



RESEARCH ARTICLE

Synthesis and characterization of interpenetrating polymer network of Fullerene based poly(acrylonitrile) and poly(α -methyl styrene).

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Abstract

A new series of fullerene based interpenetrating polymer network of poly(acrylonitrile) and poly(α -methyl styrene) is synthesized. The polymer network is characterized using infrared ¹³C NMR spectroscopy, differential scanning calorimetry, thermo gravimetric analysis, conductivity analysis and transmission electron microscopic techniques. Infrared spectral analysis of polymeric sample showing characteristic peaks for fullerene at 1445 cm⁻¹, 549 cm⁻¹ and 1600 cm⁻¹, for poly(acrylonitrile) at 2000 cm⁻¹, 1382 cm⁻¹ and 2928 cm⁻¹ and for poly(α -methyl styrene) at 3055 cm⁻¹, 1495 cm⁻¹, 2981 cm⁻¹ and 698 cm⁻¹. The peaks recorded for ¹³C NMR spectra shows the peaks for fullerene at 136 ppm, for polyacrylonitrile at 116 ppm, 32 ppm and 28 ppm and for poly(α -methyl styrene) at 128 ppm, 62 ppm, 40 ppm and 25 ppm. The glass transition temperature value obtained from differential scanning calorimetry is found to be 130°C. The initial thermal decomposition of polymer network was studied by thermo gravimetric analysis which is found to 342°C. The conductivity record reveals the semiconductor character of polymer network. Transmission electron microscopic examination reveals the dual phase morphology in the synthesized polymer network.

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INTRODUCTION

The spectacular development of polymer chemistry during the last few decades has led to the strengthening of its theoretical basis and at the same time creation of a new research field. Over few decades polymer blends showed superior performances over the conventional polymers. To overcome the poor performance of conventional polymer, a new class of polymers "Interpenetrating polymer network (IPN)" came in existence. An IPN is defined as a blend of two or more polymers in a network with at least one of the systems synthesized in the presence of another [1]. The two or more network can be envisioned to be entangled in such a way that they are concatenated and cannot be pulled apart. IPN is different from polymer blends in a way that it swells but does not dissolve in solvents [2]. IPNs constitute a rapidly developing branch of polymer blend technology which may intimately combine the properties of two cross-linked polymers in a network form. Researchers focused the desirable properties and applications differently at different time. The conclusions reported by them are in consideration of stepwise enhancement of IPN properties. Millar [3] was the first to synthesized IPN of polystyrene, Sperling et al [4]. analyzed different sequential IPNs, Frisch [5] studied properties of latex IPNs and important properties such as swelling mechanical properties of IPN was carried out by Chatterji [6], Zahao X [7] studied synthesis of elastomer and gel from IPN, Reis et al. [8] reported synthesis of hydrogels from glycidyl methacrylate, Buist and coworkers [9,10] reported the synthesis and application IPN of polyurethane containing isocyanate group. The characterization of

thermoplastic IPN prepared by melting and pressing of crystallisable polyurethane and styrene/acrylic acid random copolymer was carried by Pisis[11] et al. Thereafter for electrochemical synthesis of IPN following the electro polymerization of pyrrole was given by Gangopadhyay[12]. Buford et al[13]., used real time small angle neutron scattering technique to study the formation of IPN. Further study of terpene based IPN was carried out by Varshney Prajapati[14]. Furthermore Banerjee et al., developed an IPN based on micro spherical formulation consisting of sodium alginate and polyvinyl alcohol by the emulsion crosslinking method using glutaraldehyde as cross-linking agent [15], Kulkarni et al., developed an IPN hydrogel membranes consisting of sodium alginate and polyvinyl alcohol by solvent casting method for transdermal delivery of prazosin hydrochloride, an antihypertensive drug through skin [16]. Vlad et al., synthesized IPN with an immiscible components [17], some studies on the use of castor oil as a component in PU with IPN's have been published by Lu and Zang [18]. Gong and coworkers [19] worked out on the synthesis of IPN hydrogels using two polymers of distinctly two different chain lengths. Through these polymer networks chemically compatible desired phase morphology can be achieved [20]. IPN have found important applications in diverse technologies, including organic solar cells [21], Drug delivery [22], tissue engineering [23], polymer actuators [24] and energy harvesters [25]. Many of these mechanical properties depend on IPN for example, the IPN network with dielectric elastomer developed by Patel et al.[24], can achieve over 300% voltage-induced strain without prestretched, while the actuation strain of unprestretched common elastomer is less than 40% [26]. IPN offers the possibility of combining in network from which otherwise it is not possible to synthesize polymer with opposite properties [27] etc.

The literature discussed above reveals that enormous work has been carried on IPN but fullerene based IPN using novel vinyl monomers is still scarce. Thus the present study reveals data on fullerene based polyacrylonitrile and poly(α -methylstyrene) with interpenetrating polymer systems. The aim of the work is to develop concatenated system based on these novel vinyl monomers explaining various physicochemical and thermal phenomena of IPN [31].

EXPERIMENTAL PROCEDURE

Solvents, fullerene, washed acrylonitrile, washed α -methyl styrene and divinyl Benzene were used as received. Benzoyl peroxide was recrystallized from chloroform.

Synthesis of fullerene based Polyacrylonitrile (PAN)

The polymer samples were prepared by refluxing a suspension of acrylonitrile (Sigma Aldrich) and fullerene in toluene. The system was kept on water bath for 2.5 hours at 70 °C. The polymer was precipitated in methanol and dried to constant weight.

Synthesis of IPN

A series of IPN were synthesized via in situ polymerization by systematic variations of concentration of fullerene based PAN, α methyl styrene, divinylbenzene and Benzoyl peroxide in toluene for 3 hours at 60°C under an inert atmosphere of nitrogen. The IPN obtained were vacuum dried to constant weight.

CHARACTERIZATION OF IPN

The synthesized IPN was characterized using the spectroscopic techniques, thermal analysis techniques and transmission electron microscopic techniques

Spectroscopic technique analysis

- 1) **Infrared (IR) spectroscopic studies:** The IR spectrum of formed IPN was recorded on vertex 70 (Bruker) instrument using KBr pellet.
- 2) **^{13}C NMR Spectroscopy:** ^{13}C Nuclear magnetic resonance (NMR) spectral analysis of fullerene based IPN of poly(acrylonitrile) and poly(α -methyl styrene) sample was carried in an ECX 500-JEOL NMR spectrometer using CDCl_3 as a solvent.

Thermal Analysis

Differential scanning calorimetry (DSC) was carried out on a V2.2 Dupont calorimeter, under nitrogen atmosphere at a heating rate of 10°C/min. The sample weight was 3-5 mg.

Thermo gravimetric analysis (TGA)

TGA was carried on TGA V% V5 1A 2100, under nitrogen atmosphere at a heating rate of 10°C/min.

Transmission electron microscopy morphology (TEM)

The morphology of the IPN network was studied by TEM with a resolution of 100nm. Samples were prepared by dispersing the powder in ethanol to form a dilute suspension from which an aliquot was taken and deposited on a copper-graphite mesh grid. The sintered products were surface polished on a double jet electro polisher for TEM, the electro polishing was conducted at 230K using an electrolyte of 25% HNO_3 and 75% CH_3OH . The magnification and

electron diffraction patterns were calibrated in the TEM using a gold replica and standard procedures were followed. The samples were then scanned in a 200 kV JEOL JEM 2000 EX transmission electron microscope.

Calculation of percentage extractable materials

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

$$\% \text{ Extractable material} = [(W_b - W_a) / W_a] \times 100 \quad (1)$$

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

Swelling measurements

The cross-linked density in polymer network is usually calculated by solvent absorbency (swelling) measurements. The swelling data was calculated by soaking the sample in different polar and nonpolar solvents such as dimethylformamide (DMF), dimethyl sulphoxide (DMSO), dioxane, 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 60°C under vacuum, until an equilibrium weight was achieved. The percentage swelling was calculated according to the following relationship. [28]

$$\% \text{ Swelling} = [(W_s - W_d) / W_d] \times 100 \quad (2)$$

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

Crosslink density

IPN sample was taken and its cross-link density was determined by using the swelling data of IPN in DMF by using Flory-Rehner equation [29].

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

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 [30].

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

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.

Electrical conductivity

The conductivity measurements were taken in vacuum 10^{-5} torr by mounting the sample in specially designed sample holder. The sample holding has two parts. The upper part consists of two electrodes and an evaporation port. The samples were mounted between the jaws of two electrodes having a spring arrangement. A calibrated copper constant thermocouple was mounted very near to the sample. The resistance was measured using Keithley electrometer (model 614).

RESULTS AND DISCUSSIONS

The structural IR analysis of polymer network is studied by IR spectroscopic technique. We have determined the detailed vibrational analysis of IPN. FTIR study for pure fullerene shows peaks 1430 cm^{-1} , 527 cm^{-1} (for C-C vibration mode) and 1600 cm^{-1} (for $\text{C}=\text{C}$ mode). For PAN it shows at 2224 cm^{-1} ($\text{C}\equiv\text{N}$), 2944 cm^{-1} (aliphatic $\text{C}-\text{H}$ group vibrations), 1450 cm^{-1} ($\text{C}-\text{H}_2$ vibrations) and 1380 (aliphatic $\text{C}-\text{CH}_3$) and for the poly(α -methyl styrene), it reveals peaks at 3000 cm^{-1} (stretching vibrations), 1490 cm^{-1} ($\text{C}-\text{C}$ vibrations), 3010 cm^{-1} ($\text{C}-\text{H}$ stretching vibrations), 699 cm^{-1} (benzene ring $\text{C}=\text{C}$ bending) and 1444 cm^{-1} for bending vibrations of $\text{C}-\text{H}$ bond of $\text{C}-\text{H}_3$ group. While the IR analysis for polymer network (**fig. 1**) reveals the presence of fullerene at 549 cm^{-1} (for caged vibrations), 1600 cm^{-1} (for $\text{C}=\text{C}$ mode), for PAN it shows peaks at 2000 cm^{-1} (vibrational characteristics of $\text{C}\equiv\text{N}$), 2928 cm^{-1} (assigned to aliphatic $\text{C}-\text{H}$ group vibrations), 1445 cm^{-1} ($\text{C}-\text{H}_2$ vibrations) and 1382 cm^{-1} ($\text{C}-\text{H}_3$ vibrations) and for poly(α -methyl styrene) it shows the peaks at 3055 cm^{-1} (stretching), 1495 cm^{-1} ($\text{C}-\text{C}$ vibrations), 2981 cm^{-1} ($\text{C}-\text{H}$) and 698 cm^{-1} (benzene ring $\text{C}=\text{C}$ out of plane bending). The ^{13}C NMR spectra for pure fullerene (C_{60}) is recorded at 138 ppm and for PAN it is found to be at 120 ppm ($\text{C}\equiv\text{N}$), 33 ppm (chain carbon $\text{C}-\text{H}_2$) and 28 ppm (chain carbon $\text{C}-\text{H}$) and for poly(α -methyl styrene) it shows peaks at 128 ppm (aromatic carbon), 63 ppm ($\text{C}-\text{H}_2$), 44 ppm ($>\text{C}<$) and 25 ppm ($\text{C}-\text{H}_3$) respectively. While the ^{13}C NMR spectra for IPN (**fig. 2**) reveals peak for fullerene (C_{60}) at 136 ppm, for PAN at 116 ppm ($\text{C}\equiv\text{N}$), 33 ppm ($\text{C}-\text{H}_2$), 28 ppm ($>\text{C}-\text{H}$) and for PAMS at 128 ppm (aromatic carbon), 62 ppm ($\text{C}-\text{H}_2$), 40 ppm ($>\text{C}<$) and 25 ppm ($\text{C}-\text{H}_3$). From the observed data we find there is a shift in the peak values of fullerene, PAN and poly(α -methyl styrene), thereby showing incorporation of the polymer formed on the fullerene surface, which increases the solubility and processability of polymer network. Conductivity analysis of IPN was performed which was found to be $1.3281 \times 10^{-6} \Omega^{-1}\text{m}^{-1}$ at frequency range 20-50 Hz, which reveals the semiconductor character of IPN. The results of swelling in various solvents employing (DMF) are summarized in table 1. The variation in percentage of extractable material is shown in table 2,3,4,5 and 6. A detailed study is

performed over the effect of composition of different chemicals on the different physical and chemical properties of IPN. The relative study is discussed below.

Effect of composition

The effect of the composition of fullerene, PAN and poly(α -methyl styrene) follows a logical trend, since an increase PAN base for poly(α -methyl styrene) results in increased swelling and M_c (Table 1). This implies that the presence of PAN restricts crosslinking of poly(α -methyl styrene). Furthermore, in solution interpenetrating polymerization, it is believed that PAN becomes cross-linked to poly (α -methyl styrene). As the concentration of PAN increases the probability of interpenetration of poly(α -methyl styrene) also increases. The crystallinity of polymer network is directly proportional to the concentration increase of poly(α -methyl styrene). Thus higher amount of poly(α -methyl styrene) usually enhances polymer crystallinity and hence the higher glass transition value of IPN is obtained. On other hand according to the data obtained from table 5, the increase in concentration of PAN favors the flexibility of the IPN, but this also causes some decrease of glass transition temperature of IPN. It leads to a higher degree of crosslinking between PAN phases. A similar explanation can be given for the fact that the percentage swelling and M_c are inversely proportional to the concentration of poly(α -methyl styrene) (Table 4).

Effect of cross-linker (DVB)

The increase in concentration of DVB increases the percentage of extractable material (Table 6). The reason is that an increase of concentration of DVB increases the crosslinking between the two polymeric networks, which results in decreased swelling and decreased M_c . It is interesting to note that concentration increase in divinyl benzene enhances the crosslinking in the polymer network, and hence depresses the chain mobility. This ultimately increases the glass transition temperature.

Effect of initiator (BPO)

Table 2 presents the effect of concentration benzoyl peroxide on swelling and M_c of IPNs. It is clear that both swelling and M_c increases with increasing molar concentration of BPO.

Thermal properties

The DSC thermo gram of IPN contains crystallization peaks (**fig. 4**) at (T_g) at 130 °C, which is higher than T_g of PAN (120 °C) and lower than T_g of poly(α -methyl styrene) (173 °C). It can be caused by high crosslinking density in these samples - the crosslinking usually strongly depresses the chain mobility. In the composition of fullerene and PAN with poly(α -methyl styrene), an increase of T_g by about 10-20°C is observed. It is an evidence of restricted chain mobility. As suggested above, PAN macromolecules are entangled or even covalently bonded to crosslink poly(α -methyl styrene) (result of interpenetration). Owing to the presence of nitrogen in -CN group, PAN chains can participate in hydrogen bonding and act as 'flexible crosslinks'. **Figure 3** shows the TGA graph of IPN with initial thermal decomposition at 342°C.

Morphology

The microstructure of fullerene based interpenetrating polymer network of PAN and poly (α -methyl styrene) was observed by means of transmission electron microscopy (TEM) which reveals dual phase morphology of the synthesized IPN (**fig. 5**). 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 in the microscopic images. The surface of sample composed of fullerene, PAN and poly (α -methyl styrene) is not smooth, some protrusions of different sizes are observed. It indicates that under top layer heterogeneous domains (connected to crystallization and phase separation) were formed. In the studied IPN films, small inclusions and the regions of different morphology are observed.

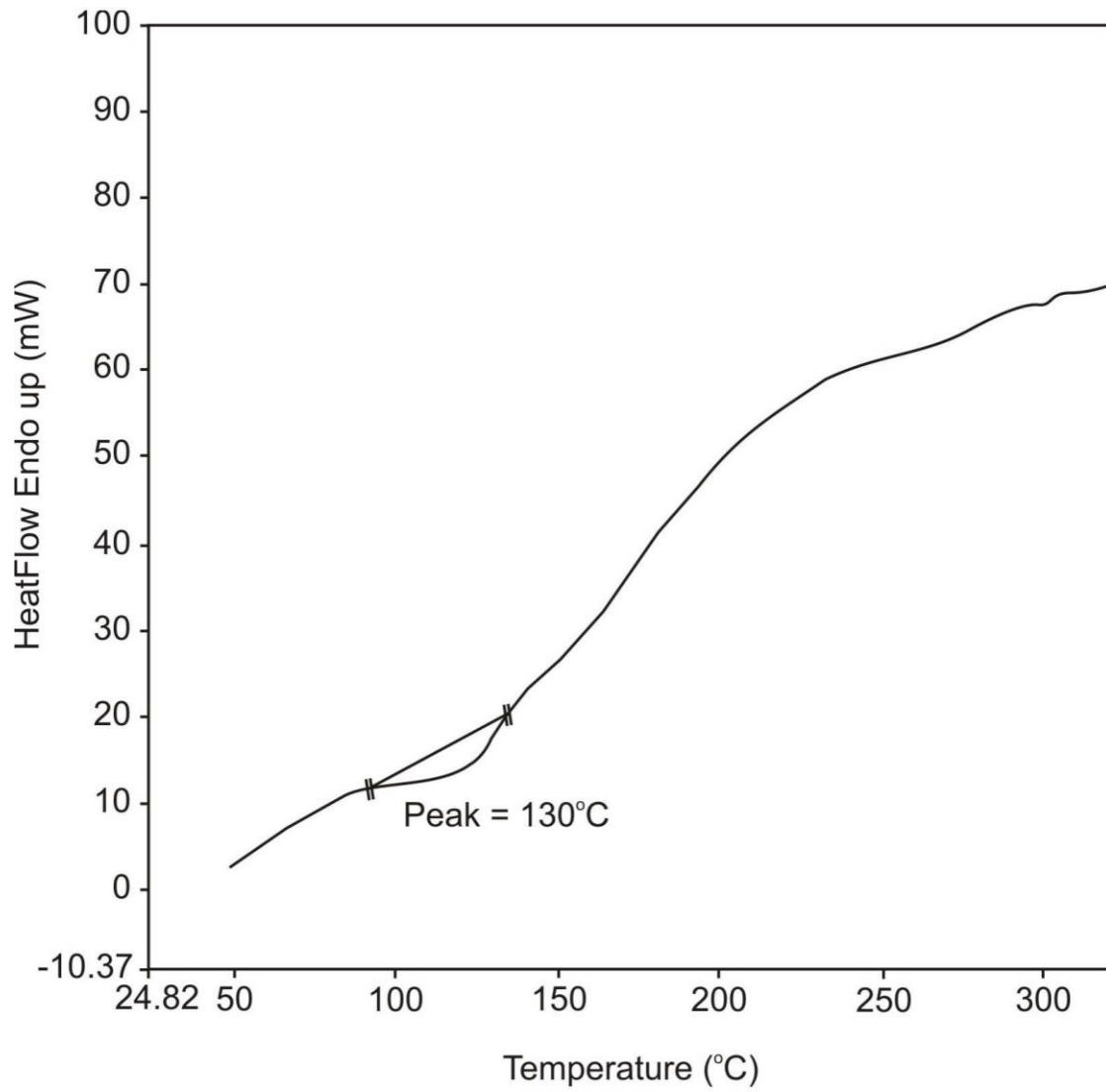
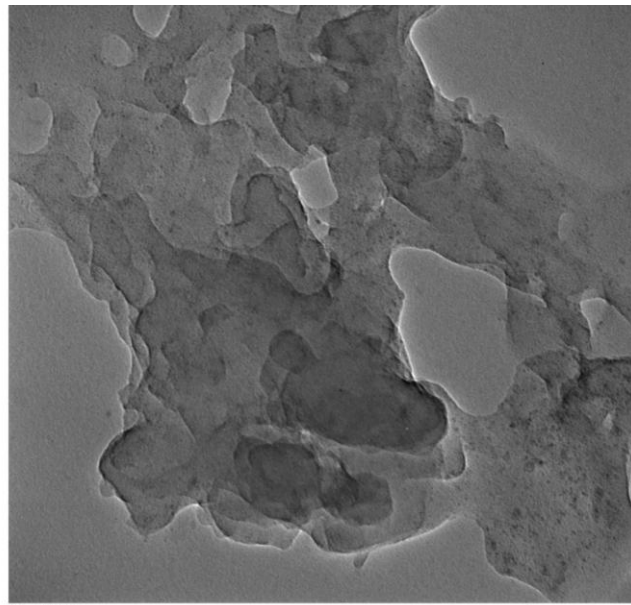


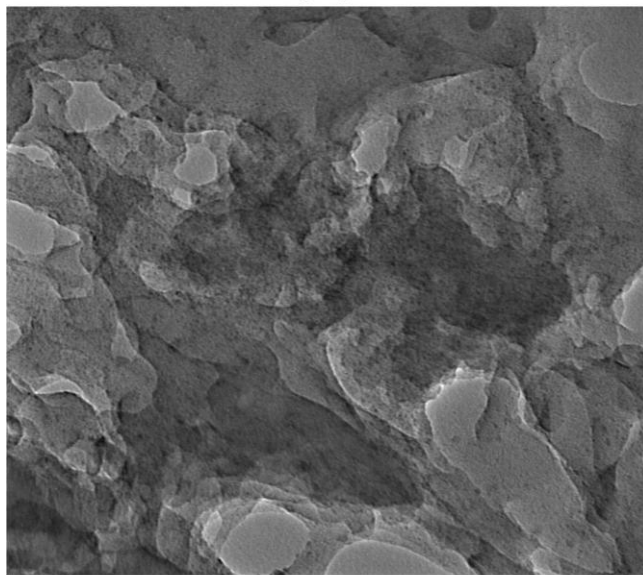
Fig. 4: DSC Thermogram of IPN 6



Altaf_004
A
Print Mag: 319000x @ 7.0 in
3:13:32 p 03/02/15

100 nm
HV=200.0kV
Direct Mag: 40000x
USIF-AMU

(a)



Altaf_009
A
Print Mag: 399000x @ 7.0 in
3:18:23 p 03/02/15

100 nm
HV=200.0kV
Direct Mag: 50000x
USIF-AMU

(b)

Fig. 5: TEM Photographs of IPN 6

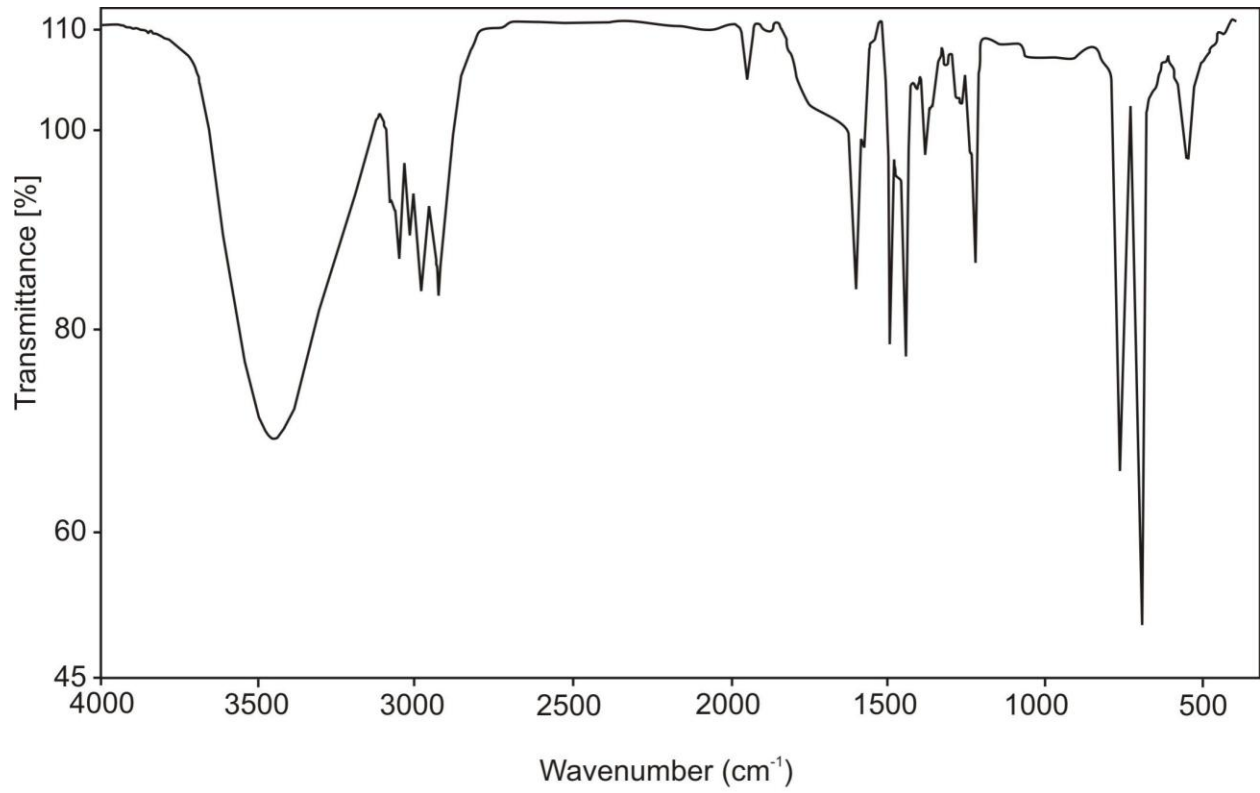


Fig. 1: IR spectra of IPN 6

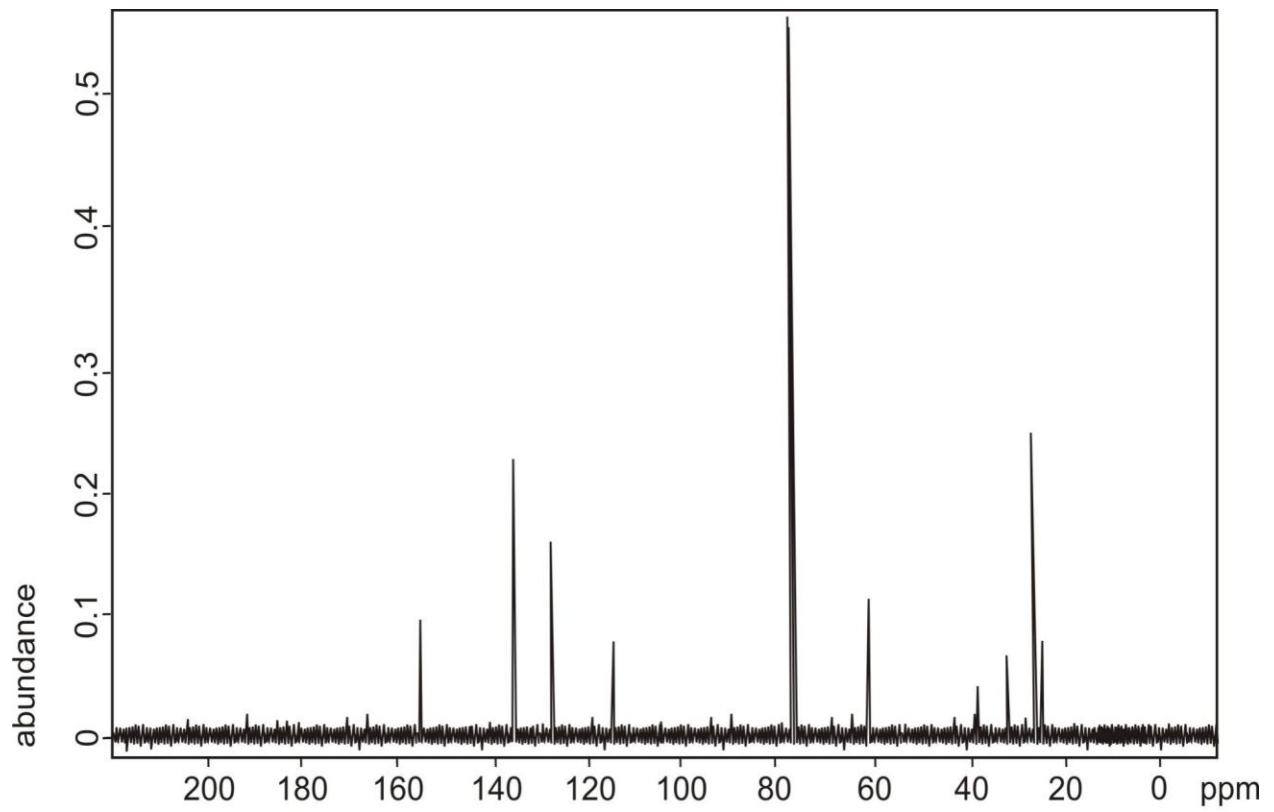


Fig. 2: ^{13}C -NMR spectra of IPN 6

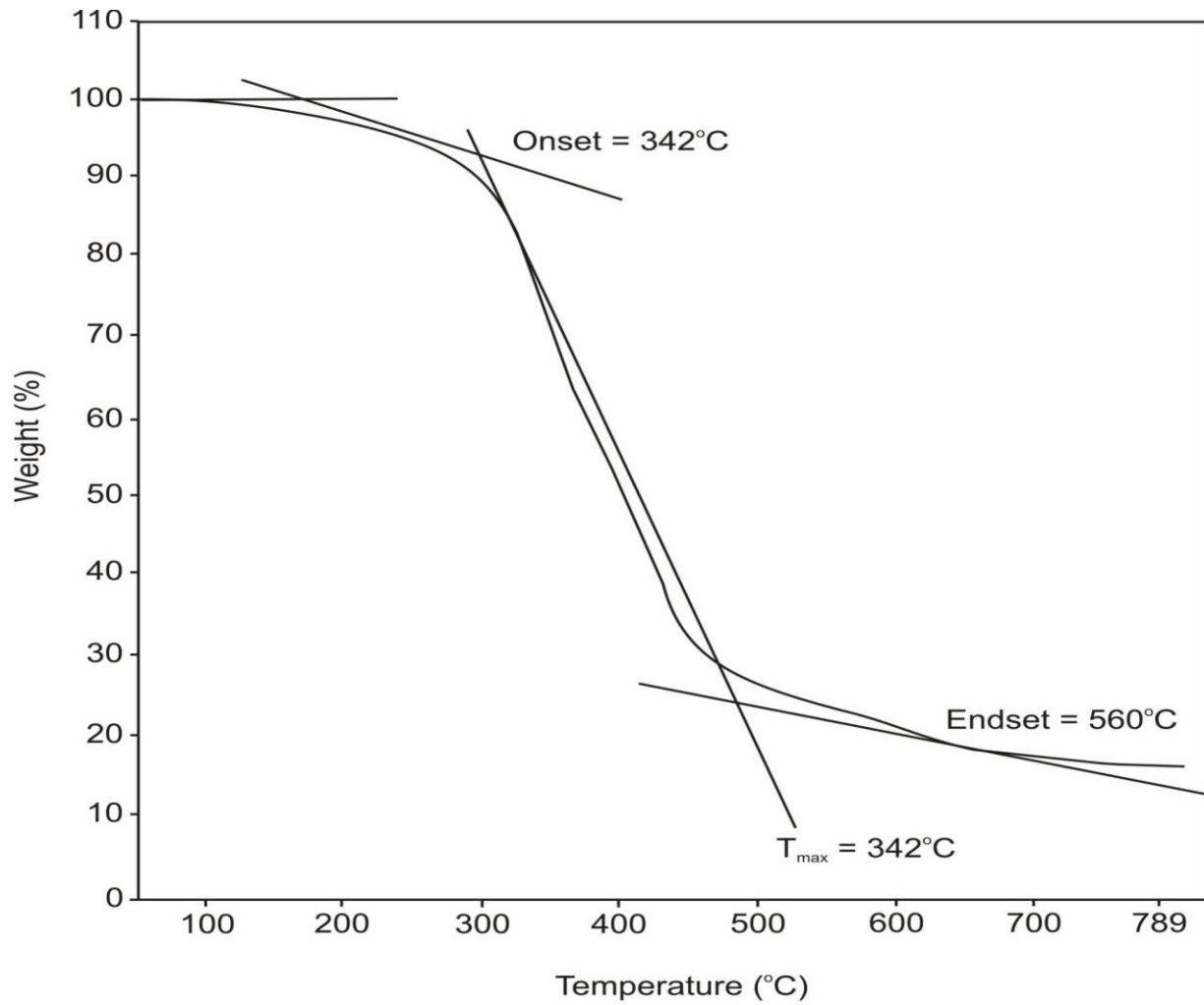
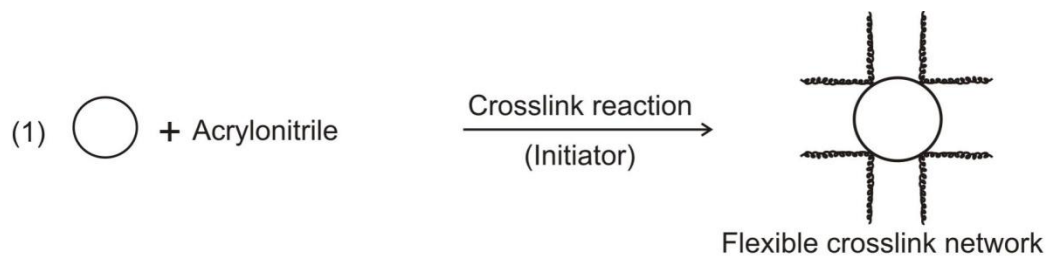
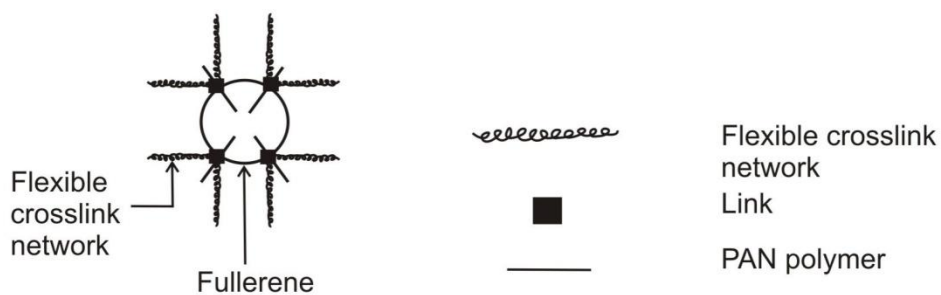


Fig. 3: TGA Thermogram of IPN 6



(2) In situ polymerization of α -methyl styrene (formation of IPN) over Fullerene-PAN base.



Scheme 1: Synthesis of IPN based on Fullerene (Containing α -methyl styrene and acrylonitrile as monomer)

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

Sample	% Swelling in DMF	In solvents		Toluene	% Extractable material
		Benzene	DMSO		
IPN 1	53	16	44	17	11.2

IPN 2	46	23	37	24	11.6
IPN 3	49	27	38	31	31.7
IPN 4	80	52	74	57	18.1
IPN 5	83	37	75	59	19.0
IPN 6	79	39	68	45	11.9
IPN 7	67	29	57	37	9.4
IPN 8	77	39	57	39	15.4
IPN 9	81	38	64	53	21.5
IPN 10	35	20	21	29	9.2
IPN 11	47	19	31	29	27.1
IPN 12	45	24	39	31	10.6
IPN 13	44	14	34	21	21.1
IPN 14	33	19	17	19	21.0
IPN 15	62	18	45	33	17.1
IPN 16	46	24	30	29	31.5
IPN 17	73	45	57	50	22.3

Table 2: Effect of BPO on IPN properties.

Sample	BPO mol/100 ml	Swelling (%) in DMF	M _c in DMF
IPN 1	0.39	8.19	166
IPN 2	0.78	13.90	149
IPN 3	1.08	10.17	159
IPN 4	1.56	14.11	189

Table 3: Effect of Fullerene on IPN properties.

Sample	Fullerene (mol / 100 ml)	Yield	Swelling (%) in DMF	M _c in DMF
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IPN 5	0.39	7.01	41	151
IPN 6	0.78	3.33	51	167
IPN 1	1.08	7.87	53	162
IPN 7	1.56	10.11	73	175

Table 4: Effect of poly(α -methyl styrene) on IPN properties.

Sample	PAMS (mol / 100 ml)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 5	0.39	7.01	41	151
IPN 6	0.78	3.33	51	167
IPN 1	1.08	7.87	53	162
IPN 7	1.56	10.11	73	175

Table 5: Effect of PAN on IPN properties.

Sample	PAN (mol / 100 ml)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 10	0.1	3.95	72	189
IPN 11	0.2	4.58	59	171
IPN 1	0.2	9.01	64	173
IPN 12	0.3	10.05	34	148

Table 6: Effect of DVB on IPN properties.

Sample	DVB (mol / 100 ml)	Yield	Swelling (%) in DMF	M _c in DMF
IPN 14	0.5	3.1	55	171
IPN 1	1.6	9.12	61	174
IPN 15	1.0	5.98	38	162
IPN 16	1.5	9.11	28	146

CONCLUSIONS

Spectral analysis of IPN of fullerene containing PAN and poly(α -methyl styrene) shows ideal polymer network formation between acrylonitrile and α -methyl styrene monomers and complete incorporation of the polymer formed on the fullerene surface. The DSC thermogram showed higher T_g for IPN as compared to the homo-polymer PAN, this is due to the higher crosslink density and restricted chain mobility. IPN microstructure calculations indicate higher acrylonitrile content along with α -methyl styrene monomer units. The compatible IPN systems resulted in higher density values and a restrained swelling behavior compared to their homo-polymers. This results from high levels of interpenetration and molecular mixing, leading to a reduced free volume and more compact network structure.

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REFERENCE

1. Sperling, L. H. and Hu, R. "Interpenetrating polymer networks," in polymer blends Handbook, L. A. Utracki, Ed., pp. 417-447, Springer, Dordrecht, The Netherlands, 2003.
2. Kudela, V., Kroschwitz, I. Hydrogels. *Encyclopedia of Polymer Science and Engineering*. J. Ed., pp. 783-807, (1987).
3. Millar J.R., 1960. *J. Chem. Soc.*, 311.
4. Sperling, H. IPN and related materials (ed, Sperling, H.) (*plenum*, New York, NY, USA, 1981).
5. Frisch, C., Klempner, D., Mukharjee, K. and Frisch, L. Stress-strain properties and thermal resistance of polyurethane-polyepoxide interpenetrating polymer network. *Appl. polym. sci. J.* **18**, 689-698 (1974).
6. Chatterjee, R. Gelatin with hydrophilic/hydrophobic grafts and glutaraldehyde crosslinks. *Appl. polym. Sci. J.* **37**, 2203 (1989).
7. Zhao X (2012) A theory for large deformation and damage of interpenetrating polymer networks. *J Mech Phys Solids* 60:319-332
8. Reis AV, Cavalcanti OA, RUIRA AF, Muniz EC (2003) synthesis and characterization of hydrogels formed from a glycidyl methacrylate derivative of galactomannan. *Int J Pharma* 267:13-25
9. Buist JM, Gudgeon H. *Advances in polyurethane technology*. London: Elsevier, 1970.
10. Hepburn C. *Polyurethane handbook*, 2nd ed. New York: : Elsevier, 1992.
11. Pissis, P., Vatalis, S., Delides, G., Georgoussis, G., Kyritis, A., Grigorieva, P., Sergeeva, M., Brovko, A., Zimich, N., Shtomptel, I. and Neagu, E. Characterization of thermoplastic interpenetrating polymer networks by various thermal analysis techniques. *Therm. Acta. J.* **371**, 87-93 (2001).
12. Gangopadhyay, R. and De, A. An electrochemically synthesized conducting Semi-IPN from polypyrrole and poly (N-vinyl alcohol). *Mater Chem. J.* **12**, 3591-3598 (2002).
13. Buford, P., Markotis, G and Knott B. Real time SANS Study of interpenetrating polymer network formation. *phys. J.* 385-386, 766-769 (2006).
14. Varshney, A. and Prajapati, K. Terpene based semi -interpenetrating polymer network initiator by p-nitrobenzyltriphenylphosphonium Ylide Synthesis and characterization. *Des monom. Poly. J.* **9**, 453-476 (2006).
15. Banerjee S, Ray S, Maiti S, et al. Interpenetrating polymer network (IPN) a novel biomaterial. *Int J Appl Pharmac* 2010, 2. 28-34.
16. Kurkarni RV, Sreedhar V, Mutalik S, Setty CM, Sa B. Interpenetrating polymer network hydrogel membranes of sodium alginate and poly(vinyl alcohol) for controlled release of prazosin hydrochloride through skin. *Int J Biol Macromol* 2010; 47: 520-7.
17. Vlad, S., A Vlad and S. Opera, " Interpenetrating polymer networks based on polyurethane and polysiloxane," *European Polymer Journal*, **38**, 829-835 (2002).
18. Zang, L., J. Zhou, J. Hunang, P. Gong, Q. Zhou, L. Zheng and Y. Du, "Biodegradability of regenerated cellulose films coated with polyurethane/natural polymers interpenetrating polymer networks," *Ind. Eng. Chem. Res.*, **38**, 4284-4289 (1999).

- 19 Gong, J.P., Katsuyama, Y., Kurokawa , T., Osada, Y., 2003. Double-network hydrogels with extremely high mechanical strength. *Adv. Mater.* **15**, 1155-1158.
- 20 Hsieh, T., Hsieh, P. and Simon, C. Interpenetrating polymer networks of 2-hydroxyethyl methacrylate terminated polyurethanes and polyurethanes. *Polymer. J.* **40**, 3153-3163 (1999).
- 21 Das, K. and Lenka, S. *Appl. polym. Sci. J.* **75**, 1487-1492 (2000).
- 22 Greco, R., Iavarone, M., Fiedlerova, A. and Borsig, E. *Macromol.Sci.pure. J.* **A37**, 433- 446. (2000).
23. Banerjee, S., Ray, S. and Maiti, S. et al. Interpenetrating polymer networks (IPN) a novel biomaterial. *ApplPharmac. Int J.* **2**, 28-34 (2010).
- 24 Patel, B., Patel,L., Shah, H. and Modasiya, K. Review on hydrogel nanoparticles in drug delivery. *Pharma. J.* **1**, 19-38 (2011).
- 25 Kim, S., Jeong, I., Kim, H., Lee, H. and Kim, H. Albumin release from biodegradable hydrogels composed of dextran and poly(Ethylene glycol) macromere. *Arch Pharm Res. J.* **24**, 69-73 (2001).
- 26 Hamidi, M., Azadi, A. and Rafeui, P.Hydrogel nanoparticles in drug delivery. *Adv Drug Deliv Rev.* **60**, 1638-1649 (2008).
- 27 Zang, L., Jeong, Y., Jang, S.andSuh, H. Kim Biocompatible and pH-sensitive hydrogels with degradable phosphoester and phosphoamide linkers end-capped with amine for controlled drug delivery. *Polym Chem.* **4**, 1084-1094 (2013).
- 28 Chatterjee, P. *Appld. Polym. Sci. J.* **37**, 2203 (1989).
- 29 Pinner, S. A practical course in polymer chemistry. Pergamon press Inc. Tarrytown, N.Y. (1961).
- 30 Collins, E. Experiments of polymer Science. *Jon Wiley and sons. J. Inc.*, N.Y (1973).
- Purushothaman, M., Santhana, P. and Nayak, S. Studies hydrophilicity and thermal stability of Poly(isoalkyl lactase methacrylate). *Journal of macromolecular science, Part A. J.* **52**, 202-209 (2015).