Advance Physics Letter

On the Studies of Thermal and Water Sorption Behavior of Vinyl Monomers

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Abstract : A novel biopolymer based Semi-IPN of polyvinyl alcohol (PVA) and polycrylonitrile (PAN) were synthesized in various proportions by redox polymerization and analyzed thermally by differential scanning calorimetry (DSC). DSC thermograms show good thermal stability, as a result of incorporation of acrylonitrile as the second network. The systematic study of their sorption behavior proves the approach to be beneficial for various biomedical applications.

I. INTRODUCTION

Thermal behaviour of polymers is one of the important features to be investigated, if one aims to adopt a polymer for some biomedical use. Acrylonitrile possesses good mechanical strength and degrades at a higher temperature. The strong nitrile dipolar interactions are believed to be the prime reason for high melting point of PAN[1]. Various researchers have put forward their efforts for the development of vinyl monomer based polymeric networks suitable for various fields such as tissue engineering[2], drug delivery[3], food industry[4], photographic technology and some others.

II. MATERIALS AND METHOD

Materials

PVA, obtained from Research Lab Chem. Mumbai, India was used without any further purification. Acrylonitrile, purchased from Research Lab, was freed from inhibitor and distilled under vaccum. N-N' methylene bisacrylamide (MBA), (Research Lab, Mumbai, India) as a crosslinking agent, potassium persulphate (KPS; Loba chemic, Delhi) as an initiator and potassium metabisulphite (KMBS; Qualigens) was used as an activator respectively and double distilled water was used throughout the experiment.

Synthesis of Hydrogel

Semi-IPNs of various compositions were prepared by redox polymerization method as reported elsewhere[5]. The reaction mixture (PVA, AN, MBA, KMBS and KPS in proper ratio) taken in a rectangular glass pellet was kept at 35^0C for a week. The soft gel, thus obtained was purified cut into equal sized square pieces, dried at room temperature for a week and stored in air-tight polyethylene bags.

III. CHARACTERIZATION

FTIR Analysis

The structural characterization of the synthesized semi-IPNs was performed, by recording FTIR spectral analysis on a Perkin-Elmer spectrophotometer (paragon 1000 FTIR).

DSC Analysis

A reasonable weight of sample was passed in the sample cup for thermal analysis on a DSC instrument in the temperature range of 30-300^0C under N_2 atmosphere and at a heating rate of 10^0C/min.

Water Sorption Measurements

The progress of water sorption process was monitored gravimetrically. In brief, pre-weighed and completly dried rectangular pieces (1cm x 1cm x 1cm) of semi-IPNs were placed in a water reservoir and allowed to swell till equilibirium. The swollen pieces were then taken out at different time intervals and gently pressed in between two filter papers to remove excess of water and finally weighed. The swelling ratio was calculated by the following equation: Swelling Ratio = Wt of swollen IPNs/Wt of dry IPNs.

IV. RESULTS AND DISCUSSION

FTIR Spectral Analysis

The IR spectra are depicted in Fig. 1 (a-c). Spectra of PVA and AN, used in this study, is in good agreement with the published ones. The IR spectra of semi-IPN, [Fig. 1(c)], not only confirm the presence of PVA and crosslinked PAN but also provide significant informiaton about the nature of network formed. The peak observed at higher frequency (3601 cm-1) due to O-H stretching of PVA suggests for formation of weak hydrogen bonds between O-H and C□ N of PAN. The spectra also contain a sharp peak at 2248 cm-1 which is

due to C≡N stretching of nitrile group indicating acrylonitrile incorporation.

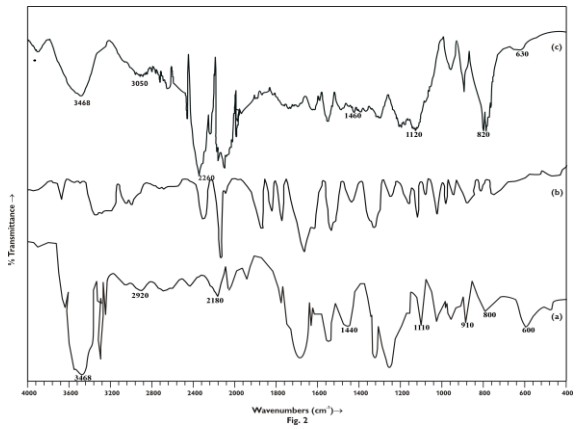

Fig.1 IR Spectra of (a) native PVA, (b) PAN and (c) semi-IPN

DSC Studies

Phase transitions and decomposition temperature of the thermally analyzed samples suggests formation of a physical gel as evident from two Tgs indicating the presence of two separate phases, one for PVA linear network and other, may be, for gel matrix. The sharp endotherm in Fig.2 depicts a gradual decrease in the second Tg, with increasing concentration of AN, but followed by an increment in the degradation temperature as well, thus, suggesting for a thermally stable nature of the semi-IPNs.

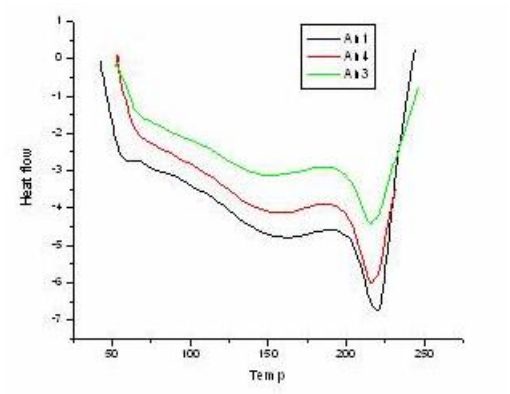

Fig.2 DSC thermograms of Semi-IPNs

Effect of PVA on swelling

PVA is a hydrophilic polymer and it's increasing amount in gel matrix is expected to enhance hydrophilicity of the network. In order to study the effect of PVA on swelling ratio, the amount of PVA was varied in the range of 1.0 g to 4.0 g . The results surprisingly reveal an initial increase in the swelling rate upto 3.0 g, but a decrease in the swelling ratio is observed for further increase in the PVA content. The initial results may be attributed to the hydrophilic nature of PVA but with increase in PVA content, the volume fraction of polymer increases, which results in a decrease in water imbibition capacity. Thus, water molecules will have to travel a longer distance through the semi-IPN to make them swell up. Also, with increasing PVA content the number of hydroxyl and methylene groups increases which consequently enhances the hydrogen bonding and hydrophobic interactions within the hydrogel network. This may lead to an initial increase but a final lower water sorption rate.

Effect of acrylonitrile on swelling

The results clearly reveal that the swelling ratio constantly decreases with the increasing concentration of AN. The noticed fall in water uptake capacity may be attributed to the hydrophobic and semi-crystalline nature of AN which may result in an enhanced hydrophobic interaction between PAN chains with more compact structure. Thus, the penetration of water molecules and subsequent relaxation of PAN chains are restrained which ultimately results in a suppressed swelling rate of the semi-IPN. Furthermore, with the increasing AN content in the semi-IPN, the increase in number of hydrogen bonds could also be the reason for decreased swelling ratio.

Effect of MBA

Properties of hydrogels can be easily modified by varying the amount of crosslinker in the semi-IPN. In the present study, the effect of crosslink density on the swelling of the network has been studied by varying the concentration of the crosslinker (MBA) in the range 0.43mM to 1.72mM in the feed mixture of the semi-IPN. The results indicates a significant increase in the swelling ratio with increasing concentration of MBA. The reason for the observed increase may be that MBA is a bifunctional monomer with hydrophilic amide and the hydrophobic -CH_2 groups. It seems that swelling rate increases due to hydrophilic characteristic of this monomer.

V. CONCLUSIONS

The semi-IPNs of PVA and PAN were successfully synthesized with quite good thermal stability. Their sorption study shows satisfactory results and being a hydrogel (water retainer) with high decomposition, the synthesized films could be tried for various biomedical applications.

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