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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF INTERPENETRATING POLYMER NETWORK OF POLY (METHYLHYDROSILOXANE) AND POLY (ACRYLONITRILE).

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Abstract

Interpenetrating polymer network (IPN) based on poly (Methylhydrosiloxane) and poly (Acrylonitrile) have been synthesized using benzyl peroxide as initiator and divinyl benzene as crosslinker in toluene under an inert atmosphere of nitrogen. The scanning electron microscopy reveals dual phase morphology of the synthesized polymer network. The properties like percentage swelling, average molecular weight between crosslink's (M_c), are the direct function of [copolymer] and initiator [benzoylperoxide] whereas inverse function of concentration of monomer (acrylonitrile) and crosslinker (divinyl benzene). A fluorescence spectrum of the material is observed in the visual range near 457 nm. FTIR spectrum confirmed the presence of PMHS and acrylonitrile and DVB in the synthesized IPN. The differential scanning calorimeter (DSC) curve showed glass transition temperature at 340°C. Thermogravimetric analysis (TGA) depicted thermal stability of IPN upto 400°C. The synthesized IPN is thermally stable upto 400°C.

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Introduction:-

In the present scenario polymers are among greatest volume chemical products in the world global market. To overcome the poor performance of conventional polymers, a new class of polymers "Interpenetrating Polymer Network (IPN)" comes in existence. An interpenetrating polymer network is defined as a combination of two crosslinked polymers such that one at least of them is synthesized and crosslinked in the immediate presence of another[1]. An IPNs can be distinguished from other in these ways: (i) in presence of solvent an IPN swells but does not dissolve (ii) creep and flow are suppressed as a result of mutual incompatibility. The term IPN introduced for the first time by Millar[2] in 1960s who studied polystyrene network. Satish Patil *et al.* [3] investigated fluoranthene and fluoranthene based fluorescent based chemosensors for the detection of NACs. A Singh *et al.* [4] reported synthesis and characterization of IPN of polyglycidyl methacrylate and acrylamide. Through these polymer networks chemically compatible desired phase morphology achieved. Sun *et al.* [5] described side chain liquid crystalline ionomer containing sulphonic acid groups with polymethyl hydrosiloxane (PMHS).

Lee and coworkers [6] made their investigation on the activity of PMHS as functional material from microfluidic chips. Firisch[7] described properties of latex IPNs and important properties such as mechanical properties and swelling properties, Vlad *et al.* prepared IPN with an immiscible component[8] Patel and coworkers[9] suggested review on hydrogel nanoparticles in drug delivery. Through these polymer networks chemically compatible desired

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phase morphology can be achieved [10]. Many of these IPNs have interesting and useful properties because of the high chain stability, low surface energy, high thermal stability and low T_g of the polysiloxane chain [11]. IPN system offer great promise for the future in view of increasing number of applications of the IPNs materials [12-13]. Now a day's polymer based composites are in demand as microwave absorber and instead of conventional metal based [14-15] materials. Nevertheless, the highly hydrophobic character of a PDMS chain has limited its use in some fields [16-17], furthermore, Banerjee *et al.* [18] synthesized an IPN based on microspherical formulation consisting of sodium polyvinyl alcohol and Alginate by emulsion crosslinking method using glutaraldehyde as crosslinking agent. Sofia *et al.* [19] synthesized polythiophene fullerene hybrid additives as potential compatibilizers of BHJ active layers. Biofabrication of IPN hydrogels was done by Sri Kumar and coworkers [20]. Meet and coworkers [21] studied electromagnetic behaviour of semi-IPN of fullerene based polyacrylonitrile and polyaniline. Literature discussed above indicates that enormous work has been carried on IPN. Use of PHMS as a polymer in synthesis of IPN is still scarce. The aim of the work is to develop a novel network system possessing inherent thermal and morphological characteristics.

Experimental Procedure

Materials:-

Purified solvents, divinyl benzene, washed acrylonitrile, polymethylhydrosiloxane were used as received. Benzoyl peroxide was recrystallized in methanol.

Synthesis of IPN

A series of 13 IPNs were synthesized by systematic variation of concentration of PMHS (Table-I), acrylonitrile (Table-II) using BPO (Table-III) as initiator and DVB (Table-IV) as crosslinking agent in toluene as solvent. The system is kept on water bath for 2.5 hours at 65°C under an inert atmosphere of nitrogen. The IPNs formed were precipitated in methanol and dried to constant weight.

Characterization Of Ipn

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

Spectroscopic technique analysis

Infrared (FT-IR) spectroscopic studies:

The IR spectrum of formed IPN was recorded Perkin Elmer spectrum version 10-03-06 instrument using KBr pellet.

SEM Morphology:

The morphology of the IPNs has been studied by the scanning electron microscopy (SEM) which has a resolution 50 Å and depth of field 30 μm. The sample were mounted on a SEM stub by graphite adhesive paste and coated with gold in a SEM coating unit. The samples were then scanned in JEOL JSM 840 Å scanning electron microscope (SEM).

Fluorescent characterization:-

The fluorescence emission spectrum of pre swollen polymer network was recorded on spectrofluorimeter (Fluorolog 3, Model FL 3-22).

Thermal Analysis

Thermal properties were examined using a Simultaneous DSC/TGA STAR^o system Mettler Toledo. The temperature range covered was 25°C – 1000°C and scanning rate 10°C under nitrogen atmosphere. The sample weight was 11.8220 mg.

Calculation of percentage extractable materials

The solute or uncrosslinked component of IPN was removed with the help of soxhlet extractor using dimethyl sulphoxide (DMSO) as a solvent, otherwise no reproducible result was obtained. The percentage extractable material was calculated using the following equation.

$$\% \text{ Extractable material} = \left(\frac{W_b - W_a}{W_a} \right) \times 100 \quad (1)$$

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

Swelling measurements

The swelling data was calculated by soaking the sample in different polar and nonpolar solvents such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), benzene or toluene until an equilibrium weight was achieved (~ 24 hrs.). Weight measurements were made by blotting the samples and immediately weighing them. The solvent was then removed by heating the samples to 65°C under vacuum, until an equilibrium weight was achieved. The weight of the swollen film in each solvent was recorded at different time. The swollen percentage is calculated according to the following relationship [22].

$$\% \text{ Swelling} = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (2)$$

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

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[23].

$$\frac{1}{M_c} = - \frac{\left(\ln(1 - V_p) + V_p + X_{12} V_p^2 \right)}{\rho V_1 (V_p^{1/3} - V_p/2)}$$

Where, M_c = average molecular weight of network between crosslinks, ρ = 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 [24].

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

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.

Results And Discussion

FTIR:

The presences of functional groups in the prepared IPN samples were evaluated via FTIR spectra as shown in the (fig.1). FTIR study for pure PMHS shows peak at 2167 cm^{-1} and 2966 cm^{-1} corresponding to Si-H and C-H groups of respectively and Si-H bending vibration at 924 cm^{-1} , for PAN it shows at 2224 cm^{-1} (CN), 2944 cm^{-1} (aliphatic -CH) group vibrations, 1450 cm^{-1} (-CH₂ vibration) and 1380 (aliphatic -CH₃). While the FTIR analysis for polymer network (Fig.1) indicate that the broad absorption band at 3430 cm^{-1} is described for the existence of -NH group. The bond at 1555 cm^{-1} is ascribed to stretching flexural vibrations of N-H groups and Si-H bending at 894 cm^{-1} . For PAN shows peaks at 2168 cm^{-1} (vibrational characteristics of -CN), 2967 cm^{-1} (assigned to aliphatic -CH group vibrations), 1451 cm^{-1} (CH₂ vibrations) and 1409 cm^{-1} (-CH₃ vibrations). The vinyl bonds at 1680 cm^{-1} did not appear in spectra indicating that all monomeric groups are involved in polymerization reaction.

Fluorescent Characterization:-

Fluorescence emission spectra of polymeric network (Fig.2) reveals fluorescent excitation and emission spectra of the synthesized IPN. The fluorescent excitation and emission spectra of IPN depict that the polymeric network exhibit analogous excitation and emission. The emission spectra reveal a broad peak centered at about 457 nm, owing to $n \rightarrow \pi^*$ electronic transition found in polymeric network. Emission spectra generated by radioactive decay of excitations exhibit a maximal peak at 457 nm, suggesting that the synthesized IPN are typically high intensity blue light emitting materials.

Morphology-

SEM is an excellent tool for the examination of surface morphology of the microstructure of novel vinyl based IPN of PMHS and PAN which indicate that dual phase morphology of the synthesized IPN (Fig.3). The network structure is diversified which indicates sample heterogeneity of solution used for film separation. This is clearly distinguished in the microscopic images. The surface of sample composed of PMHS and PAN is not smooth, some protrusions of different size are observed. Dual phase morphology of different regions is observed in IPN film which is due to the presence of both components.

Thermal properties:-

The DSC Thermogram (Fig.4) of IPN reveals glass transition temperature (T_g) at 400°C which is higher than T_g of PAN and T_g of PMHS. This might be caused a high crosslink density in these samples. The crosslinking usually strongly depresses the chain mobility. It is an evidence of restricted chain mobility. As suggested above, PAN macromolecules are entangled or even covalently bonded to crosslink PMHS (result of interpenetration) owing to the presence of nitrogen in –CN group, PAN chains can participate in hydrogen bonding and act as a flexible crosslinks. As shown in (Fig.5) the TGA graph of IPN sample containing PMHS and PAN is stable upto 350°C. Rapid decomposition is observed at 457°C – 490°C almost complete volatilisation of IPN occurred around 600°C.

Effect of Composition

The study of effect of composition of copolymer results in the increased swelling with increase in concentration of copolymer. This indicated that the presence of copolymer restricted crosslinking of polyacrylonitrile. This restriction is due to overall decrease in concentration of acrylonitrile. Furthermore, it is believed that PMHS must be crosslinked to polyacrylonitrile. As the concentration of the copolymer increases the probability of grafting by acrylonitrile must have also enhanced which resulted is crosslinking between the two polymers. A similar explanation is given for the percentage swelling and M_c which is the inverse function of concentration of acrylonitrile (Table-II).

Effect of Initiator (BPO):-

The data depicts that swelling and M_c increase with increasing molar concentration of BPO. Table-III shows that the effect of concentration of benzoylperoxide on swelling and M_c of IPN.

Effect of Crosslinker (DVB):-

Table-IV indicates that as the concentration of crosslinker DVB increase, 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 enhance the crosslinking in the polymeric network and hence depress the chain mobility. This ultimately increases the glass transition temperature. The swelling behavior could be envisaged from Table-V which represents the effect of various solvent on swelling of IPN. The variation in percentage of extractible material is shown in Table I-IV. A detailed study is performed over the effect of composition of different solvents on the different chemical and physical properties of IPNs.

Conclusion:-

Spectral analysis of IPN containing PMHS and PAN shows ideal polymer network formation between polymethylhydrosiloxane and acrylonitrile monomeric unit. The DSC thermogram revealed higher T_g for IPN as compared to the homopolymer PMHS. This is due to the higher crosslink density and restricted chain mobility of the units. The IPN exhibit characteristics dual phase morphology indicating crosslinking between the two components. M_c is the direct function of (copolymer), (initiator) where as inverse function of monomer and crosslinker.

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Table I:-Effect of variation PMHS on IPN properties.

Sample	PMHS mol l ⁻¹	Yield	Swelling (%) in DMF	M_c in DMF
IPN 1	0.053	350	56	168
IPN 2	0.079	480	73	182
IPN 3	0.106	750	80	190
IPN 4	0.132	900	86	198

Table II:-Effect of (acrylonitrile) on IPN properties

Sample	Acrylonitrile (mol l ⁻¹)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 5	2.28	1.240	65	166
IPN 6	3.05	1.170	55	162
IPN 7	3.82	1.000	42	158
IPN 8	4.58	0.950	28	155

Table III:-Effect of (BPO) on IPN properties.

Sample	BPO (x 10 ⁻² mol l ⁻¹)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 1	0.412	350	56	168
IPN 9	0.619	850	62	181
IPN 10	0.825	1.560	68	189
IPN 11	1.030	3.150	72	198

Table IV:-Effect of variation of DVB on IPN properties.

Sample	DVB (mol l ⁻¹)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 1	0.70	350	56	168
IPN 12	1.05	550	50	162
IPN 13	1.40	1.680	42	155
IPN 14	1.75	2.130	33	139

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

Sample Used	% Swelling in DMF	In solvents		Toluene	% Extractable material
		Benzene	DMSO		
IPN 1	56	25	48	35	15.2
IPN 2	73	35	58	42	12.6
IPN 3	80	43	65	54	13.5
IPN 4	86	48	75	65	28.0
IPN 5	65	24	32	28	12.3
IPN 6	55	22	38	25	9.4
IPN 7	42	28	47	40	14.3
IPN 8	28	26	38	32	20.5
IPN 9	62	38	57	46	35.3
IPN 10	68	19	40	32	23.0
IPN 11	72	21	35	30	13.6
IPN 12	50	32	45	38	11.3

IPN 13	42	17	36	31	9.1
IPN 14	33	15	25	20	10.5

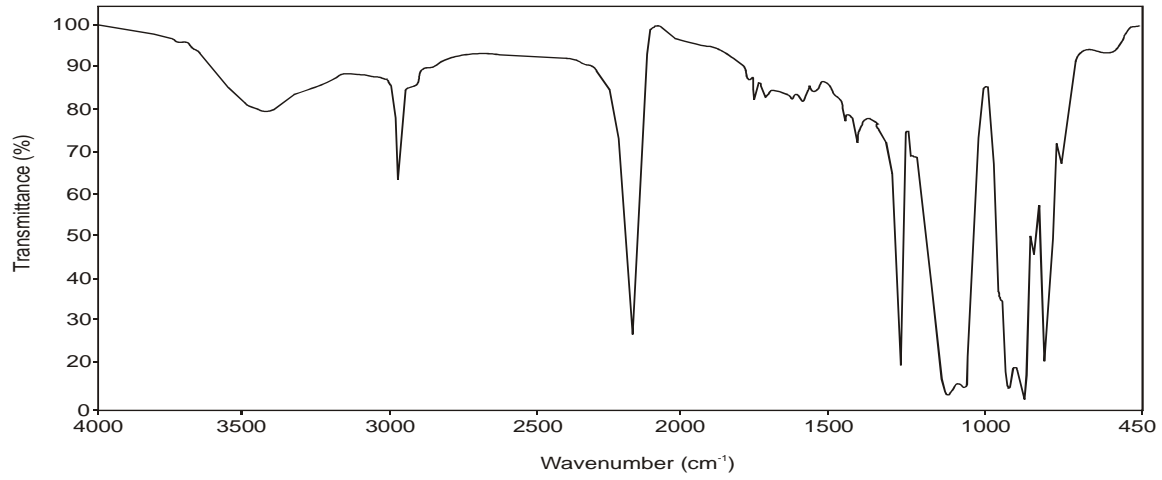


Fig. 1 : IR spectrum of IPN

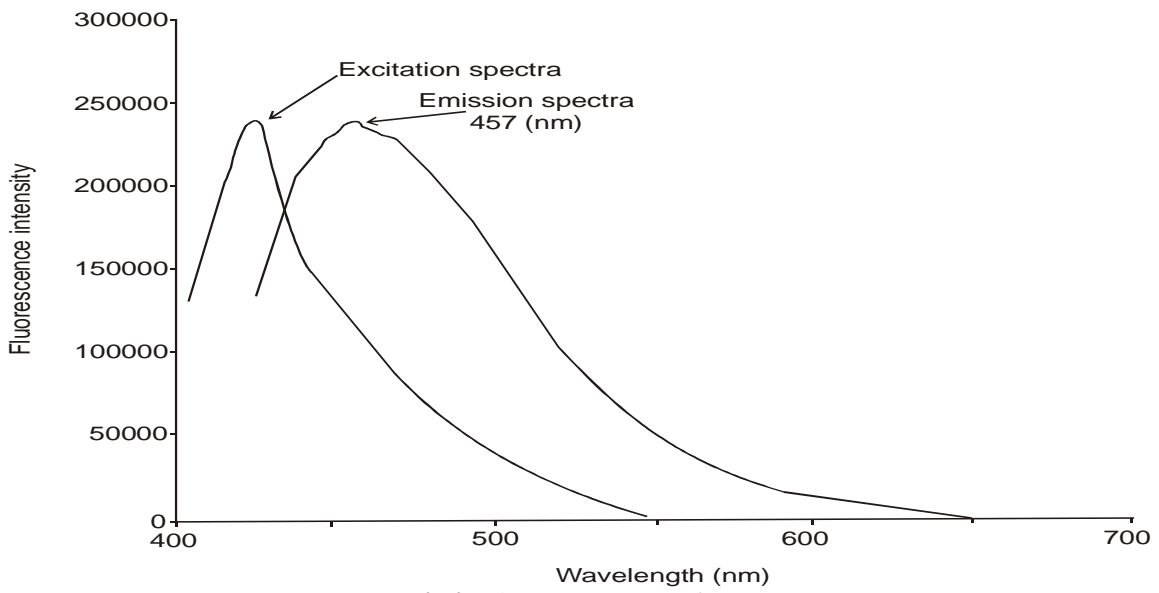


Fig 2:-Fluorescent curve of IPN

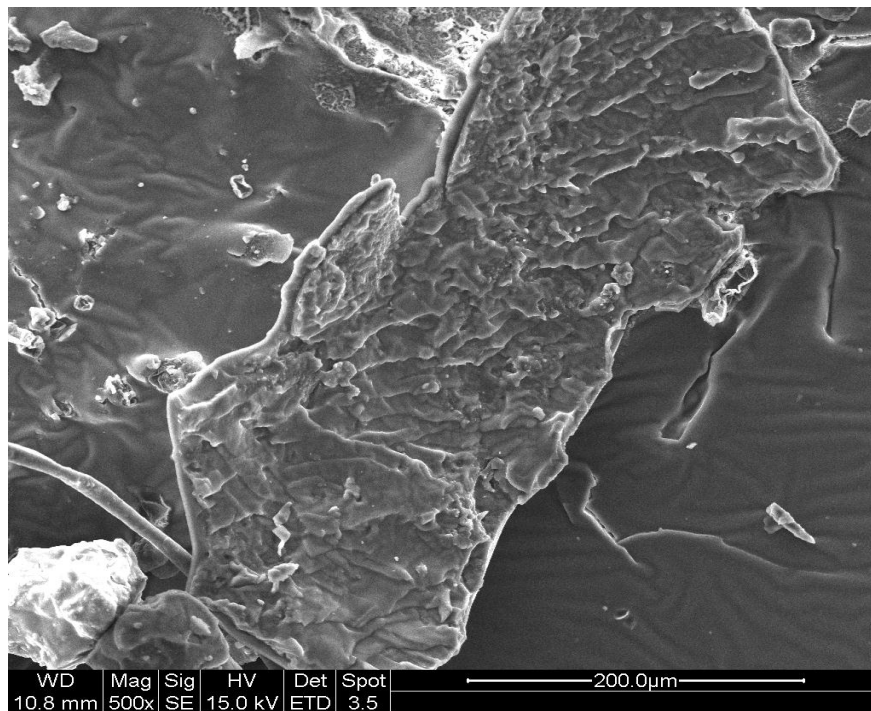
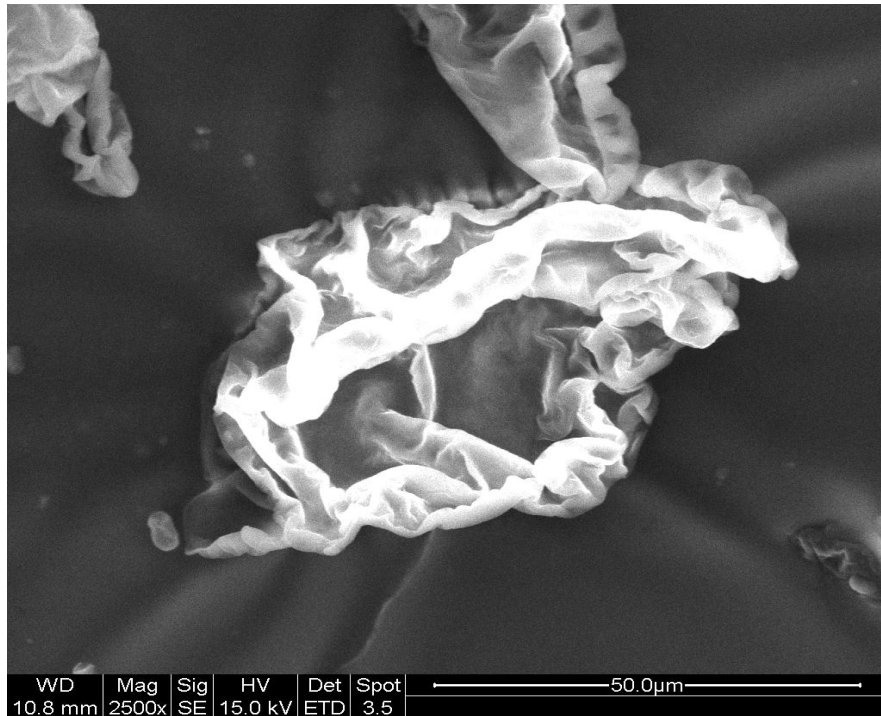


Fig. 3 : SEM photographs of IPN

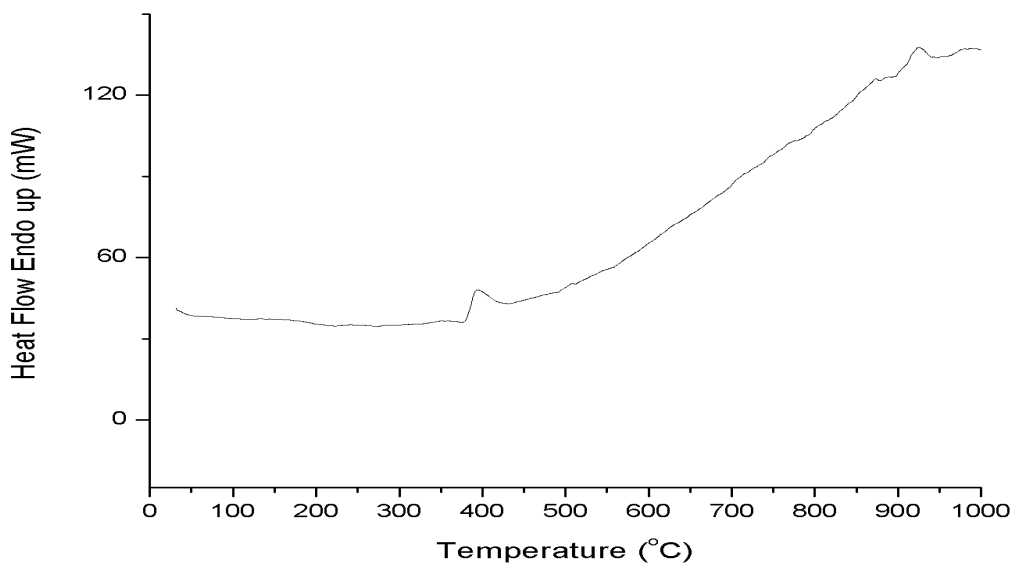


Fig 4:-DSC curve of IPN

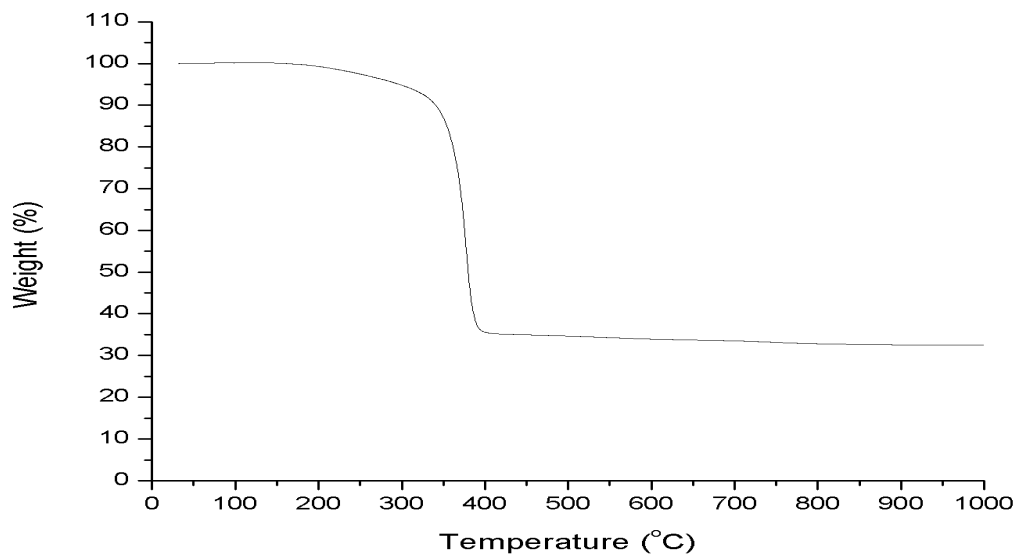


Fig 5:-TGA curve of IPN

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