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# Radiation synthesis, characterization and amidoximation of *N*-vinyl-2-pyrrolidone/acrylonitrile interpenetrating polymer networks

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#### Abstract

Interpenetrating polymer networks (IPNs) were synthesized by irradiating acrylonitrile solutions of poly(*N*-vinyl-2pyrrolidone) with <sup>60</sup>Co- $\gamma$  rays. The conversion to insoluble IPN structure was characterized using FT-IR and thermal analysis methods. The amidoximation of polyacrylonitrile moieties of IPN was carried out in aqueous solutions of NH<sub>2</sub>OH · HCl– NaOH at 50°C. The conversion of amidoximation was followed by using FT-IR spectrophotometer and conversion of nitrile groups to amidoxime was determined as percentage. The structure of amidoximated IPN was characterized by FT-IR and thermal methods as well. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Interpenetrating polymer networks; <sup>60</sup>Co-y rays; Amidoximation; FT-IR and TGA

## 1. Introduction

As the name implies IPNs are obtained by the simultaneous polymerization and crosslinking together of two or more monomers or polymers dissolved in some monomers. IPNs can be applied in many areas from controlled drug delivery to immobilization of enzyme and separation systems [1-3]. The diverse application possibilities arise from the incorporation of polymers with different properties in a given IPN structure.

There are numerous studies on the use of hydrophilic polymers with chelating functional groups in the preparation of IPNs [4–8]. Poly-

mers with specific functionalities can be obtained by changing some groups on existing polymers or copolymers with suitable reactants. It has been determined that the polymers containing amidoxime groups have a tendency to form a complex with metal ions. Since there are no easily available monomers with pendant amidoxime groups, these types of polymers were synthesized by polymer-polymer conversion reactions where acrylonitrile type polymers were reacted with hydroxylamine hydrochloride [9]. In this study it is aimed to prepare IPN of and poly(N-vinyl-2-pyrrolpolyacrylonitrile idone) (PVP) with the anticipation of preparing amidoximated PVP networks. IPN was synthesized by irradiation of dissolved PVP in acrylonitrile solution in  ${}^{60}$ Co- $\gamma$  source. The

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structure of IPNs, after synthesis and amidoximation reaction, were characterized by means of FT-IR and thermal analysis methods.

### 2. Experimental section

## 2.1. Synthesis of IPN

The poly(N-vinyl-2-pyrrolidone) used in this study was supplied by Serva Company with a molecular weight of 25 000. Acrylonitrile (AN) and hydroxylamine hydrochloride (NH<sub>2</sub>OH · HCl) were obtained from Merck. In a typical IPN preparation 3 g of PVP was dissolved in 6 ml AN (this is pre-determined to be the composition of a saturated solution), and the solution was irradiated in straws in  ${}^{60}$ Co- $\gamma$  source. Gammacell 220 in air at room temperature at a dose rate of 0.5 kGy/h. The PVP-AN solutions thus prepared were irradiated to different doses, and their percent conversion to insoluble network was determined gravimetrically. Irradiated mixtures were extracted with dimethylformamide to remove the soluble fractions.

#### 2.2. Characterization

In order to characterize the IPN structure, the samples were ground and dried in vacuum oven. KBr pellets were prepared from these powders and spectra were taken with Nicolet 520 FT-IR Spectrophotometer. The thermal characterization was performed by using Du Pont 951 Thermogravimetric Analyzer.

## 2.3. Amidoximation

IPNs obtained were first brought to constant weights and further reacted in 0.05 M hydroxylamine hydrochloride solution (1 : 1 in NH<sub>2</sub>OH · HCl-NaOH) at 50°C. During the amidoximation reaction, samples were taken from the reaction medium occasionally and the conversion to amidoxime structure was determined by following the changes in C=N bands of AN from FT-IR spectra. After the completion of amidoximation reaction, the amidoximated IPN taken from the reaction medium was washed with distilled water and separated by centrifuging then dried at  $35^{\circ}$ C in a vacuum oven.

# 3. Results and discussion

# 3.1. Synthesis and characterization

One of the most straightforward methods used in the preparation of IPNs is the simultaneous irradiation by ionizing radiation of a solution of a polymer in a given monomer provided that they are mutually soluble. The most important advantage of this method is the possibility of carrying out the polymerization reaction at room temperature. In the present work first we have synthesized the PVP-PAN IPNs by irradiating the solutions of PVP in AN to various doses. The conversion of this solution into insoluble network structures was determined gravimetrically. The percent conversions reached at different dose values are plotted in Fig. 1. As it is seen, the maximum conversion was reached at around 10 kGy dose. In this study, 15 kGy of dose was selected for the preparation of IPNs later used for amidoxime conversion reactions. PVP, as one of the IPN components, determines the swelling properties in water whereas PAN provides the gels durability and convertibility to other useful



Fig. 1. Percent conversion-dose plot for IPN system.

chemical structures. The samples prepared after irradiation to 15 kGy dose were first treated with water and dimethylformamide in order to selectively dissolve the uncrosslinked PVP and PAN respectively. The composition of IPNs were thus found to be 31/69% by weight for PVP/PAN respectively. The IPNs thus synthesized were first characterized spectroscopically and thermally.

The FT-IR spectra of polyacrylonitrile (PAN), PVP and IPNs are collectively shown in Fig. 2. In PAN's FT-IR spectrum at 2220  $\text{cm}^{-1}$ a sharp band characterizing C=N groups, and between 1000-1100 cm<sup>-1</sup> characteristic C-N stretching vibrations can be seen. In PVP's FT-IR spectrum there is a strong band for C=O stretching vibration at 1650  $\text{cm}^{-1}$ , and a wide strong band due to -OH stretching vibration at 3500 cm<sup>-1</sup>, and the bands between 670–730 cm<sup>-1</sup> illustrate C-H ring bending vibrations. In the FT-IR spectrum of IPN, the bands belonging to both components can be seen, such as at 2220  $cm^{-1}$  for  $\hat{C} \equiv N$  stretching, at 1650  $cm^{-1}$  for C=O stretching, between  $1000-1100 \text{ cm}^{-1}$  for C–N stretching, and between  $670-730 \text{ cm}^{-1}$  for C-H ring bending vibration together with broad

-OH band are characteristic bands of both components.

The structure of IPN was also characterized with a thermal analysis method. In order to observe IPN's thermal behavior, the IPN was ground into fine particles, and its thermogravimetric analysis (TGA) was performed in an N<sub>2</sub> atmosphere. The TGA thermogram in Fig. 3 is for pure PVP. As can be observed from this thermogram, PVP can keep its thermal stability until 400°C and shows maximum degradation rate at around 460°C. The weight loss of PVP was around 95% in the heating process of up to 600°C. In the TGA thermogram taken for pure PAN, the thermal stability of PAN was seen to be higher than PVP's, Fig. 4. The degradation of PAN was only around 35% in the heating process of up to 600°C. The starting point of degradation temperature for PAN is however, 280°C. This initial degradation is known to be due to the formation of rings among the adjacent C=N groups in the PAN structure which further increases its thermal stability. The thermogram resulting from IPN's degradation in Fig. 5 shows PAN's characteristic degradation at around 290°C, and PVP's characteristic degra-



Fig. 2. FT-IR spectra of (a) PAN, (b) PVP and (c) PVP/AN IPNs.





dation at 460°C. It should be noted that a residue of about 40% remains after degrading the IPN at 600°C. This, as noted before is because of the thermally stable cyclic structure of PAN moieties in the IPN. Consequently, FT-IR and thermal studies confirm that the

obtained structure of IPN is composed of PAN and PVP.

Since the two major thermal degradation processes of PAN and PVP are taking places at rather different temperatures and the corresponding derivative peaks are not overlapping,



Fig. 5. TGA thermogram of PVP/AN IPNs.

it was possible to calculate the composition of the IPN from the respective derivative peak areas. Such an evaluation yielded an average composition of 30–70% by weight in PVP and PAN respectively, which is in very good agreement with the result obtained in selective dissolution method.

#### 3.2. Amidoximation

As indicated in the experimental section the conversion of PAN segments into amidoxime structures is shown in Scheme 1.

In order to follow the course of the above reaction FT-IR analysis was used. The samples

taken from the reaction medium at certain intervals during the amidoximation reaction process were dried, and their FT-IR spectra were taken. As can be seen from Fig. 6 the intensities of C=N bands in IPN decrease proportionally with the reaction time. The relative decrease in the intensity of characteristic C=N bands in PAN as a function of reaction time, is shown in Fig. 7. Practically the conversion is 95% complete in 12 h and 99% of C=N groups in IPN were transformed into amidoxime groups in 20 h. Fig. 8 shows the FT-IR spectra of PVP/PAN IPN together with the amidoximated IPN at the end of 20 h of conversion time. After the amidoximation reaction, the characteristic



IPN

Scheme 1. Amidoximation reaction of IPN.



Fig. 6. FT-IR spectra of amidoximated IPNs with reaction time.



Fig. 7. The change in the relative intensity of C=N band with reaction time.

bands of IPN, which was mentioned earlier in synthesis and characterization section have been observed to change. According to the Scheme 1, C=N groups are expected to be replaced with  $H_2N-C=NOH$  at the end of the reaction. Thus, the sharp band observed in amidoximated IPN spectrum (in Fig. 8b) at 1650 cm<sup>-1</sup> belongs to C=O (PVP) stretching vibration, and the newly appearing band observed at 1600 cm<sup>-1</sup> belongs to C=N stretching vibration of the amidoximated groups [10]. As a result of amidoximation, at around 900  $\text{cm}^{-1}$  there is a newly formed band belonging to N-O stretching vibration. The wider band which can be seen at  $3400 \text{ cm}^{-1}$  is resulted from both newly formed N-H groups on amidoximated IPN groups and the diffuse H-bonding to the C=O groups. The main reason for the background change observed in amidoximated IPN spectrum could be resulting from the intramolecular hydrogen bonds among the newly formed NH<sub>2</sub> groups, and C=O groups. The sharp C=N band of PAN, although decreased significantly did not disappear completely. The IPN particles that did not swell well enough in aqueous media before amidoximation reaction, began to better and efficiently swell with the conversion due to replacement of hydrophobic nitrile groups with the hydrophilic amidoxime groups.

The consequences of nitrile–amidoxime conversion on the PAN moieties in the IPNs were also observed by the changes in the thermal properties. Before analyzing the converted IPNs thermally however, first pure PAN samples were reacted with hydroxylamine hydrochloride for 20 h as indicated in the experimental part in order to obtain so-called amidoximated PAN.



Fig. 8. FT-IR spectra of (a) PVP/AN IPNs and (b) amidoximated IPNs.

Fig. 9 shows the dynamic thermogram and its derivative for amidoximated PAN. Comparison of thermograms depicted in Figs. 4 and 9 which are for pure PAN and converted one respectively clearly shows the effect of replacement of C=N groups by amidoxime. While no weight

loss was observed for pure PAN up to around 270°C, already 25% loss in weight takes place in amidoximated polymer. The thermal instability of converted PAN is also obviously seen from a second stepwise thermal degradation at around 475°C. When the thermogram and derivative



Fig. 9. TGA thermogram of amidoximated PAN.



Fig. 10. TGA thermogram of amidoximated IPNs.

given in Fig. 10 which represent the degradation of amidoximated IPN is investigated, typical steps observed for the degradation of PVP, Fig. 3, and those appearing in Fig. 9 can be seen to be overlapping in the thermal degradation of converted IPN.

In conclusion, in the present work we have attempted to show that gamma irradiation of acrylonitrile solutions of PVP yields easily IPNs of PVP and PAN. The conversion of nitrile groups in the PAN backbone can be achieved at rather mild reaction conditions with an almost complete change into amidoxime groups. Amidoximated PVP based IPNs show good swelling behavior in aqueous media due to the presence of PVP chains and the functional amidoxime groups are effective in the adsorption of various metal ions. Adsorption capacity of these IPNs will be published separately.

#### References

- A.S. Hoffman, A. Afrassiabi, L.C. Dong, J. Cont. Rel. 4 (1986) 213.
- [2] T.G. Park, A.S. Hoffman, Appl. Biochem. Biotechnol. 19 (1988) 1.
- [3] F.A. Freitas, E.L. Cussler, Chem. Eng. Sci. 42 (1987) 97.
- [4] H. Nishide, E. Tsuchida, Makromol. Chem. 177 (1976) 2295.
- [5] H. Tbal, J. Morcellet, M. Delporte, M. Morcellet, J. Macromol. Sci. - Pure Appl. Chem. A 29(8) (1992) 699.
- [6] H. Egawa, N. Kabay, T. Shuto, A. Jyo, J. Appl. Polym. Sci. 46 (1992) 129.
- [7] E. Bayer, P. Grathwohl, K. Geckeler, Angew. Makromol. Chem. 113 (1983) 141.
- [8] S. Kobayashi, K. Hiroishi, M. Tokunoh, T. Saegusa, Macromolecules 20 (1987) 1496.
- [9] F. Arranz, M. Sanchez-Chaves, M.M. Gallego, Angew. Makromol. Chem. 218 (1994) 183.
- [10] W. Lim, Y. Lu, H. Zeng, J. Appl. Polym. Sci. 47 (1993) 45.