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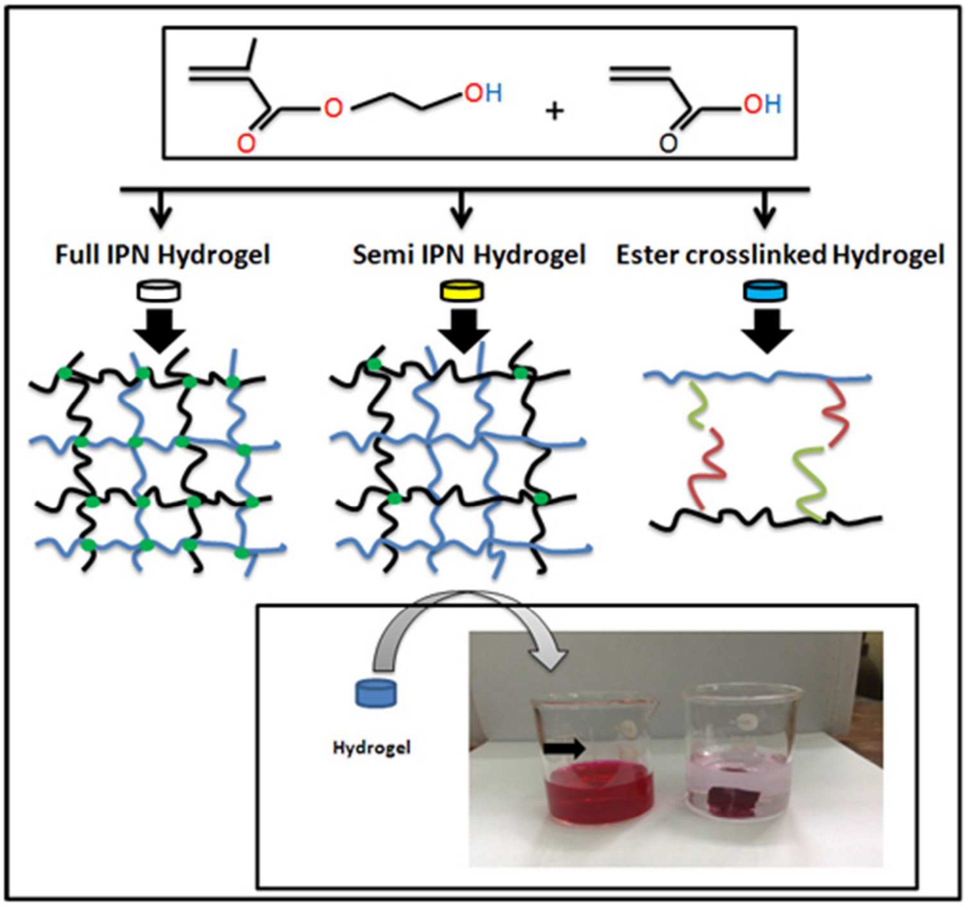
Three different methods have been developed to crosslink the poly(acrylic acid - 2-hydroxyethyl methacrylate) to form the hydrogels having tunable swelling, rheological and morphological properties with applicability in dye and heavy metal removal.



Synthesis and characterization of Acrylic acid - 2-Hydroxyethyl methacrylate IPN hydrogels

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Abstract

Interpenetrating polymer networks (both full and semi) and ester crosslinked hydrogels have been synthesized from acrylic acid and 2-hydroxyethyl methacrylate by using various monomer feed composition. No crosslinker have been used in case of ester crosslinked gel, instead the neighboring polymer chains are crosslinked by esterification reaction, which is established by FTIR and ^{13}C NMR spectroscopy. Swelling of the hydrogels has been found to be strongly dependent on the pH, temperature and ionic strength of the medium. The rheological properties of the hydrogels are found to be dependent on the mode of crosslinking and composition of the gel (only in case of ester crosslinked gel) as well. The flexibility of the gel is also dependent on the method of preparation of the hydrogel. Rheological study in normal force sweep mode reveals the high shape and size regain ability of the gel. The cryo SEM images show the porous structure of the gels. The hydrogels especially ester crosslinked gels have been found quite effective in separation of cationic dyes and heavy metal ions (copper and iron) from their corresponding aqueous solutions.

Keywords: IPN; hydrogel; dye removal; SEM; rheology.

1. Introduction

Hydrogels are special kind of soft polymeric materials having three-dimensional crosslinked networks that can absorb large quantities of water or aqueous solutions without dissolving in it [1]. There are some polymers that can change their structure and eventually their properties in response to physical or chemical changes in the environment, such as pH [2], temperature [3-4], ionic strength, electric field [5], magnetic field [6] etc. They are known as intelligent or smart polymers. Environment responsive hydrogel gains enormous interest in the biomedical fields [7, 8], organic dye and heavy metal ion separation [9-13] etc. Recently IPN hydrogels have gained popularity due to its ability to combine multicomponent polymer materials without any phase separation, structural rigidity and improved mechanical properties [14].

Interpenetrating polymer network (IPN) is a blend of two or more polymers in a network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the others. In case of IPN (full and semi) hydrogels, due to presence of interlocking structures between the polymers, they have more improved mechanical properties, excellent weather and creep resistance. The rate or the extent of release or the adsorption can be controlled by monitoring the extent of interpenetration and degree of crosslinking in the IPN system [15-17].

Both the full and semi IPN hydrogels are prepared by simultaneous and sequential technique of IPN preparation. In case of full IPN, by simultaneous method the monomers and the crosslinker (either one common for all monomers or different for different monomer) are polymerized and crosslinked all at a time [18-20]. In case of semi IPN formation by simultaneous method, a single crosslinker (which has no possibility of any interaction with the second polymer) is used for a particular monomer and polymerized simultaneously with the other monomer such that the first polymer gets crosslinked and intermingled with the other linear polymer [21-23]. But in case of sequential method, full IPN hydrogels are prepared by two step process. One of the monomers is polymerized and crosslinked in one step and then the crosslinked polymer I is soaked in solution of the other monomer along with its own crosslinker and initiator followed by its polymerization [24-25]. Semi IPN hydrogels are prepared by sequential method in the similar way as that of the full IPN synthesis except using no crosslinker in the second step of polymerization [26]. Semi IPN I is the one in which monomer I is polymerized and crosslinked while the polymer II remain linear. In the semi IPN II the reverse is true i.e. polymer I is linear and polymer II is crosslinked.

Poly(2-hydroxyethyl methacrylate) has some desirable properties such as its strength, durability, nontoxicity and favorable tissue compatibility [27-28]. The presence of hydrophilic hydroxyl and carbonyl groups in the same molecule makes the polymer water compatible. On the other hand, mechanical strength of the polymer is derived from its hydrophobic backbone part [29]. Sometimes poly HEMA has been used to enhance the mechanical strength of other mechanically weak gels [30]. But the main drawback associated with the poly HEMA is its low swelling ability. Many researches are being carried out to increase the hydrogel characteristics (mostly the swelling), as well as imparting the stimuli responsive character into the poly HEMA gel [31-33]. Semi and full IPN hydrogels of HEMA and acrylic acid were prepared in the matrix of PVA by Mandal et al [34].

Literature survey so far conducted reveals very few reports on the semi and full IPNs of only neat HEMA and acrylic acid. Most of the articles investigated so far, deal with the acrylic acid-HEMA copolymer [35] or their IPN with a third polymer [34,36-37].

The present work focuses chiefly on the crosslinking of both poly AAc and poly HEMA for full IPN and only poly AAc for semi IPN. In addition to these two types of novel blends, a third and an unique method of blending has been followed where simultaneous polymerization of AAc and HEMA and crosslinking of the two polymer networks, through covalent crosslink (inter molecular) formation by means of esterification reaction between the –COOH group of AAc and –OH group of HEMA has been carried out. The properties of all these three types of hydrogels (semi IPN of poly AAc/poly HEMA; full IPN of poly AAc/poly HEMA and inter crosslinked poly AAc/poly HEMA) have been investigated in terms of swelling efficiencies, morphology, rheology and applicability in organic dye and heavy metal ion separation and compared thoroughly. For all practical purposes such types of studies have been found to be very rare.

In brief, the objective of the present work is to synthesize mechanically flexible, smart polymeric hydrogels with reasonably good flow characteristic and investigate its effective properties of dye and heavy metal ion separation from aqueous solution.

2. Experimental

2.1. Materials

2-hydroxyethyl methacrylate (Loba Chemie), acrylic acid (Merck, Darmstadt, Germany), ethyleneglycol dimethacrylate (EGDMA) (Aldrich), ammonium persulfate (APS) (Merck) and sodium bisulphite (SBS) (Merck) were used as received. *N,N′*-methylenebisacrylamide (MBA) (Loba Chemie) was used without further purification. Methane sulphonic acid (MSA) was purchased from Sigma Aldrich. Buffer capsules were used as supplied by Merck. Distilled water was used for synthesizing hydrogels as well as for swelling.

2.2. Method of hydrogel preparation

2.2.1. Full IPN hydrogel

Measured amounts of HEMA and acrylic acid are taken in a conical flask with measured amount of water. Aqueous solution of EGDMA as crosslinker of both the polymers formed in situ and APS, SBS as redox initiator are sequentially added to the said conical flask containing the monomers under nitrogen atmosphere. Then the reactant solution was kept at room temperature (25°C) for 8 hours. The molar proportions of the individual reactant are given in table 1. The polymer gel formed in each is taken out from the test tube, washed well by water several times and cut into pieces. The pieces are further subjected to washing by keeping it immersed first in water and then in methanol for 7 days with the routine change of the solvent twice a day. The prepared hydrogel samples were dried by keeping in the oven at the temperature of 45-50°C and at certain time intervals the samples were weighed. The process was continued till the constant weight was reached. The gel samples are denoted by FAH2, FAH6 and FAH10 respectively.

2.2.2. Semi IPN hydrogel

Crosslinked poly acrylic acid is first prepared by following the above said procedure. Then the aqueous solution of HEMA and the initiators are absorbed in the previously synthesized polyacrylic acid gel. MBA is taken as crosslinker in place of EGDMA. MBA crosslink the poly acrylic acid but the poly HEMA remains uncrosslinked. The gel samples are denoted by SAH2, SAH6 and SAH10.

Table 1: Composition of the reactant used in hydrogel synthesis

Hydro gel	Acrylic acid		HEMA		MBA		EGDMA		APS		SBS		MSA
	mol %	mol	mol %	mol	mol %	mol	mol %	mol	mol %	mol	mol %	mol	ml
FAH2	98	0.49	2	0.01	-	-	0.1	0.0005	1	0.005	1	0.005	-
FAH6	94	0.47	6	0.03	-	-	0.1	0.0005	1	0.005	1	0.005	-
FAH10	90	0.45	10	0.05	-	-	0.1	0.0005	1	0.005	1	0.005	-
SAH2	98	0.49	2	0.01	0.1	0.00049	-	-	1	0.005	1	0.005	-
SAH6	94	0.47	6	0.03	0.1	0.00049	-	-	1	0.005	1	0.005	-
SAH10	90	0.45	10	0.05	0.1	0.00049	-	-	1	0.005	1	0.005	-
AHE2	98	0.49	2	0.01	-	-	-	-	1	0.005	1	0.005	0.5
AHE6	94	0.47	6	0.03	-	-	-	-	1	0.005	1	0.005	0.5
AHE10	90	0.45	10	0.05	-	-	-	-	1	0.005	1	0.005	0.5

2.2.3. Chemical blending/grafting and interwinding through condensation reaction

HEMA and acrylic acid are esterified using MSA as catalyst under N_2 atmosphere in sealed container for 7 days at 25 ºC. After that the hydrogel formed is taken out, washed using the same procedure applied for the full IPN. Thus, the gel is prepared without the use of any crosslinker but only through esterification reaction between the constituents. The gel samples are denoted by AHE2, AHE6 and AHE10.

2.2.4. For ^{13}C NMR spectroscopy, poly (Mac-HEMA) was prepared by polymerization of the monomer mixture without using any crosslinker.

For dye removal study, crosslinked poly acrylic acid and crosslinked poly HEMA were prepared by using *N,N′*-methylenebisacrylamide (MBA) as crosslinker.

2.3. Characterization

2.3.1. Spectroscopic analysis

2.3.1.1. FTIR study

FT IR measurements of the dried gels have been carried out in ATR mode by using FTIR spectrophotometer (Perkin Elmer, Japan) in the range of 4000–600 cm^{-1}.

2.3.1.2. ^{13}C NMR study

Solid state ^{13}C NMR studies have been carried out in JEOL RESONANCE, USA at the field strength of 400 MHz in order to prove the ester formation through intermolecular condensation between AAc and HEMA. The other experimental parameters are as follows: contact time: 3.5 ms, scans: 1420, X_Resolution: 34.3618 Hz, Relaxation delay: 5 s.

2.3.2. Swelling study

Dried hydrogel samples are allowed to swell in distilled water at different temperatures and in buffer solutions of different pH. The swollen gels are taken out at certain time intervals, wiped on its surface with tissue paper and then weighed and the process is repeated until the constant weight is reached. Swelling percentage (%) is measured from the following equation:

Swelling percentage = $\frac{We-Wd}{Wd} X 100\%$ … … … … … … … … … … … … …(1)

Where W_e is the weight of the swollen gel and W_d is the weight of the dry gel.

2.3.3. Morphological study

The scanning electron micrographs of the hydrogel samples in swollen condition are taken by using cryogenic SEM apparatus, CARL ZEISS EVO18, Special edition, Germany. Before up-taking the images, the samples are cryo fractured at -187°C followed by platinum coating with coating time of 2 minutes in argon atmosphere at -150° to -160°C temperature. Pore size distribution is analyzed using the software “Smart SEM V-05.04.05.00”.

2.3.4. Rheological study

In order to investigate the mechanical stiffness of the hydrogel, the rheological measurements of the cylindrical hydrogel samples are performed by frequency, stress and normal force sweep test in Anton Paar, UK oscillatory rheometer at 25°C with a parallel plate geometry (plate diameter= 25 mm, gap= 10 mm) from 100 to 0.1 rad/s frequency, 0.1 to 1000 Pa stress and 0 to 5 N normal force respectively.

2.3.5. Applicability test of the hydrogel

2.3.5.1. Separation of organic dye

To investigate the efficiency in removal of organic dye (methyl violet and fuchsine) from aqueous solution, poly(AAc-HEMA) hydrogels (0.5 gm) are placed in 25 ml aqueous solutions of dye having strength 50 mg/Lt and allowed to reach equilibrium for 7 days at room temperature. After that period the concentration of the dye remaining in the solution is determined spectrometrically by using UV spectrophotometer Parkin Elmer USA Lambda 25. Aqueous solution of methyl violet and fuchsine shows the maximum absorption peak at about 585 and 549 nm respectively. The equilibrium concentration of dye molecules are determined from the calibration curve obtained with the solutions of known concentrations of the dye.

2.3.5.2. Separation of heavy metal ions

Efficiency of the poly(AAc-HEMA) hydrogels in separating heavy metal ions is determined by keeping 0.5 gm of the gel immersed in 25 ml of standard metal ion solution (0.1 moles/Lt) for 7 days. Then the concentration of the metal ions remaining in the solution is determined conductometrically from a previously experimented conductance versus metal ion concentration calibration curve. Images are captured using canon powershot A3500.

3. Results and discussion

3.1. Spectroscopic study

3.1.1. FT IR study

Fourier transform infrared (FT-IR) spectroscopy in ATR mode has been used to indicate the chemical composition of the different gels under study, any interaction involving the functional groups of HEMA, acrylic acid and their various crosslinkers and shown in Fig 1(a). The characteristics absorption peaks of the monomeric units, HEMA, acrylic acid, EGDMA and MBA, appear at their usual wave numbers in the FTIR spectra of the hydrogel samples. The observed and the reference peaks are given in the table 2, separately for each series of hydrogels.

In case of the full IPN gels (FAH), the C=O peak of ester is found to appear at around 1700 cm^{-1} and that of –COOH group at 1655 cm^{-1} [38]. There is a probability of formation of hydrogen bonding between the C=O group of the ester in HEMA and the H atom of the –COOH group of AAc unit in the ultimate crosslinked structure which might have shifted the C=O peaks to the lower value [39-40]. O-H peak of the carboxylic acid (-COOH) group is observed at 2925 cm^{-1}. The peaks at around 1017 and 1072 cm^{-1} are assumed to be due to C-O bond vibration [40]. Besides there are two consecutive peaks at around 1390 and 1450 cm^{-1} which may be attributed to alkane C-H rocking and bending respectively.

In case of the semi IPN samples (SAH) the peaks for C=O, C-O, O-H and C-H are observed in the similar frequency ranges as that of the FAH hydrogel samples. There is however, an extra peak for N-H bond at 3430 cm^{-1} which arises from MBA used as crosslinker for AAc.

Ester crosslinked hydrogels (AHE) also exhibit the similar spectral pattern as those of the FAH samples. The only difference in the two spectrums with the others (FAH and SAH) is that the peaks at 1017 and 1072 cm^{-1} are more intense and sharp in case of the AHE samples. It can be rationalized by the formation of new ester linkages and the C-O bonds which increases the peak intensity corresponding to the C-O bonds.

Table 2: FT IR peaks of the hydrogel samples

	Functionality	Reference peak (cm^{-1})	Observed peak (cm^{-1})
FAH Samples	C=O of ester	1735-1750	~1700
	C-O	1000-1300 (2 or more bands)	~1017 & ~1072
	O-H of acid	2500-3300	~2930
	O-H of alcohol	3200-3700	~3300
	N-H stretch of amide	3100-3500	-
SAH Samples	C=O of ester	1735-1750	~1700
	C-O	1000-1300 (2 or more bands)	~1017 & ~1072
	O-H of acid	2500-3300	~2930
	O-H of alcohol	3200-3700	~3300
	N-H stretch of amide	3100-3500	~3430
AHE Samples	C=O of ester	1735-1750	~1700
	C-O	1000-1300 (2 or more bands)	~1017 & ~1072 (sharp peak)
	O-H of acid	2500-3300	~2930
	O-H of alcohol	3200-3700	~3300
	N-H stretch of amide	3100-3500	-

3.1.2. ^{13}C NMR study

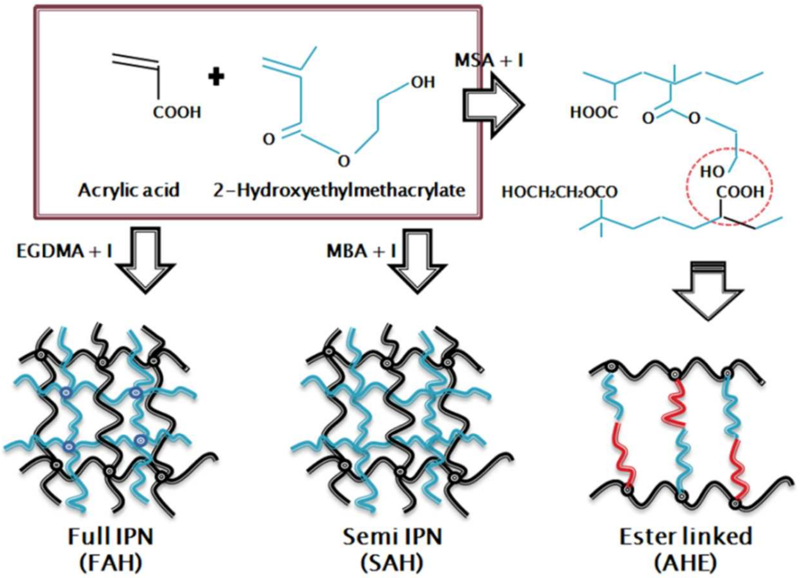
The crosslinking by esterification reaction in case of the ester crosslinked gel (AHE system) was also confirmed by ^{13}C nmr spectroscopy. The investigation was carried out with poly (acrylic acid-HEMA) and one ester crosslinked gel (AHE10). It is apparent from the figure 1(b) that both the spectra contain the similar peaks at around 176, 61, 45, 41, 34 and 19 ppm. The assignment of the peaks is given in figure 1(b) [41].

There is an extra peak in the spectrum of AHE10 sample at 53 ppm. The peak may be attributed to the presence of methylene C in the alkyl-oxygen bond of the ester [41] which is absent in the copolymer system as shown in the figure.

3.2. Swelling study

Variation in swelling of the hydrogels at different temperatures occurs due to phase transition controlled by the hydrophilic-hydrophobic balance of the polymer network. Hydrogels with interpenetrating polymer network structure of poly (acrylic acid) as one of the component and with intra-molecular hydrogen bonding also undergo a phase transition in water. In this case the repulsive ionic interaction due to increased ionization at higher temperature controls the vacant space and thus, governs the transition temperature [42]. Figure 2 (a) shows that the swelling of all present poly (AAc-co-HEMA) IPN gels are temperature dependent. Swelling of the all hydrogel increases with the temperature of the medium. The order of equilibrium swelling values is identical as that in water at room temperature [figure 2(a)].

Scheme 1. Schematic diagram of the reactions occurred during gel formation.



EGDMA: Ethyleneglycoldimethacrylate, MBA: N,N'-methylene bisacrylamide
MSA: Methane sulphonic acid, I: Initiator couple $K_2S_2O_8$+$NaHSO_3$

Since swelling of acrylic acid based hydrogel is strongly influenced by pH of the medium the measurements of swelling efficiency of the hydrogels were carried out in different pH medium. The results were collected in fig. 2 (b). In both the acidic and almost neutral medium the swelling characteristics of the gels follows a decreasing pattern with increase in HEMA content for all the full IPN, semi IPN and ester cross-linked chemical blends. In the basic pH range however the swelling for all the three varieties is much higher. Here also we find in all the cases of FAH, SAH and AHE that the extent of swelling is maximized at the lowest HEMA content under study and gradually decreases with increase in HEMA content. The behavior of the three systems under swelling at higher pH has been attempted to explain with some hypothetical models in the figure 2 (c). At higher pH the carboxylic acid (-COOH) group gets completely ionized to form the carboxylates (-COO-) ions. The ionization creates charged blocks in the polymer segments at pH 9.2. This increases inter-chain repulsion in the inter-wind polymer matrix which may lead to increase in cell dimensions during swelling. But the phenomenon is suppressed for the semi IPN and the ester linked gel as well. In case of semi IPN lateral movement of the cross-linked polymer chain may release the tension created by repulsive interaction of ionized groups. For the ester-linked gel the decrease in concentration of carboxylic acid group lead to complete destruction of strained ionic atmosphere (which is created in case of full IPN). This may explain the observed swelling responses in terms of structural point of view. Decrease in concentration of carboxylic acid group results in decrease in pH sensitivity as well.

To emphasize the effect of HEMA content the equilibrium swelling percentage data were plotted in figure 2(d) against the concentration of HEMA used with the assumption that all the HEMA was consumed during crosslinking reaction. The swelling of all the hydrogels under study is however higher than the bare poly HEMA gel. In case of the full IPN the sharp fall in equilibrium swelling percentage for increase in HEMA content from 2-6% is quite mentionable. With further increase in HEMA content the drop in swelling % occurs slowly. From the statistical analysis as given in table 3 it can be stated that the standard deviation is minimum in case of the semi IPN hydrogel when compared to the same values for the full and ester crosslinked hydrogel. It might be expected that the effect of hydrophobicity remaining the same, it is the number of cells which predominates in the matrix of the full IPN where both the polymeric networks are completely cross-linked and inter-wined, In case of semi IPN however the PHEMA phase being linear and a sequential process of IPN formation being followed it seldom contributes to the cell formation.

In case of gel (AHE) swelling follows decreasing pattern with the increase in HEMA content. As no gel is formed in absence of MSA it may be assumed that crosslinking occurs through the flexible ester linkages to give cellular structure (Scheme 1). The behavior is well explained by the hypothetical models presented in the figure 2(c).

Table 3: Equilibrium swelling values and statistical analysis of the hydrogel samples

Equilibrium swelling (%)				Statistical values			
HEMA Content (mol %)	**FAH**	**SAH**	**AHE**	**Hydrogels**	**Mean (μ)**	**Variance (σ^2)**	**Standard deviation (σ)**
2	177.4	106.1	61.5	**FAH**	97.7333	3375.2288	58.0967
6	75.3	81.6	41.1	**SAH**	87.4333	547.1649	23.3916
10	40.5	74.6	22.6	**AHE**	41.7333	757.2067	27.5174

3.3. Rheological study

Frequency sweep

Figure 3(a) shows the storage moduli of the various gels as functions of angular frequency. All the gels under study exhibit a marginal decrease in G' values as the angular frequency decreases. The two full IPN hydrogels exhibit almost identical pattern with negligible changes in storage moduli over the entire range of frequency. It may thus, possibly be inferred that the elastic modulus of the full IPNs are hardly dependent on PHEMA content. The semi IPNs under consideration also show similar behavior although their storage modulus are somewhat lower than those of the full IPN.

In case of the ester crosslinked hydrogels, G' is strongly dependent on the AAc/HEMA copolymer composition. Increment in the HEMA content (from 2 to 10 mole percent) results in increase in G' substantially. At higher HEMA concentration, the possibility of formation of crosslinking by esterification reaction between the HEMA and the corresponding amount of AAc part increases and so the elastic modulus and stiffness also increases. It supports the assumption of crosslinking by esterification reaction.

It is quite noteworthy that the storage moduli values always remain higher than the loss moduli one. This is the typical characteristics of gel/hydrogel [43].

Yield stress

Low values of yield stress implies higher spreadability but lower retention and the vice versa. There are different methods in determining the yield stress as discussed by Malana et al. [44]. In the present paper storage modulus have been plotted as a function of shear stress in which the point of deflection denotes the yield stress of the gel sample according to the method used by Rajat k. Das et al. [45]. The yield stress values decreases from full IPN samples to semi IPN and further reduces in ester crosslinked hydrogel sample, i.e. the spreadability or the flexibility is maximum in AHE hydrogel sample among the three types of gels studied. Hence it can be said that the hydrogels of different flexibility can be obtained as needed by following the different methods of hydrogel synthesis.

Normal force sweep

In normal force sweep study storage moduli have been measured as function of different normal force in the range 0-5 N in three consecutive cycles and it is plotted as function of time in seconds in figure 4(a). All the three type of gels are found to possess good memory effect, i.e. they have the ability to regain their structure and shape. It is best understood by the figure 4(b) in which G' at zero normal force have been plotted as function of number of cycles. The figure depicts that the ester crosslinked gels have got almost no change in G' in three consecutive cycles but it decreases slowly in case of FAH and SAH samples, which means regain ability is maximum for AHE hydrogels among the three types of hydrogels studied.

Cole-Cole plot

Figure 5(a)-(c) describe the behavior of cole-cole plot for full IPN, semi IPN and ester crosslinked gel respectively. All the polymer systems are prepared from a binary mixture of two different monomer but crosslinked in three different ways. It is the general practice to use cole-cole plot for investigation of the inter phase compatibility of the polymer blends. Wu et al [46], Yeganeh et al [47] and Xu et al [48] pointed out that a homogeneous polymer system results a single semicircular arc where as an immiscible or partially miscible blend results in two consecutive semicircular arcs. However from the observation of Wu et al [46] it can be said that the distinctions between this two arcs disappear with increase in the miscibility or decrease in the phase separation. This may be used for differentiation of IPN and semi IPN system also. It is observed from the figure 5(a) that both the IPN systems show single clear semicircular arc. This clearly emphasizes that no distinct phase separation present between the two polymer system crosslinked with two different crosslinker at the same time. So this can be taken as a direct proof of IPN formation which only may be the reason of such binary polymer system to behave like a homogeneous one.

The semi IPN system [Fig 5(b)] shows a single semicircular arc but skewed to left. Interfacial tension between the crosslinked network of the polymer and the uncrosslinked one may results such deviations. Single arc clearly indicate a single distinct phase structure of the binary polymer system. This intern can be considered as a proof of semi IPN formation in terms of rheology.

The esterification mediated gel AH2E and AH10E results in same type of semicircular single arc cole-cole plot [Fig 5(c)]. This indicates a homogeneous crosslinked network system formed by the crosslinking using esterification reaction. The results show esterification of HEMA and acrylic acid system leads to a homophasic network system.

3.4. Morphological study by Cryo SEM

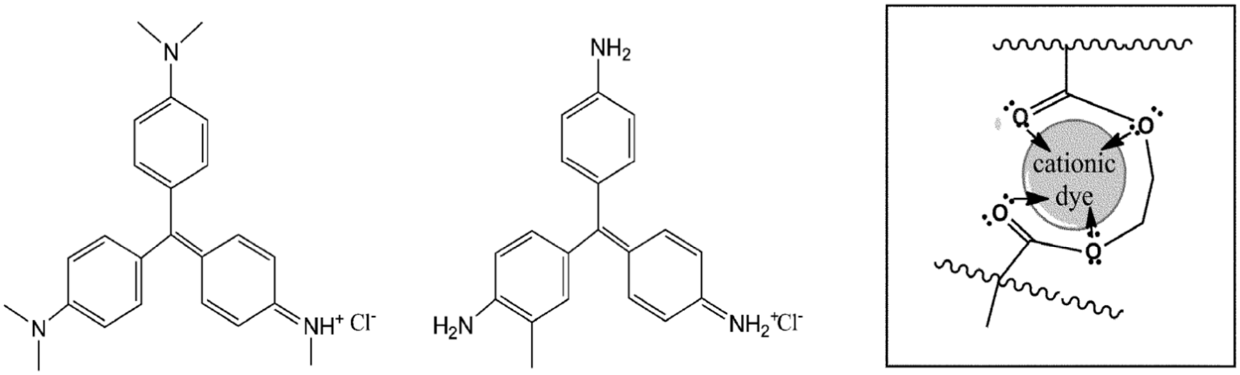
Figure 6(a) and (b) show the cryo SEM images of the hydrogel FAH2 and SAH2 respectively with individual pore size distribution. Both the images contain homogeneously distributed multilayered porous structures. In both the cases the most of the pores are circular and sometimes it is elliptical of different diameter, though the mean pore diameter is greater in case of hydrogel FAH2. Pore size distribution is seemed to be skewed towards larger pore diameter for the full IPN. The larger multi layered pores in FAH sample enables the polymer network to absorb and hold greater volume of water or aqueous solution within it compared to SAH samples which corroborates the results of the swelling experiment (figure 2) discussed earlier. Thus, the gel appears to absorb higher volume of water in its crosslinked structure.

3.5. Applicability test of the gel

3.5.1. Application in dye removal

All the prepared poly (AAc-HEMA) copolymer hydrogels were found to be able to separate dyes from its aqueous solution efficiently [Fig 7(a)-(b)]. However the virgin poly AAc gel can absorb only about 30-40% dye and poly HEMA gel is not at all effective in removal of any dye from its aqueous solution. The percentage of the basic dye (methyl violet and fuchsine) removal of the gel varies from 80-98 % (Table 4). Since all the hydrogels contain ionizable –COOH groups that can easily interact with the cationic groups of the basic dye. Other types of interaction such as hydrogen bonding and hydrophobic interaction may also play the role in holding the dye molecules within the gel network [49]. Hydrogen bonding may occur with the amine N atom of dye and –COOH group of the gel. The hydrophobic aromatic rings of the dye may interact effectively with the hydrophobic part of the HEMA unit (scheme 2). These effects either in combination or in isolation lead to highly efficient removal of dye from the aqueous solution. The efficiency of separation is more prominent in basic medium where almost 99 % dye removal becomes possible with the present hydrogel.

Scheme 2. Structures of the two dye molecules, methyl violet and fuchsine; and Schematic representation of their interaction with the polymer network.



Methyl violet

Fuchsine

Dye absorption by chelation

Table 4: Dye separation valuation of the hydrogels

Hydrogel	Removal (%) in Methyl violet		Removal (%) in Fuchsine	
	Neutral medium	Basic medium	Neutral medium	Basic medium
SAH2	99.2±1.9	99.3±2.0	92.3±1.8	93.3±1.8
SAH6	88.9±1.8	99.9±2.0	93.5±2.1	95.2±2.0
SAH10	80.9±1.6	99.9±2.0	95.3±1.9	95.5±2.0
FAH2	97.8±1.9	99.9±2.0	91.2±1.8	94.2±1.8
FAH6	98.7±2.0	99.8±2.0	93.0±2.0	96.1±2.0
FAH10	98.9±1.8	99.8±1.9	95.2±2.0	97.2±2.0
AHE2	92.1±1.9	99.8±2.0	95.8±2.0	96.8±2.0
AHE6	96.9±2.0	99.8±2.0	93.6±1.9	93.6±1.9
AHE10	96.2±2.0	99.2±1.8	97.8±2.0	96.8±2.0
Poly AAc gel	33.6±2.4	37.2±1.8	30.2±2.3	31.3±2.1
Poly HEMA gel	3.5±0.2	3.2±0.3	2.5±0.8	2.0±0.3

3.5.2. Application in heavy metal ion separation

Hydrogels are used now a day to separate the metal ions as well. In case of poly electrolyte hydrogel the anionic groups form chelate complexes with the metal ions [39]. The poly (AAc-HEMA) gel can separate Cu^{2+} ion from the aqueous solution of $CuSO_4$. The percentage of Cu^{2+} adsorption varies from 68-78 % as shown in figure 7(c)-(d).

The gel also absorb Fe^{3+} ion as well from the aqueous solution of $Fe_2(SO_4)_3$ and the adsorption varies from 36-47 %.

Table 5: Cu^{2+} and Fe^{3+} metal ion removal by the hydrogels

Hydrogel samples	Cu^{2+} Removal (%)	Fe^{3+} Removal (%)
FAH2	74±3.7	38±1.9
SAH2	74.2±3.71	47±2.35
AH2E	79±3.95	36±1.8

4. Conclusion

Full IPN, semi IPN and ester crosslinked gels of poly (AAc-HEMA) copolymer have been prepared with the monomers acrylic Acid and HEMA. Ester crosslinked gels have been synthesized by esterification reaction at room temperature without using any crosslinker. All the gels are pH and temperature responsive. The incorporation of HEMA unit in the crosslinked network of poly acrylic acid increases the mechanical strength of the gel.

The gels may find application in removing basic dyes from aqueous solution. The dye molecules get trapped within the gel. The gels may be used in separation of heavy metal ions from their aqueous solutions as well. The gels have the ability to absorb and retain transition metals (like Cu^{2+}, Fe^{3+}) within itself due to the formation of chelate complex with carboxylic acid groups. Ester linked gel has been found to behave in better way from all aspects like swelling, mechanical rigidity, cationic dye and heavy metal ion removal ability along with low cost and easy development procedure.

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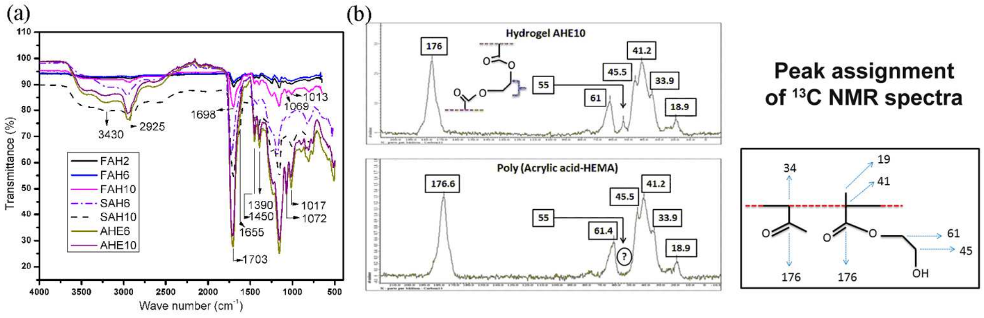

Fig. 1: (a) FTIR-ATR spectroscopy of the oven dried hydrogels and (b) 13-C NMR spectroscopy of the hydrogels AHE10, poly (Acrylic acid-HEMA) and the corresponding peak assignments.
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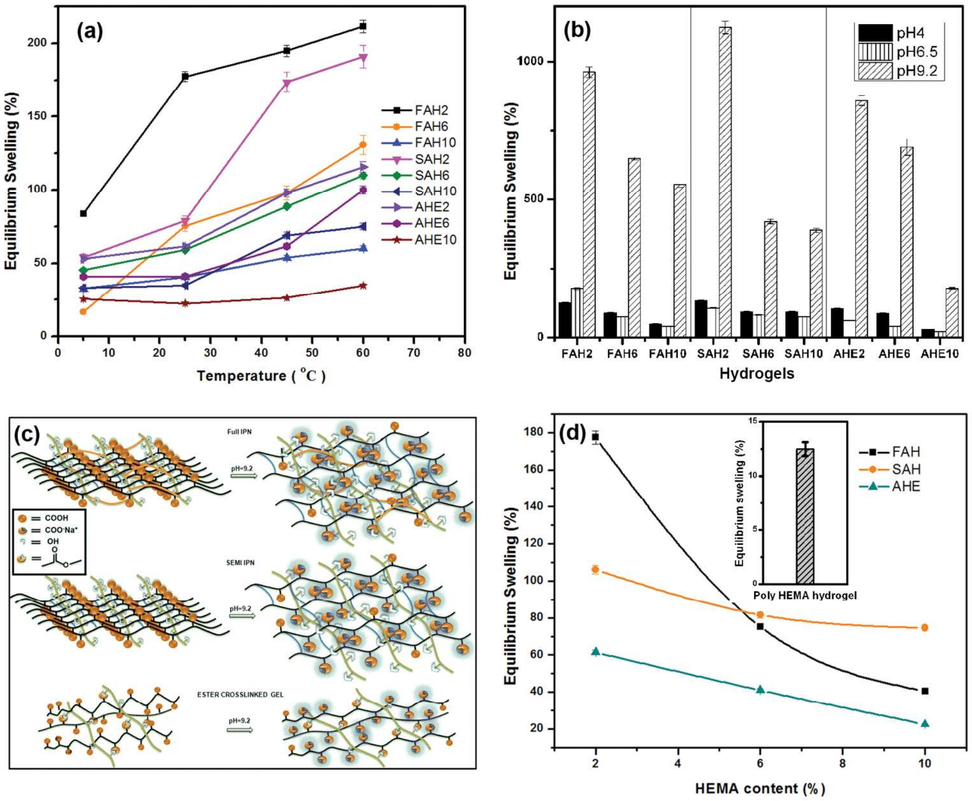

Fig. 2:Variation of equilibrium swelling percentage (%) of the hydrogels with the (a) temperature, (b) pH and (d) HEMA content; (c) Hypothetical models to draw structure-property relationship for the three systems during change in pH of the swelling media.
160x130mm (300 x 300 DPI)

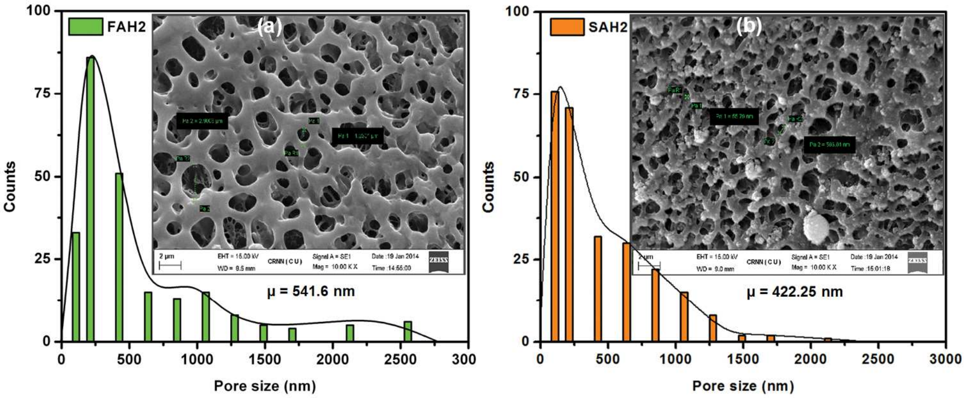

Fig. 3: Scanning electron microscopic study and the respective pore size distribution of the (a) Full IPN and (b) semi IPN.
168x69mm (300 x 300 DPI)

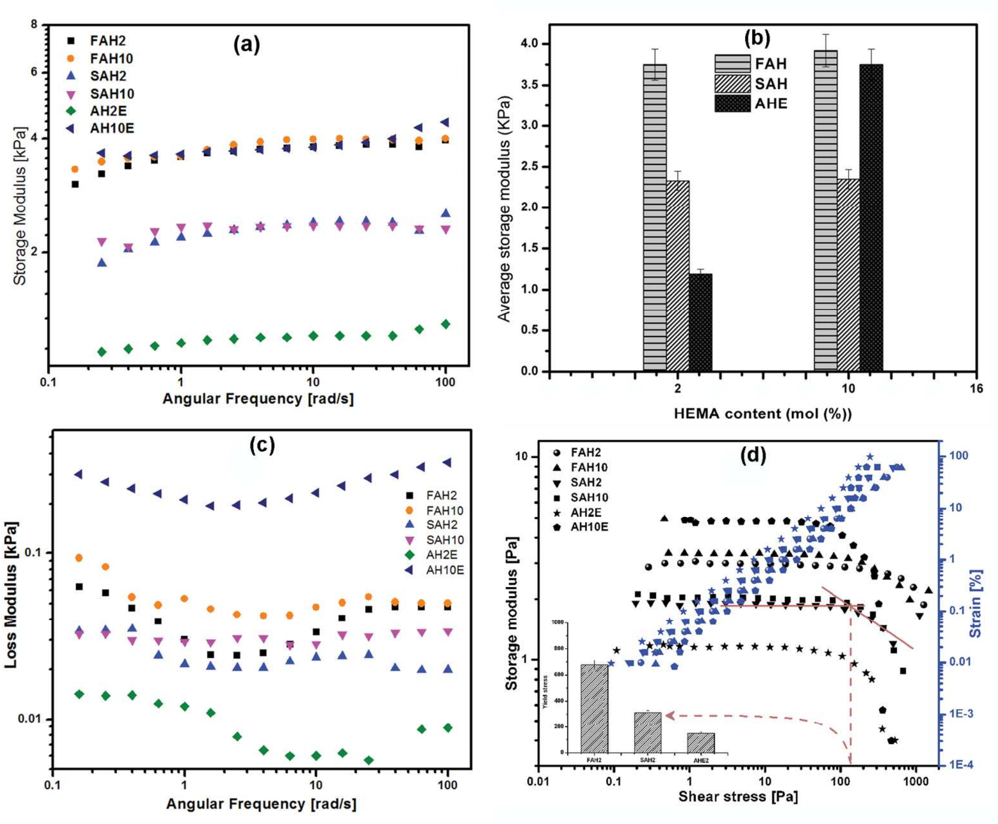

Fig. 4: Variation of (a) storage and (c) loss moduli for the gels with the increase in angular frequency; and variation of storage modulus with (b) the HEMA content and (d) the increase in shear stress (determination of yield stress).
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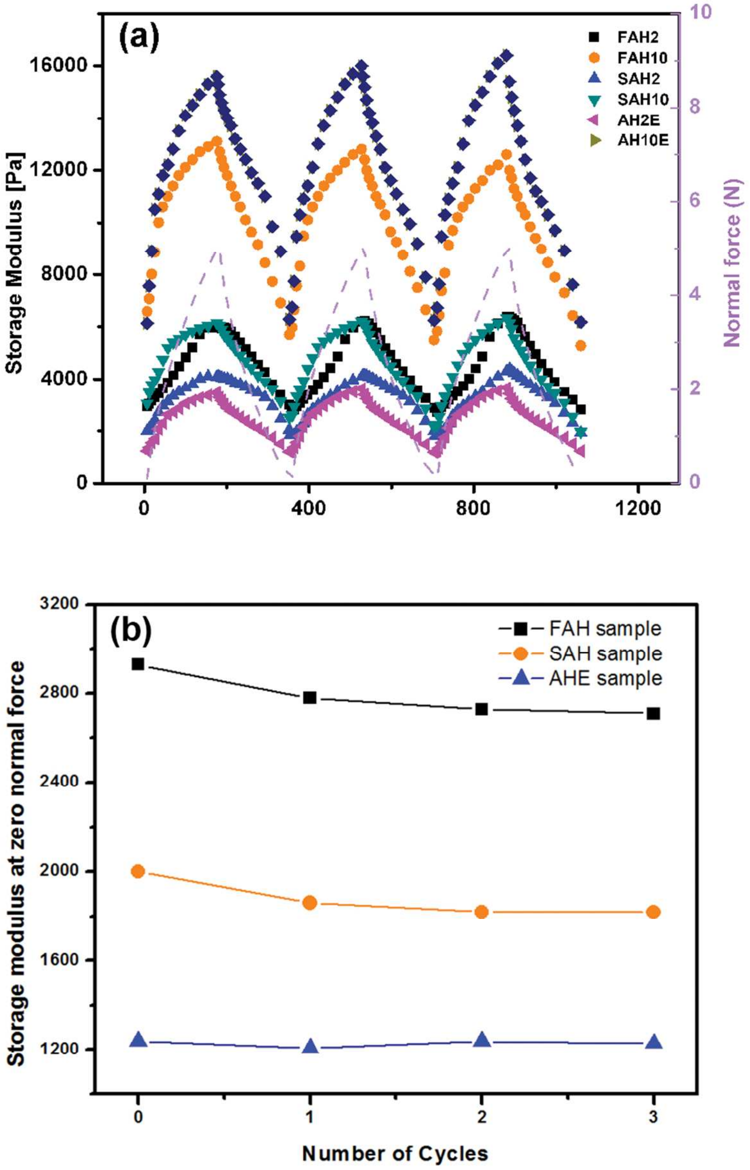

Fig. 5: Variation of (a) storage modulus with the normal force for the gels (up to 3 cycles) and (b) storage modulus at zero normal fore with the number of cycles of applying force.
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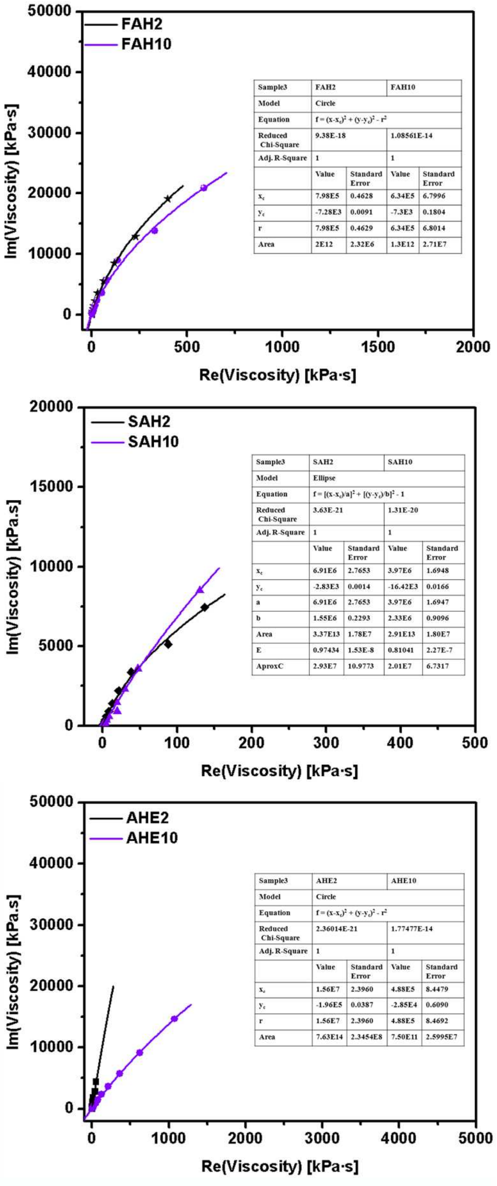

Sample3	FAH2		FAH10	
Model	Circle			
Equation	$f = (x-x_c)^2 + (y-y_c)^2 - r^2$			
Reduced Chi-Square	9.38E-18		1.08561E-14	
Adj. R-Square	1		1	
	Value	Standard Error	Value	Standard Error
x_c	7.98E5	0.4628	6.34E5	6.7996
y_c	-7.28E3	0.0091	-7.3E3	0.1804
r	7.98E5	0.4629	6.34E5	6.8014
Area	2E12	2.32E6	1.3E12	2.71E7

Sample3	SAH2		SAH10	
Model	Ellipse			
Equation	$f = [(x-x_c)/a]^2 + [(y-y_c)/b]^2 - 1$			
Reduced Chi-Square	3.63E-21		1.31E-20	
Adj. R-Square	1		1	
	Value	Standard Error	Value	Standard Error
x_c	6.91E6	2.7653	3.97E6	1.6948
y_c	-2.83E3	0.0014	-16.42E3	0.0166
a	6.91E6	2.7653	3.97E6	1.6947
b	1.55E6	0.2293	2.33E6	0.9096
Area	3.37E13	1.78E7	2.91E13	1.80E7
E	0.97434	1.53E-8	0.81041	2.27E-7
AproxC	2.93E7	10.9773	2.01E7	6.7317

Sample3	AHE2		AHE10	
Model	Circle			
Equation	$f = (x-x_c)^2 + (y-y_c)^2 - r^2$			
Reduced Chi-Square	2.36014E-21		1.77477E-14	
Adj. R-Square	1		1	
	Value	Standard Error	Value	Standard Error
x_c	1.56E7	2.3960	4.88E5	8.4479
y_c	-1.96E5	0.0387	-2.85E4	0.6090
r	1.56E7	2.3960	4.88E5	8.4692
Area	7.63E14	2.3454E8	7.50E11	2.5995E7

Fig. 6: Cole-Cole plot for (a) full IPN hydrogels, (b) semi-IPN hydrogels and (c) ester linked hydrogels with the symmetry parameters at the inset of each plot.
80x193mm (300 x 300 DPI)

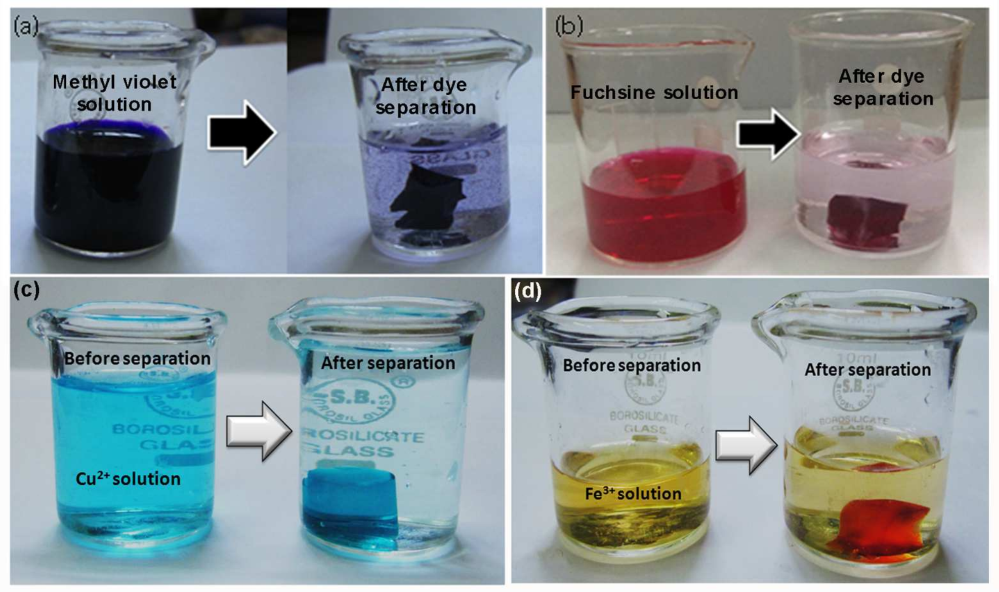

Fig. 7: Images regarding the experiment determining removal efficiency of (a) Methyl violet, (b) Fuchsine, (c) Cupper (2+) ion and (d) Iron (3+) ion from the aqueous solution of them.
160x95mm (300 x 300 DPI)