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Semi-Inter Penetrating New Polymer Network

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Abstract

New semi interpenetrating polymer network (s-IPN) was prepared and characterized by using FTIR, SEM, EDX, XRD and TGA measurements. These micro particles were prepared using two different polymers; sodium alginate (Na-Alg) and hydrolyzed carboxy-methyl cellulose grafted poly acrylonitrile (h-CMC-g-PAN) with $CaCl_2$ as a cross-linker.

Keywords: H-CMC-g-PAN, SA, s-IPN.

Introduction

Recently, the use of cross-linked carboxymethyl cellulose (CMC) in gel formations using grafting technique with selected monomers have been reported [1-3]. Polymer modification is required to bring specific properties, such as enhancing their thermal stability, multiphase physical responses, compatibility, flexibility, and rigidity [4-7]. The prime techniques for polymer modifications are grafting, crosslinking, blending, and composite formation, are all multicomponent polymer systems. Among those, acrylonitrile (AN), which specified by high grafting efficiency [8,9], that improving its thermal resistance [10] as well as subsequent alkaline hydrolysis of the grafting product to obtain water absorbents hydrogels [8,11]. Sodium alginate (SA, polyanionic copolymer consist of 1-4 glycosidically-linked β-D-mannuronic acid (M) and its C-5 epimer α-L-guluronic acid (G) residues), tends to form hydrogels in presence of Ca(II) ions [12] through ionotropic crosslinking, which occurs particularly between the cations and the G-blocks of alginate [13,14]. Mechanical strength of the corresponding hydrogels can be enhanced by preparing s-IPNs [15], by blending two polymers, as one polymer is cross-linked in presence of the other polymer to produce an additional non-covalent interaction between the two polymers [16-18]. S-IPNs are of interest since they have been applied in many areas, and the outstanding performance of such materials was obtained by the construction of s-IPN structure [19].

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Experimental Procedure

Materials

All preparations were performed under anaerobic conditions, under N_2 atmosphere. The chemicals and solvents were used as received. Chemicals were obtained from Sigma-Aldrich Chemie GmbH, Merck and Fluka.

Instrumentations and Measurements

FT-IR spectra were measured as KBr discs on a Matson 5000 FT-IR spectrometer. Thermal analysis measurements (TGA) were made in the range of 20°C to 800°C at the heating rate of 10°C min^{-1}, using α- Al_2O_3 as a reference, on a Shimadzu Thermogravimetric analyzer TGA-50. XRD spectra were performed using a Shimadzu x-ray diffractometer XRD-6000. SEM samples were performed using JOEL JSM 65101v. EDX was performed using JED-2300 analysis station.

Synthesis of chelating s-IPNs

Preparation of CMC-g-PAN: CMC (0.5 gm; 60 mL water) was mixed with AN monomer (3 mL), and the reaction mixture was stirred for 10 min. at 35°C. Cerric ammonium nitrate (CAN; 2.74 g in 50.0 mL of 1M HNO_3) was added (3.5 mL). The reaction mixture was stirred for 2 h. Hydroquinon solution (0.5 wt%, 2 mL) was added, and the reaction mixture was cool, followed by the addition of few drops of 1M NaOH solution. The precipitate was obtained after the addition of methanol, filtered off, washed with methanol and dried at 50°C for 1 h [20].

Alkaline hydrolysis of CMC-g-PAN (h-CMC-g-PAN): CMC-g-PAN (0.5 g) was added to 1M NaOH (20 mL), and the mixture was refluxed with stirring for 0.5 h, upon which the color was changed to light yellow. The mixture was allowed to cool to room temperature, neutralized to pH 8.0 by acetic acid (10 wt%). The gelled product was cut to small pieces and poured onto methanol (200 mL) for 2 h. and the hardened particles were filtered off and dried at 50°C for 10 h [21].

Preparation of s-IPN: Aqueous solution of h-CMC-g-PAN and SA (1:1 W/W) was stirred at room temperature for 24 h, and the solution then extruded as small drops by means of syringe into a stirred solution of 0.2 M $CaCl_2$ (cross-linker). The microspheres were left in the solution for 24 h to be hardened. The resulting beads were removed and washed with distilled water (to remove excess Ca (II) ions).

Results and Discussion

New s-IPN was prepared and characterized. Results were discussed as following:

3.1. Characterization of s-IPN

The existence of a sharp intense peak at 2244 cm^{-1} in IR spectrum of CMC-g-PAN, is an evidence of grafting of acrylonitrile monomer onto CMC backbone, while the sharp intense peak at 1661 cm^{-1} is due to the carbonyl group (FIG. 1a).

After alkaline hydrolysis of CMC-g-PAN, the spectrum shows a broad band at 3443 cm^{-1} and another sharp one at 1637 cm^{-1}, can be attributed to carbonyl stretching of ($COO^- Na^+$ and $CONH_2$) and N-H stretching of the carboxamide group, respectively. In addition, the sharp band corresponding to -CN groups is completely disappeared after hydrolysis (FIG. 1b).

The spectrum of SA, FIG. 1c, shows absorption bands regarding hydroxyl, ether and carboxylic functional groups. The Stretching vibration of OH groups of alginate is appeared in the range of 3000-3600 cm^{-1}, while those at 1620 and 1418 cm^{-1} are due to asymmetric and symmetric stretching vibrations of carboxylate group, respectively. The bands at 1097 and 948 cm^{-1} are attributed to C–O stretching of the pyranosyl ring and the C–O contributed from C–C–H and C–O–H deformation, respectively. S-IPN, FIG. 1d, shows significant different bands in comparison to the IR spectrum of SA, as the stretching vibrations of OH bands appears narrower than that in SA. This difference arises from the participation of hydroxyl and carboxylate groups of SA to Ca (II) ions in order to form chelating structure and consequent decrease in hydrogen bonding between hydroxyl functional groups. The asymmetric stretching vibration of carboxylate ion shifted to lower wave numbers, Ca (II) ions replaced Na(I) ions in SA. As the charge density, radius and atomic weight of the cation changed; and hence shifting should be expected.

The surface morphologies of S-IPNs were examined by scanning electron microscope (SEM). The bead diameter is round 950 μm (FIG. 2). The EDX spectrum (FIG. 3) shows beaks corresponding to carbon and oxygen. XRD pattern of s-IPN (FIG. 4) exhibits crystalline peaks at 29, 47 and 77.

The TGA thermogram of s-IPNs showed higher thermal stability than CMC sodium salt. The thermosgram of s-IPNs shows three weight-loss steps, come from the decomposition of full CMC and part of CMC units, parts of CMC, and CO2 fragments , leaving residue of CaO.

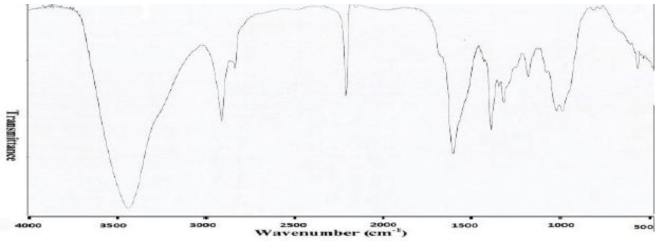

FIG.1a. **FTIR of CMC-g-PAN.**

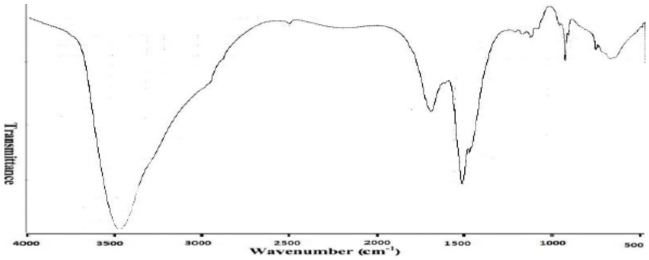

FIG.1b. **FTIR of h-CMC-g-PAN.**

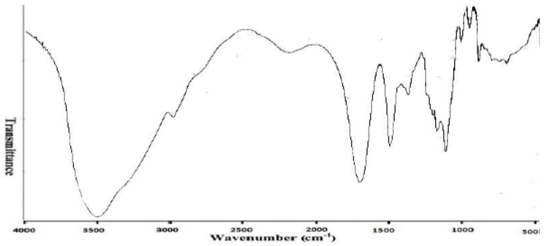

FIG. 1c. **FTIR of sodium alginate.**

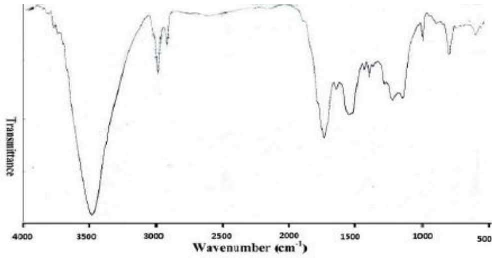

FIG. 1d**. FTIR of s-IPN.**

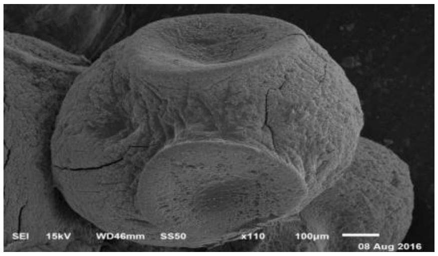

FIG. 2 **SEM of s-IPN.**

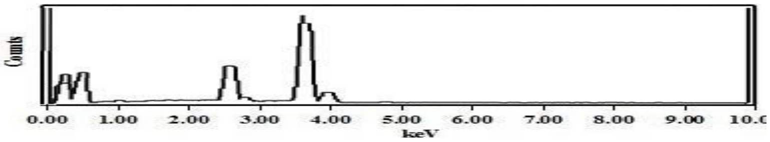

FIG. 3 **EDX of s-IPN.**

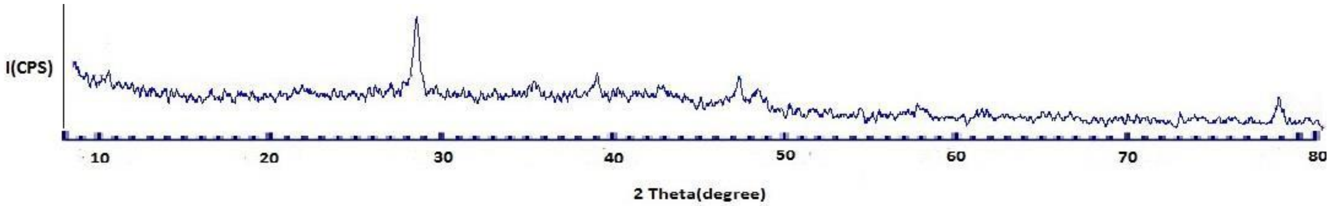

FIG. 4 **XRD of s-IPN.**

Conclusion

New semi-interpenetrating polymer networks were prepared and characterized using different spectral and thermal measurements. These micro spheres were prepared using sodium alginate (Na-Alg) and hydrolyzed carboxy-methyl cellulose grafted poly acrylonitrile (h-CMC-g-PAN) with $CaCl_2$ as a cross-linker.

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