKP and CMTKP-g-PAN samples were taken in KBr pellets using Fourier transform infrared spectrophotometer (Perkin Elmer, USA) between 400 and 4000 cm^{-1}.

2.4.2. Thermogravimetric analysis

Thermal behaviour of CMTKP and CMTKP-g-PAN was recorded under constant nitrogen purge of 100 ml/min in a temperature range of 25–600 °C at heating rate of 10 °C/min with the help of simultaneous thermal analyzer (SDT,Q-600, TA Instruments, USA).

2.4.3. X-ray diffraction

Powder diffraction spectra of CMTKP and CMTKP-g-PAN samples were recorded employing X-ray diffractometer (Miniflex II, Rigaku Japan) copper Kα-radiation generated at 40 kV and 35 mA in the differential angle range of 0–80° (2θ).

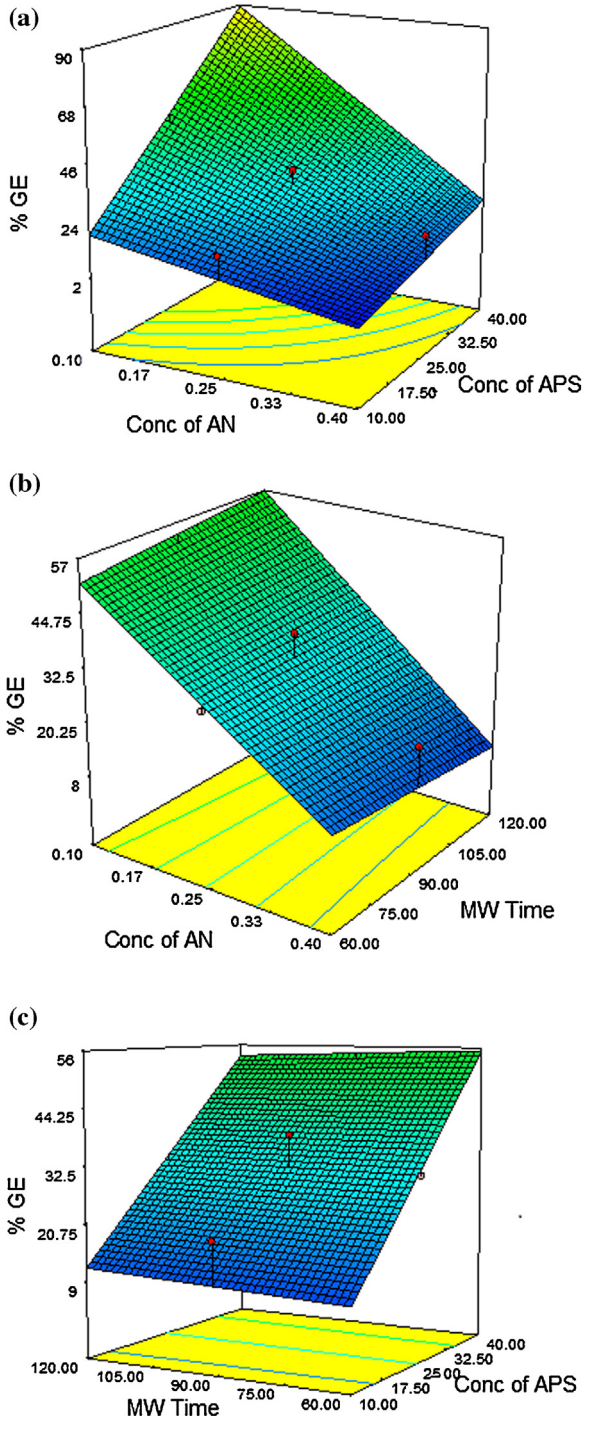

Fig. 1. Response surface plots showing the combined effect of (a) concentrations of acrylonitrile and ammonium persulphate, (b) concentration of acrylonitrile and MW exposure time and (c) concentration of ammonium persulphate and MW exposure time.

2.4.4. Scanning electron microscopy

Scanning electron micrographs of CMTKP and CMTKP-g-PAN powder samples were recorded using SEM (JEOL, JSM-6100). The photomicrographs were taken at accelerating voltage of 15 kV.

2.4.5. Swelling behaviour

Swelling behaviour of optimized batch of CMTKP-g-PAN was studied at pH 2.0, 6.6 and 8.0. An accurately weighed sample of optimized batch of graft copolymer was placed in basket of