Synthesis And Characterization Of Interpenetrating Polymer Network Of Poly (METHYLHYDROSILOXANE) And Polystyrene

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Abstract: A series of Interpenetrating Polymer Network (IPN), of poly(methylhydrosiloxane) and polystyrene was synthesized, using divinyl benzene (DVB) as cross linker and benzoyl peroxide (BPO) as an initiator. The characterization of the sample is done by FT-IR spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogrametric analysis (TGA) and fluorescent technique. FT-IR spectra reveals presence of poly(methylhydrosiloxane) at 1048 cm^{-1} and polystyrene at 1451 cm^{-1}. Shifting in band positions depict formation of IPN. SEM images show a clear dual phase morphology. DSC thermogram shows glass transition temperature (T_g) value of the polymer is network at 380°C. TGA graph shows thermal stability of IPN upto 345°C. Proton NMR spectra of IPN reveals presence of poly(hydrosiloxane) at 4.7 ppm, 1.2 ppm and poly(styrene) 7.2 ppm. Fluorescence spectra of IPN observed in emission spectra of excitations of IPN reveals a maximal peak at 445 nm, which suggest typical high intensity blue emitting property of the polymer network.

Keywords : Poly(methylhydrosiloxane), Polystyrene, glass transition temperature, dual phase morphology, interpenetrating polymer network and crosslinker.

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1 INTRODUCTION:

An IPN is a network of two or more polymer entangled such that they are unable to pulled apart from one another [1]. An IPN is neither a blend of two polymer nor a co-polymer. It may be classified as a separate form of polymer application i.e. interpenetrating polymeric unit [2]. First effort towards IPN study was emphasized by Millar in 1960, who put forward his idea of interpenetration of polymers [3]. Then after several researches developed different theories and gave out surprising facts about IPN. IPN has found important applications in diverse technologies, including organic cells, tissue engineering and polymer actuators [4] etc. Besides IPN structures, there is another polymeric species which reveals a broad spectrum properties and application in the present scenario of polymer world [5]. This is silicon based polymers such as polymethyl hydrosiloxane. Taking into consideration the above mentioned structure and properties of discussed molecular form viz. Polystyrene and polymethyl-hydrosiloxane and IPNs [6], [7]: the possibility may be explored for their future applications. A variety of research work has been carried out to investigate the thermal and morphological properties yet IPNs of polystyrene is still scarce [8]. The aim of research work is to synthesize a polymeric network based on novel vinyl monomer styrene and polymethylhydrosilaxane which elaborate various physiochemical and thermal properties. Attempts have been made to provide flexibility and better thermal properties of IPN [9].
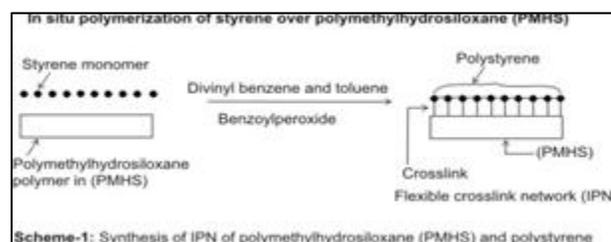
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2 EXPERIMENTAL PROCEDURE:

Materials:
Poly(methylhydrosiloxane) (Sigma-Aldrich) solvents (Merck) and divinyl benzene (Merck) were used as received. Benzoylperoxide (BPO) was recrystallized in methanol. Styrene (CDH 98%) washed before use.

Synthesis of IPN:
A series IPNs were synthesized by systematic variation of concentration of poly(methylhydro- siloxane) and styrene using benzoyl peroxide as an initiator and divinyl benzene as a crosslinker and toluene as a solvent. The system kept on water bath for 50 to 70 minutes at 65 ± 1°C under nitrogen atmosphere. The IPN obtained was precipitated in methanol and vacuum dried until a constant weight was obtained.

Scheme-1: Synthesis of IPN of polymethylhydrosiloxane (PMHS) and polystyrene

2 CHARACTERIZATION OF IPN:
FT-IR Measurements:
Transparent thin film of IPN was characterized by FT-IR spectroscopic study using a Perkin Elmer spectrum version 10-03-06 instrument (using KBr pallet).

^{1}H-NMR Spectroscopy:
^{1}H-NMR spectral analysis of synthesized IPN of poly(methyl-hydrosiloxane) and polystyrene sample was carried out in an ECX500-JEOL NMR spectrometer).

Surface Morphology:
The surface morphology of the synthesized IPN network was studied by scanning electron microscopy (SEM) at different magnifications. The IPN was studied from gold-coated films by a (JEOL JSM 840Å).

Fluorescent Characterization:
The fluorescent emission / excitation spectrum of pre-swollen IPN was recorded on spectrofluorimeter (Fluorolog 3, Model FL 3.22)

Thermal Analysis:
Measurement of thermal properties were examined using a simultaneous DSC/ TGA SDTQ600V20.9 Build 20 system with a heating rate of $10^{o}C$ min^{-1}. The sample weight was found to be 15.94 mg.

Calculation of Percentage Extractable Materials:
The uncrosslinked component was removed with the help of soxhlet extractor using dimethylsulphoxide (DMSO) as a solvent. The % extractable material was calculated as:
% Extractable material $=(W_b-W_a) / W_a \times 100$ (1)
Where the W_a and W_b are the weights of the IPN after extraction and before extraction, respectively.

Swelling measurements: Swelling data were calculated by soaking the sample in 10 ml of different solvents such as DMF, benzene, DMSO, toluene until an swollen equilibrium was achieved (~24 hrs). Weight measurements were made using filter paper. The sample was dried and immediately weighed. The weight of the swollen IPNs in each solvent was recorded. The swollen percentage was then calculated as:
        % swelling = $(W_s-W_d) / W_d \times 100$ (2)
Where W_s and W_d weight of swollen IPN and dry IPN, respectively.

Crosslink density $(1/M_c)$:
 The IPN sample was taken and its crosslink density of the network was calculated by using the swelling data of IPN in DMF with the help of Flory-Rehner equation [10]
$1/Mc= - [\ln (1-Vp) + Vp +X_{12} Vp^2] / \rho V_1[Vp^{1/3} – Vp / 2]$ (3)
Where M_c = average molecular weight of network between crosslink density, ρ = density of the network, V_1 = molar Volume of solvent, Vp = Volume fraction of polymer in swollen gel, X_{12} = polymer solvent interaction parameter, calculated by the following equation [11].
        $X_{12}=B+V_1(\delta_p-\delta_s)^2/RT$ (4)
Where δ_p and δ_s = solubility parameter of polymer and swelling solvent respectively and B = lattice constant, the value of which is taken as 0.34

3 RESULTS AND DISCUSSION:

FT-IR DATA:
IR spectroscopy of the synthesized polymeric network was studied which reveals the presence of several important functional groups. IR study for pure poly(methylhydrosiloxane) shows peak position at 1050 cm^{-1} (Si–O), 1250 cm^{-1} (Si–C), 2225 cm^{-1} (Si–H) and 3000 cm^{-1} (C–H), respectively and IR study for pure poly(styrene) depicts bond position at 1490 cm^{-1} (–C–C–) vibrations and at 699 cm^{-1} (benzene ring C=C bending). While IR spectra (Fig.1) of the synthesized IPN depicts presence of

poly(methylhydrosiloxane) at band position 1048 cm^{-1} (Si–O), 1261 cm^{-1} (Si–C), 2168 cm^{-1} (Si–H) and 2967 cm^{-1} (C–H), respectively and for poly(styrene) it shows presence of (–C–C–) vibration at 1451 cm^{-1} and benzene ring C = C bending at 710 cm^{-1}. The shifting is band position clearly indicates the possibility of interpenetration between the two units i.e. formation of interpenetrating polymer network.
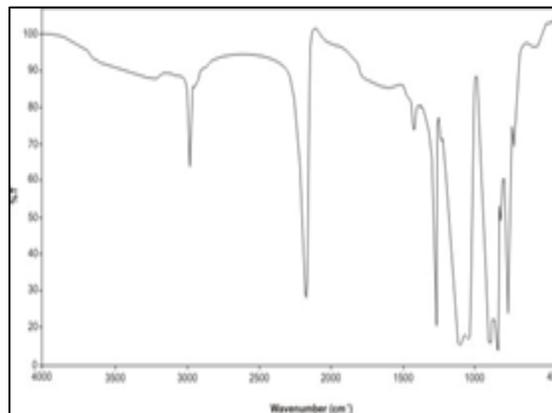

Fig. 1: IR spectra of IPN 3

^{1}H-NMR spectral study:
The ^{1}H NMR spectra for pure poly(methyl hydroxysiloxane) (PMHS) is found to be at 5.1 ppm and 0.5 ppm and for pure synadiotactic polystyrene is recorded at 6.6 ppm (for Phenyl group) and at 6.9 ppm (CH group). But the NMR spectral (Fig.2) study for the fabricated polymeric network reveals the presence of PHMS at 4.6 ppm and 1.2 ppm and for polystyrene it is observable that band position for CH group and phenyl group get merged and produce single peak at 7.2 ppm. Thus a considerable deviation of IPN sample from the ideal ^{1}H spectra depicts possibility of interpenetration and network formation between the two polymers (PMHS) and polystyrene.
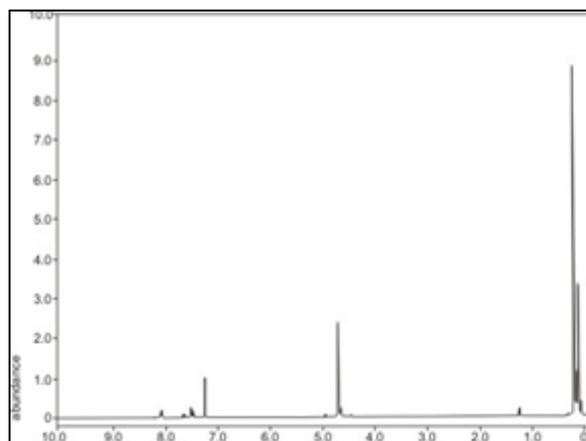

Fig. 2: Proton NMR spectra of IPN 3

Fluorescent analysis:
The Fluorescent emission spectra of polymeric network were analyzed on spectrofluoremeter. The fluorescent excitation and emission spectra of IPN (Fig.3) film reveals that the polymeric network exhibits analogous excitation (A) and emission spectra (B). The excitation spectra depict a

414

broad peak centered at 400 nm, owing to n→□* electronic transition found in polymeric network. Emission spectra produced by radioactive decay of excitations exhibit a maximal peak at 445 nm, suggesting that the fabricated polymeric network is typically high intensity blue light emitting materials.
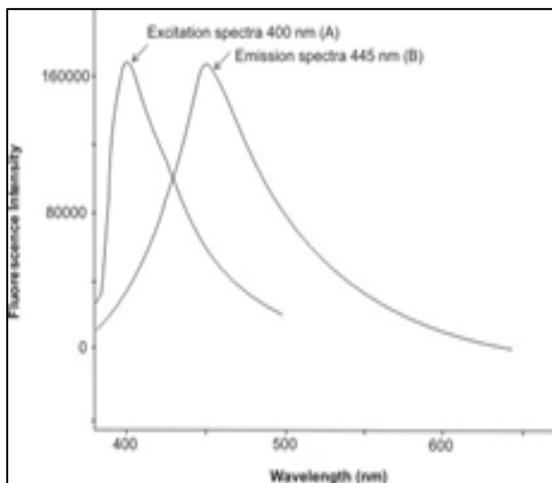

Fig. 3: *Fluorescent of IPN 3*

Morphology:
The morphological analysis of interpenetrating polymer network of poly(methylhydro-siloxane) and polystyrene by SEM technique reveals a clear dual phase morphology (Fig.4). The network structure is variegated, indicating sample heterogenity of solution. The surface of IPN is not serene. Some projections of different sizes are observable. This indicates that under top layer there is a presence of heterogeneous regions, depicting a clear dual phase morphology.
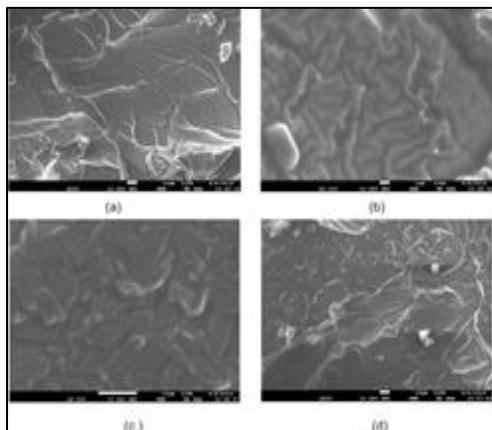

Fig. 4 : *SEM images of IPN 3*

DSC characterization:
 DSC thermogram of polymeric network (Fig.5) reveals glass transition temperature value (T_g) at 380°C which is higher than the reacting species. This enhanced, T_g value clearly indicates the crosslinking between the two units.
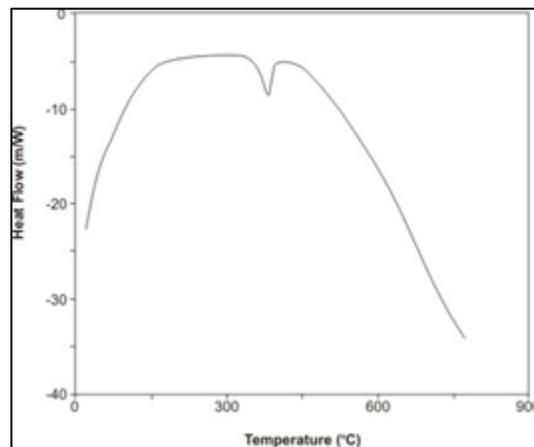

Fig.5: *DSC thermogram of IPN 3*

TGA characterization:
 Figure 6 shows TGA graph of IPN with initial thermal decomposition temperature at 345°C. The thermal decomposition pattern of polymeric network ranges between the polystyrene and polymethylhydrosiloxane. This result indicates the incorporation of polystyrene units in the polymeric network.
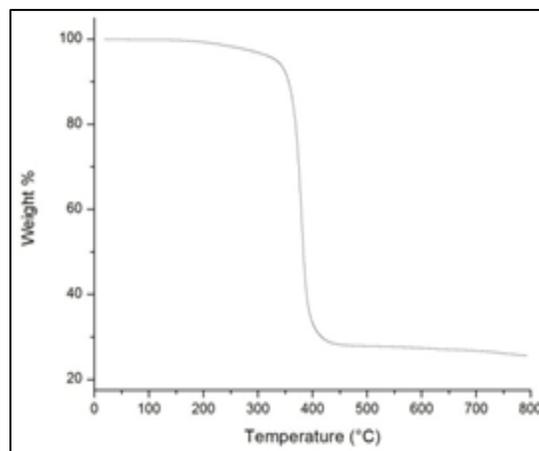

Fig.6: *TGA curve of IPN-3*

Effect of Composition:
The swelling behavior could be envisaged from (Table-I) which represent the percentage swelling of IPN in different solvent such as toluene, DMF, DMSO, benzene and percentage extractable material. The study reveals a proportion effect of variation poly(methylhydrosiloxane) (Table-II) over increased swelling and molecular weight (M_c). This indicates which shows that with increase is concentration of PMHS there is increase is Mc values. From the analyse data of table III increase in concentration of polystyrene decreases the value of Mc which shows that the presence of polystyrene restricts crosslinking of poly(methylhydrosiloxane). This restriction is due to overall decrease in concentration of crosslinking of styrene. Furthermore, it is believed that poly(methylhydro-siloxane) must be crosslinked to polystyrene.

415

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

Sample used	Toluene (%)	Benzene (%)	DMSO (%)	DMF (%)	Extractable Material (%)
IPN 1	53	26	48	32	13.5
IPN 2	71	37	55	38	15.3
IPN 3	80	39	61	62	16.3
IPN 4	84	43	68	57	26.5
IPN 5	49	21	39	28	13.6
IPN 6	47	18	35	24	11.3
IPN 7	44	32	42	36	14.8
IPN 8	57	38	45	39	36.7
IPN 9	63	23	41	33	24.3
IPN 10	68	25	34	27	13.2
IPN 11	46	27	47	39	12.4
IPN 12	38	22	34	33	10.5
IPN 13	29	12	27	21	11.8

Table-II: Effect of variation poly(methylhydrosiloxane) on IPN properties

Sample	PMHS (mol l^{-1} x 10^3)	Yield	Swelling % in toluene	M_c in DMF
IPN 1	53	1.257	53	163
IPN 2	79	1.380	71	178
IPN 3	106	1.732	80	187
IPN 4	132	1.850	84	193

Table-III: Effect of variation of (styrene) on IPN properties

Sample	Styrene (mol l^{-1})	Yield	Swelling (%) in toluene	M_c in DMF
IPN 1	0.87	1.257	53	163
IPN 5	1.30	1.138	49	156
IPN 6	1.74	0.850	47	151
IPN 7	2.18	0.453	44	147

Effect of initiator (BPO):

The data depict (Table IV) that increasing molar concentration of initiator increases M_c and swelling behaviour.

Table-IV: Effect of variation of (BPO) on IPN properties

Sample	BPO ($\times 10^{-2}$ mol l^{-1})	Yield	Swelling (%) in toluene	M_c in DMF
IPN 1	0.412	1.257	53	163
IPN 8	0.619	1.750	57	182
IPN 9	0.825	1.468	63	194
IPN 10	1.030	2.156	68	199

Effect of crosslinker (DVB):

Table-V indicates that as the concentration of crosslinker increases, the value of percentage swelling and M_c decreases. This is due to an increase of concentration of crosslinker which increases the crosslinking between the two polymeric chain resulting decreased M_c and swelling. It is interesting to note that increase in concentration of crosslinker enhances the crosslinking in the polymeric network and hence depress the chain mobility. This ultimately increases the glass transition temperature. It is an evidence for crosslinking between two components.

Table-V: Effect of variation of (DVB) on IPN properties

Sample	DVB (mol l^{-1})	Yield	Swelling (%) in toluene	M_c in DMF
IPN 1	0.70	1.257	53	163
IPN 11	1.05	1.457	46	156
IPN 12	1.40	1.538	38	151
IPN 13	1.70	2.131	29	131

4 CONCLUSION:

Spectral analysis of IPN containing poly(methyl-hydrosiloxane) and polystyrene indicates ideal IPN formation. The DSC thermogram revealed higher T_g for IPN. The reason is that higher crosslink density and restricted chain mobility of the units. The IPN shows characteristics dual phase morphology. The fluorescent excitation and emission spectra at 445 nm shown that such IPN system exhibit a typical high intensity blue light emitting property.

5 ACKNOWLEDGMENT:

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