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POLY (N-VINYLCARBAZOLE) AND (α-POLMETHYLSTYRENE) BASED SEMI INTERPENETRATING POLYMER NETWORK: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

A series of interpenetrating polymer network (IPN) based on poly(N-vinylcarbazole) and poly(α-methylstyrene) were synthesized using benzoylperoxide (BPO) as initiator and divinyl benzene as crosslinker. The IPNs were characterized using infrared spectroscopic technique, differential scanning calorimetric analysis, thermal gravimetric analysis and scanning electron microscope techniques. FTIR spectra of the synthesized polymeric network revealed the band positions for poly(N-vinylcarbazole), at 2923 cm^{-1}, 1600 cm^{-1} and 1629 cm^{-1}, and for poly(α-methylstyrene) at 3019 cm^{-1}, 1484 cm^{-1}, 707 cm^{-1} and 1451 cm^{-1}. The relatively shortened peak value (1595 cm^{-1} $CH\text{-}CH_2\text{-}$) of vinyl group in poly(α-methylsytrene) justify the disappearance of double bond which is a clear indication of bonding between the two polymer networks leading to IPN formation. The differential scanning calorimetry (DSC) graph showed glass transition temperature (T_g) at 449ºC, which indicate crystalline nature of synthesized IPN. Thermogravimetric analysis (TGA) graph showed thermal stability of IPN upto 395ºC. Fluorescence spectra of IPN at the visual range near 450 nanometer also predicts its good optical properties. The SEM image showed a transparent and dual morphology of the synthesized polymeric network. The properties like percentage swelling, average molecular weight (Mc) between crosslinker are in direct function of initiator (benzoyl peroxide) and poly(N-vinyl carbazole) but inverse function of monomer (α-methylsytrene) and crosslinker (divinyl benzene).

Keywords: Swelling, Morphology, Network, Crosslinker, Fluorescence.

1. INTRODUCTION

In the present polymer world, interpenetrating polymer network is defined as a combination of two or more crosslinked polymers in a network with at least one of the system synthesized or crosslinked in the presence of another. These reactions may be simultaneous. Carbazole based interpenetrating polymer networks are of considerable scientific and industrial interest due to their attractive approach of combining to different properties easily and bears good optical properties also. Among carbazole polymers, a central place is reserved for poly(N-vinyl carbozole) because it is easily synthesized. This is an applicable approach and has been employed by a number of scientists to describe novel IPN systems for commercial applications. Investigators discussed their view regarding enhancement of IPN study. Millar [1] was the first person to use the concept of 'IPN' and prepared from identical styrene - divinyl benzene production with polymer networks. A mass of studies are reported in the literature about the IPNs of PUI. The first reported work is by Sperling et al. [2]. Ekici and co-worker [3] synthesized a special IPN, carrying drug release properties. They worked out to prepare IPN hydrogel of chitosan poly (N-vinyl pyrrolidone) and poly(acrylic acid) with N, N'-methylene bisacrylamide (MBA). This was a unique IPN hydrogel which holds better swelling properties along with upgraded thermal and mechanical properties. The individual polymer is linked together by crosslinking but not chemically linked [4]. Zahao and co-workers [5] reported synthesis of elastomers and gel from IPN. Synthesis and characterization of interpenetrating polymer network poly(glycidyl methacrylate) and acrylamide using selenenium ylide as an initiator and divinyl benzene as crosslinker was done by Anamika Singh [6]. Peerasak et al. [7] synthesized styrene and 4-vinyl pyridine with poly(ethylene tetraphthalate) using benzoyl peroxide. Prashantha et al. [8] formed polyurethane epoxy IPNs and widely applied to fibers, foams, coating, leathers and other applications. Kyriakos et al. [9] described versatile synthetic methodology that leads to the generation of nonconjugated 3D luminescent semi interpenetrating aliphatic network. Tamrin and coworker [10] synthesized IPN from composite base on poly composite polyurethane-natural rubber assisted montmorillonite as Filler. It showed the improve mechanics, morphology and thermal properties of IPN. Netu et al. [11] studied photoluminescence spectroscopy property as an important tool which has been used (TiO_2/SnO_2) sensing of gas. Meet and coworker [12] described conductivity behaviour of semi IPN of fullerene based polyacrylonitrile and polyaniline. Petra et al. [13] reported synthesis of semi IPN by ring opening polymerization of ε-caprolactone and the poly (styrene-co-divinyl benzene) which has a pronounced effect on the morphology of obtained polystyrene frame works. Further, Ruima et al. [14] synthesized IPN based on Trisocyanate-terminated and modified poly (urethene-imide) with superior mechanical properties.

A lot of work has been carried on silicon polymers and vinyl monomers. But synthesis of vinyl carbazole based IPN is still scare. Therefore, the present study emphasized on synthesis of IPN based on interaction of poly(N-vinyl carbazole) and poly(α-methyl styrene). The aim of the research work is to fabricate a network system to describe various physiochemical and thermal properties. The vinyl monomeric repeating units of α-methyl styrene provides a great sense of interpenetration where as poly(N-vinylcarbozole) is a temperature resistant thermoplastic polymer.

2. MATERIAL AND METHODS

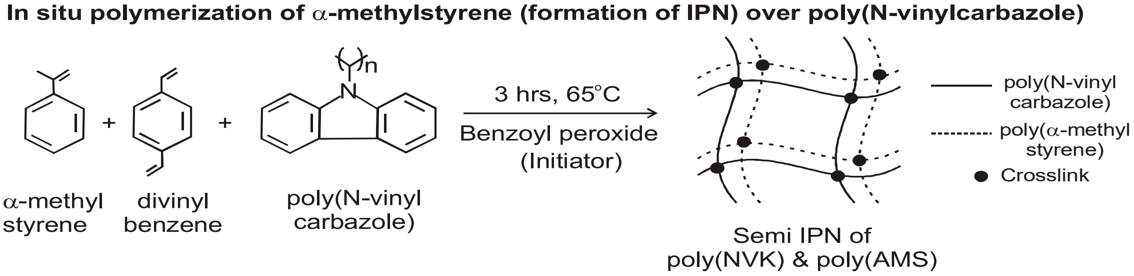
N-vinylcarbazole (NVK 98%) (Sigma Aldrich) and Benzoyl peroxide (Merck 98%) was recrystallized thrice from methanol. Divinyl benzene, solvents (Merck) were used as received. α-methyl styrene (98%) (Kemphasol) was purified by recrystallization from methanol. All other material were used without further purification.

2.1. Preparation of poly (N-vinylcarbozole)

N-vinylcarbazole (19.3 gm or 0.1 mole) was placed in a conical flask (250ml). Benzolyl peroxide (0.5 g) was dissolved in 100 ml acetonitrile and added to the flask which was heated at 70°C over a 4 hours period. The polymer was precipitated by methyl alcohol and washed with acetone and dried under constant weight.

2.2. Synthesis of IPN

Interpenetrating polymer network of poly(N-vinylcarbazole) and poly(α-methyl styrene) were synthesized by systematic variation of concentration of poly (N-vinylcarbazole) and α-methyl styrene using benzoyl peroxide as initiator and divinyl benzene as crosslinking agent in toluene as solvent. The system was kept on water bath for 3 hours at 70°C under an inert atmosphere. The IPNs was obtained after evaporating the solvent. The IPNs formed were precipitated in methanol and vacuum dried to constant weight.



Scheme 1: **Synthesis of IPN based on poly(N-vinylcarbazole) and α-methylstyren**

2.3. Characterization of IPN

The IPNs were formulated and characterized using spectroscopic technique, thermal techniques and scanning electron microscopic techniques.

2.3.1. FTIR Measurement

The IR spectra of synthesized IPNs were recorded by a Perkin-Elmer spectrum version 10-03-06 instrument using the dry KBr at room temperature. The IR spectrum was carried out at wavelength 500-4000 cm^{-1}.

2.3.2. Thermal analysis

Thermal properties were analyzed by Simultaneous DSC/TGA technique on the instrument model SDTQ 600 V 20.9 Build 20. All spectra were recorded under nitrogen atmosphere upto 800°C using programmed rate of 10°C /minute.

2.3.3. Fluorescent characterization

The fluorescence emission and excitation spectrum of IPNs were recorded on a spectrofluorimeter (Fluorolog 3, Model FL 3-22).

2.3.4. SEM Morphology

The morphology images of the synthesized IPNs have been studied by the SEM technique with varying magnification. The IPN samples were Gold Sputter coated carried out using model JEOLJ SM 840 Å scanning electron micrsoscope (SEM).

2.3.5. Swelling measurements

Swelling behaviour of IPNs sample were calculated by soaking the sample in 10 ml of different solvents such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), benzene or toluene until an equilibrium weight was achieved (~24 hrs). The solvent was removed by heating the sample to 60°C under vaccum until equilibrium was achieved. The weight of the swollen film in each solvent was recorded at different time. The swollen percentage was calculated according to the following relationship [15].

$$\%\ \text{Swelling} = \left(\frac{W_s - W_d}{W_d}\right) \text{x } 100$$

where W_s = weight of swollen IPN and W_d= Weight of dry IPN.

2.3.6. Calculation of percentage extractable materials

The uncrosslinked component of IPN was removed with the help of Soxhlet extractor using dimethyl sulphoxide (DMSO) as solvent, otherwise no reproducible results were obtained. The percentage extractable material was calculated using the following formula:

$$\%\ \text{Extractable material} = \left(\frac{W_b - W_a}{W_a}\right) \text{x } 100$$

where W_b = Weight of IPN before extraction and W_a = Weight of IPN after extraction.

2.3.7. Crosslink density (1/Mc)

The IPN sample was taken and its crosslink density (1/Mc) of the network was determined by using the swelling data of IPN in DMF with help of Flory-Rehner equation [16, 17].

$$\frac{1}{M_c} = -\frac{\left(\mathrm{In}\,(1 - V_p) + V_p + X_{12}V_p^{\,2}\right)}{pV_1\,(V_p^{\,1/3} - V_p/2)}$$

where, M_c= average molecular weight of network between crosslinks, p = density of the network, V_1= molar volume of solvent, and V_p = volume fraction of polymer in swollen gel, X_{12} = polymer solvent interaction parameter, calculated by the expression [18].

$$X_{12} = B + \frac{V_1\,(\delta_p - \delta_s)^2}{RT}$$

where δ_p and δ_s = solubility parameters of polymer and swelling solvent, respectively, and B = lattice constant, the value of which is taken as 0.34.

3. RESULTS AND DISCUSSION

3.1. FTIR spectral analysis

The structural analysis of polymeric network was studied by FTIR spectroscopic technique. We have examined the detailed vibrational FTIR spectra of the synthesized IPN. FTIR study for pure poly(N-vinyl carbazole) (PNVK) (Fig. 1) revealed, peaks at 2964 cm^{-1} (C-H a symmetric), 2927 cm^{-1} (for C-H symmetric stretching), 1595 cm^{-1} (for C=C stretching in vinylidene) and 1639 cm^{-1} (for C=C stretching in aromatic ring) and for poly(α-methyl styrene) it depicted peaks at 3000 cm^{-1} (stretching vibrations), 1490 cm^{-1} (for C-C vibrations), 3010 cm^{-1} (for C-H stretching vibrations), 699 cm^{-1} (benzene ring C=C bending) and 1444 cm^{-1} (for bending vibrations of C-H bond of $-CH_3$ group). While IR spectra for the synthesized IPN (Fig.3) revealed the peaks for poly(N-vinyl carbazole) at 2923 cm^{-1} (C-H asymmetric stretching), 1600 cm^{-1} (C=C stretching in vinylidene) and 1629 cm^{-1} (C=C stretching in aromatic ring) and for poly(α-methyl styrene) it is depicted peaks at 3019 cm^{-1} (stretching vibration), 1484 cm^{-1} (for C-H vibration), 3019 cm^{-1} (for C–H stretching vibration), 707 cm^{-1} (for benzene ring C=C bonding) and 1451 cm^{-1} (for bending vibration of C-H bond of $-CH_3$ group). For companion FTIR spectra of α-methyl styrene also been depicted is Fig. 2.

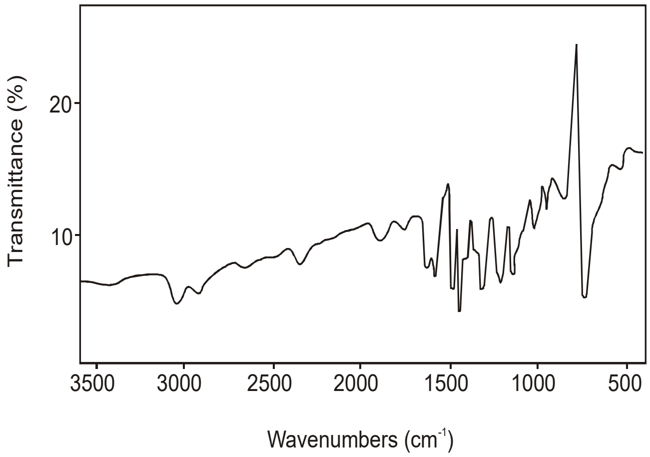


Fig. 1: IR spectra of poly(N-vinylcarbazole)

Moreover, the shortened and relatively broadened peak value (1595cm^{-1}, -CH–CH$_2$-) of vinyl group in poly (α-methyl styrene) justify the disappearance of the double bond. This band shifting revealed the interpenetration of poly(α-methylstyrene) is poly (N-vinylcarbazole) matrix.

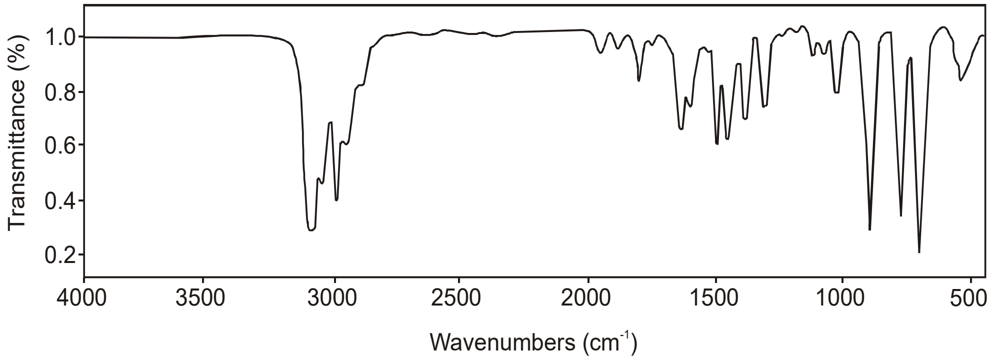


Fig. 2: IR spectra of α-methylstyrene

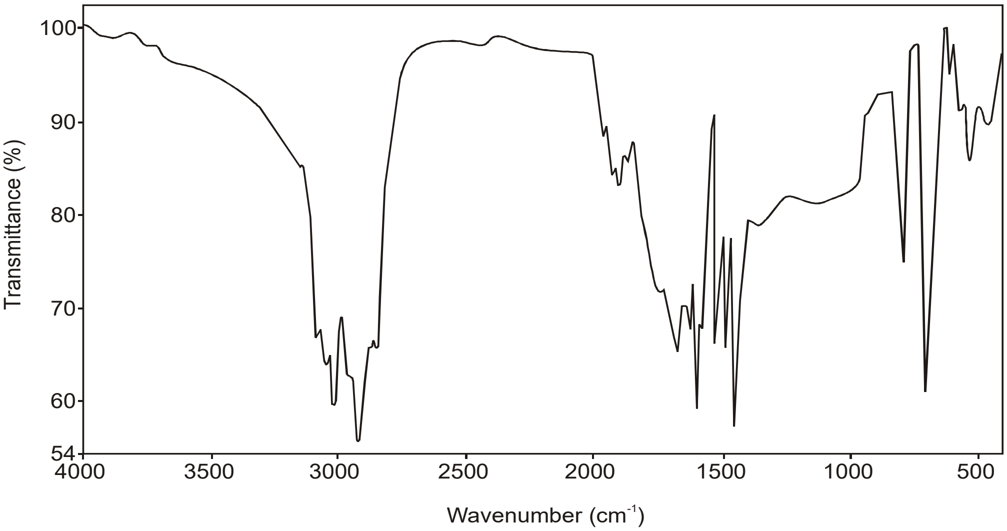


Fig. 3: IR spectra of IPN

3.2. Thermal Analysis

3.2.1. DSC

DSC thermogram of IPN sample contain crystalline peak (Tg) at 447ºC (Fig.4), which is in higher than Tg of poly(α-methyl styrene) (435ºC) and poly(N-vinyl carbozole) (225ºC). It might be caused by high crosslinking density in the IPN. It is an evidence of strong restricted chain mobility. N-vinylcarbozole macromolecules are entangled or even covalently bonded to crosslink. Poly(α-methylstyrene) (result of interpenetration). Poly(N-vinyl carbozole) has stiff backbone length which provides stiffness to polymer network and poly(α-methylstyrene) has comparatively thermal resistant backbone and participate in properties of IPN.

3.2.2. TGA

Thermal stability of the IPN was studied by TGA from 25 to 800ºC. It displaced degradation upon gradual heating of the sample during the entire thermogram from Fig.5. This shows that initial thermal decomposition at 390ºC. The thermal decomposition pattern of IPN ranges between the poly(N-vinylcarbozole) and poly(α-methylstyrene). This result indicates the incorporation of α-methylstyrene unit in the polymer network.

3.2.3. Fluorescent characterization

Fluorescence emission spectra of polymeric network (Fig.6) reveal fluorescent excitation and emission spectra of the synthesized IPN. The fluorescent excitation and emission spectra of IPN nanosheets depict that the polymeric network exhibit analogous excitation and emission. The emission spectra reveal a broad peak centered at about 450 nm, owing to n→π* electronic transition found in polymeric network. Emission spectra generated by radioactive decay of excitations exhibit a maximal peak at 450 nm, suggesting that the synthesized IPN nanosheets are typically high intensity blue light emitting materials.

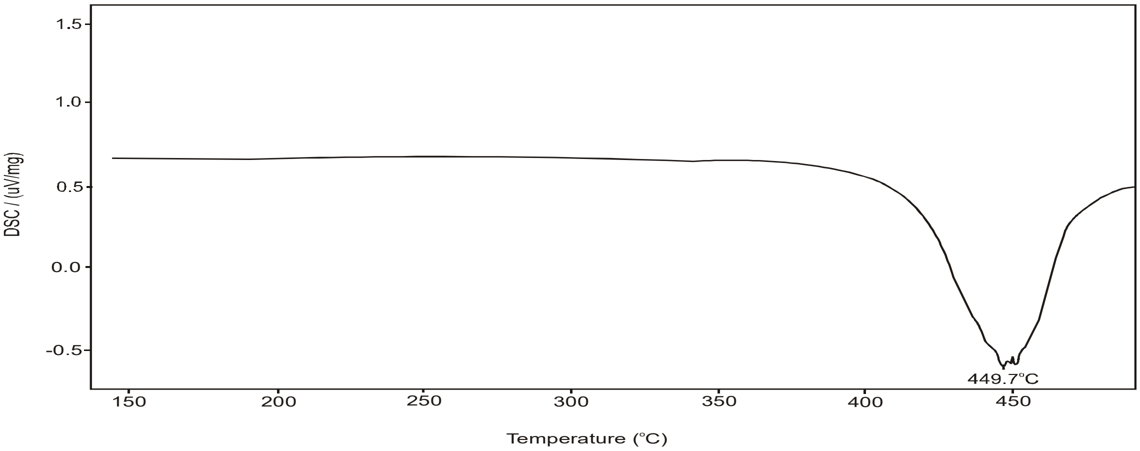


Fig. 4: DSC thermogram of IPN

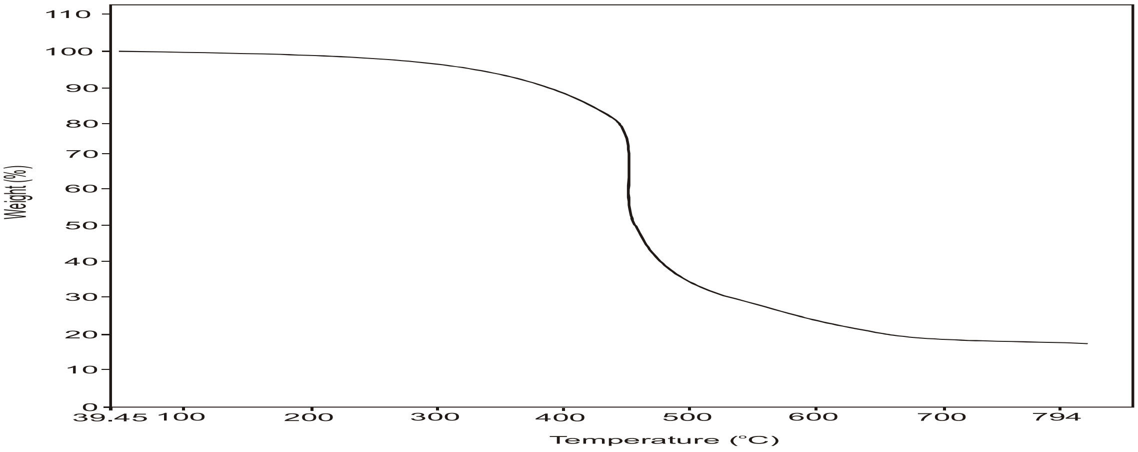


Fig. 5: TGA curve of IPN

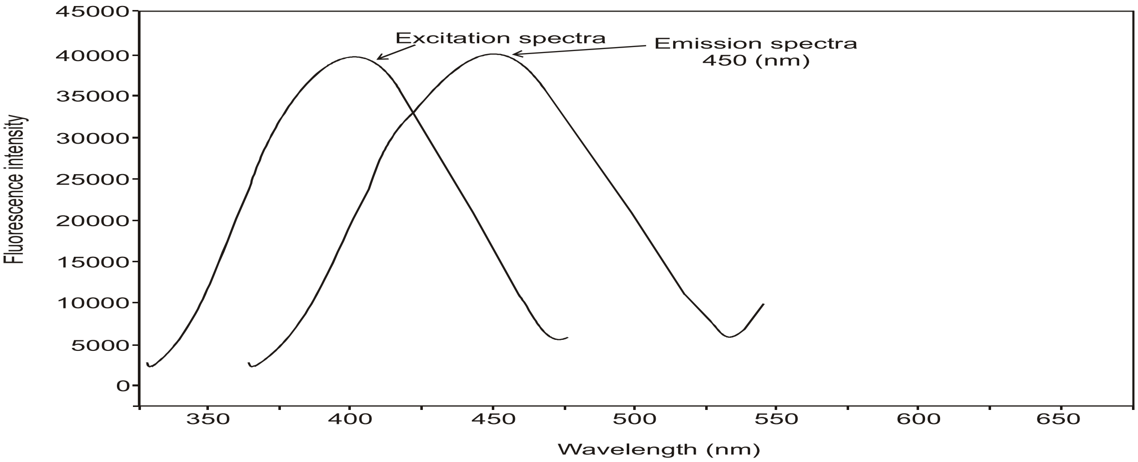


Fig. 6: Fluorescent excitation and emission spectra of IPN

3.2.4. Morphology

The micro structure of interpenetrating network of poly (N-vinylcarbozole) and poly(α-methylstyrene) is observed. The SEM images indicate dual phase morphology of synthesized IPN (Fig. 7). The network structure is diversified, which indicate sample heterogeneity of solution used for film preparation. It means phase separation has occurred just after solvent evaporation which is clearly distinguished.

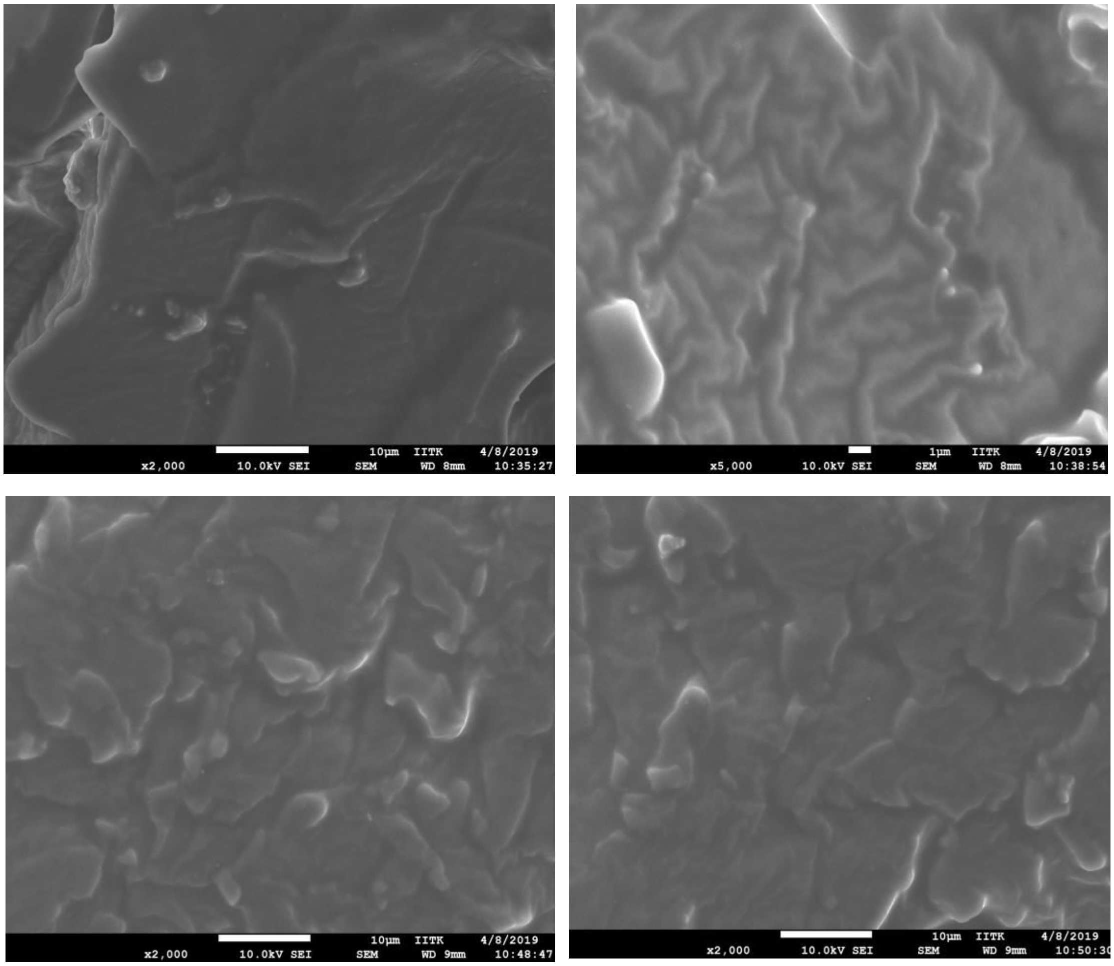


Fig. 7: SEM photograph of IPN

3.2.5. Effect of composition

The swelling behaviour could be envisaged from Table 1 which represents the effect of various solvent in swelling and percentage of extractable material on the different physical and chemical properties of IPN. The study of effect of composition of poly(N-vinylcarbazole) and poly(α-methylstyrene) shows as trend, since an increase in concentration of poly(α-methylstyrene) for poly(N-vinylcarbozole) result in increased swelling and molecular weight (Mc) (Table 2). It shows that poly(N-vinylcarbozole) restricts crosslinking of poly(α-methylstyrene). As the concentration of poly(α-methylstyrene) increases, interpenetration of poly(N-vinylcarbazole) also increases. The crystallinity of polymer network is directly proportional to the concentration increases of poly(N-vinylcarbazole). Thus higher amount of poly(N-vinylcarbazole) usually enhances polymer crystallinity and hence the higher glass transition temperature value of IPN is obtained. On the other hand, according the data obtained from Table 2 and 3, the increase in concentration of α-methylstyrene favours the formation of crosslinked network, but also some decrease of glass transition temperature of IPNs. It leads to a higher degree of crosslinking between poly(α-methylstyrene) phase. Similarly explanation can be given for the fact that percentage swelling and Mc vary inversely proportional to the concentration of poly(N-vinylcarbozole).

3.2.6. *Effect of initiator (BPO)*

The variation and effect of BPO concentration over swelling and molecular weight (Mc) of IPN is shown in Table 4. It is clear that both swelling and molecular weight increases with increase molar concentration of benzoylperoxide.

3.2.7. Effect *of crosslinker (DVB)*

Table 5 indicates that as the concentration of crosslinker DVB increases, the value of crosslink density and percentage swelling decreases. The reason is that an increase of concentration of DVB increases the crosslinking between the two polymeric networks which results decreased swelling and M_c. It is interesting to note that concentration increase in DVB enhances the crosslinking in the polymeric network and hence depress the chain mobility. This ultimately increases the glass transition temperature. The IPN does not dissolve, but swells in DMF. It is an evidence for crosslinking between two components.

Table 1: Percentage swelling of IPN in different solvent and extractable material (%)

Sample used	DMSO (%)	Benzene (%)	Toluene (%)	DMF (%)	Extractable Material (%)
IPN 1	48	27	41	33	13.6
IPN 2	60	36	49	35	15.2
IPN 3	71	40	52	55	16.0
IPN 4	82	42	56	52	26.8
IPN 5	42	21	37	25	13.6
IPN 6	39	17	32	22	11.4
IPN 7	40	15	28	35	14.0
IPN 8	54	42	39	39	36.2
IPN 9	61	25	34	33	24.1
IPN 10	67	23	32	27	13.4
IPN 11	38	26	48	41	12.0
IPN 12	31	23	25	36	11.5
IPN 13	22	11	25	23	12.8

Table 2: Effect of variation poly(N-vinylcarbozole) on IPN properties

Sample	Poly(NVK) (mol l^{-1} x 10^{-3})	Yield	Swelling (%) in DMSO	M_c in DMF
IPN 1	76.9	1.157	48	160
IPN 2	11.5	1.386	60	175
IPN 3	153.8	1.722	71	181
IPN 4	192.3	1.850	82	189

Table 3: Effect of variation of α-methylstyrene on IPN properties

Sample	α-methylstyrene (mol l^{-1} x 10^{-3})	Yield	Swelling (%) in DMSO	M_c in DMF
IPN 1	62	1.157	48	160
IPN 5	93.1	1.138	42	152
IPN 6	124.1	0.850	39	149
IPN 7	155.2	0.453	40	136

Table 4: Effect of variation of (BPO) on IPN properties

Sample	BPO($\times 10^{-2}$ mol l^{-1})	Yield	Swelling (%) in DMSO	M_c in DMF
IPN 1	0.412	1.157	48	160
IPN 8	0.619	1.750	54	175
IPN 9	0.825	1.468	61	183
IPN 10	1.030	2.156	67	189

Table 5: Effect of variation of (DVB) on IPN properties

Sample	DVB (mol l^{-1})	Yield	Swelling (%) in DMSO	M_c in DMF
IPN 1	0.70	1.157	48	160
IPN 11	1.05	1.550	38	149
IPN 12	1.40	1.680	31	136
IPN 13	1.70	2.130	22	123

4. CONCLUSION

The present work has given rise to the formation of tough and strong conducting polymer network of poly(N-vinylcarbazole) and α-methylstyrene, which reveals a proper packing with the monomeric species. The DSC thermogram indicate that high value of glass transition temperature as compared to poly(N-vinylcarbazole) and α-methylstyrene. This might have been occurred because high crosslink density and better interpenetration of poly(N-vinylcarbazole) and poly(α-methylstyrene). SEM photograph reveals a clear dual phase morphology of polymer network. The fluorescent emission and excitation spectral study of polymeric network depicts emission spectra generation by radioactive decay of excitation which exhibit a maximum peak value at 450 nanometer. This indicates typical high intensity blue light emitting property of the IPN. The synthesized IPN may be applicable in thermal resistant polymers bearing good fluorescent property and photo conducting light emitting diodes.

5. ACKNOWLEDGMENT

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