

# SYNTHESIS AND CHARACTERIZATION OF POLY (ACRYLIC ACID) AND POLY (VINYL ALCOHOL) BASED MAGNETIC HYDROGEL

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**ABSTRACT:** The hydrogels are very much useful in the bio-medical engineering field. The wide applications of hydrogel urged us to do the present investigation. Hydrogel between poly(acrylic acid) (PAA) and epichlorohydrin (ECH), and poly(vinyl alcohol) (PVA) and ECH were prepared by simple chemical grafting reaction. The hydrogels were prepared in the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticle (NP) at 45°C under nitrogen atmosphere. Thus synthesized magnetic Nanocomposite hydrogels were characterized by fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), vibrating sample magnetometer (VSM) and field emission scanning electron microscopy (FESEM) like analytical methods. The FESEM results clearly indicated that the size and shape of NP can be altered by the polymer chains. The results are critically compared with the literature.

**Keywords:** Hydrogel, Fe<sub>3</sub>O<sub>4</sub>, synthesis, characterization

## Introduction

Recently, the polymer scientists turned their attention towards the synthesis of magnetic responsive hydrogels, a class of smart materials due to the positive proper response to the applied magnetic force. For example, Liu *et al.*<sup>1</sup> synthesized a PVA based magnetic sensitive hydrogel by physical cross-linking method. Effect of magnetic NP on the thermal properties of some hydrogels was studied by Goiti and co-workers<sup>2</sup>. PVA-ferrogels and films were reported in the literature<sup>3</sup>. Wu *et al.*<sup>4</sup> reported about the physically cross linked PVA hydrogel with magnetic field. In 2004, magnetic hydrogels for hyperthermia application was studied by Lao and research team<sup>5</sup>. Magnetic hydrogel with its mechanical behavior was reported in the literature<sup>6</sup>. PVA based magnetic hydrogels were synthesized towards water sorption study<sup>7</sup>. In 2013, PAA based magnetic hydrogel for controlled drug release was reported<sup>8</sup>. PAA magnetic hydrogel was synthesized and their dielectric study was done by Berkum *et al.*<sup>9</sup>. Other authors also studied about the magnetic hydrogels synthesized by

various methods<sup>10,11</sup>. By thorough literature survey, we found few reports are available on the PAA based magnetic hydrogel. The novelty of the present investigation is a comparative study of PAA and PVA based magnetic hydrogels. The thermal, VSM and their morphology were compared with each other.

## Experimental

**Materials:** FeCl<sub>2</sub>, FeCl<sub>3</sub> and sodium hydroxide (NaOH) were purchased from CDH chemicals, India. PVA (M<sub>w</sub>-1, 25, 00 g/mol) and PAA (M<sub>w</sub>-25,000 g/mol) were purchased from Nice Chemicals, India. ECH was purchased from Spectrum chemicals, India and used as received. Double distilled (DD) water was used for solution preparation purpose.

### Synthesis of Fe<sub>3</sub>O<sub>4</sub>:

10 g FeCl<sub>3</sub> and 5 g FeCl<sub>2</sub> were mixed with 100 mL of DD water and stirred for about half an hour at 45°C under nitrogen atmosphere. The stirring was continued for another 2 hrs at room temperature for nucleation. With this 5 g NaOH in 10 mL of DD water was added to the mixture

in drop wise manner under mild stirring<sup>12</sup>. This resulted in the formation of a black colored precipitate and it was dried in the oven for about 6 hrs at 110°C. Thus obtained black color powder was weighed and stored in a zipper lock cover.

### Synthesis of Magnetic Hydrogel:

5 mL of PAA solution was taken in a 100 mL round bottomed flask (RBF). 25 mL of DD water was added under vigorous stirring condition. 1.0 g NaOH pellet was dissolved in 10 mL DD water separately and poured into the RBF under vigorous stirring condition. The PAA was converted into PAA-Na. With this, 5 mL ECH was added. The ECH functionalized PAA was formed with the removal of NaCl. The reaction should be carried out for 6 hours at 40°C under nitrogen atmosphere. Thus obtained brown color gel was washed with water and dried by using a drying paper. The same procedure was repeated in the case of PVA at 75°C. The other experimental conditions were maintained as constant.

### Characterization Techniques:

Magnetic measurements (VSM) were carried out with a superconducting quantum interference device magnetometer (Lakesore-7410-VSM, USA) with magnetic fields up to 7 T at 32 °C. DSC and TGA were measured by using Universal V4.4A TA Instruments (simultaneous DSC and TGA analyzer) under nitrogen atmosphere at the heating rate of 10 K/min from room temperature to 373K. FTIR spectrum was taken by using Shimadzu 8400 S, Japan model instrument from 4000-400 cm<sup>-1</sup> by KBr pelletisation method. FESEM was used to examine morphological behaviour of polymer with the help of FESEM – Hitachi S4800 Japan, instrument.

### Results and Discussion

**FTIR spectroscopy:** **Figure 1a** indicates the FTIR spectrum of PAA-g-ECH system. A broad peak at 3400 cm<sup>-1</sup> indicates the –OH stretching of water molecules. The C-H symmetric and anti-symmetric stretching observed at 2882 and 2946 cm<sup>-1</sup> respectively. The C=O stretching of PAA appeared at 1726 cm<sup>-1</sup>. The bending

vibration of water is noted at 1643 cm<sup>-1</sup>. The ester C-O-C linkage and C-H out of plane bending vibration was noted at 1042 and 751 cm<sup>-1</sup> respectively. The Metal-Oxide stretching of Fe<sub>3</sub>O<sub>4</sub> appeared at 573 cm<sup>-1</sup>. **Figure 1b** indicates the FTIR spectrum of PVA-g-ECH system. Here also the above said peaks appeared, particularly a small hump at 1734 cm<sup>-1</sup> is associated with the conversion of secondary alcoholic group of PVA into a keto group<sup>13</sup>. The remaining peaks were also appeared here with slight shifting. The M-O stretching of Fe<sub>3</sub>O<sub>4</sub> was clearly explained by our research team<sup>12,14</sup>. The –OH, C-H, C=O and C-O-C stretching in PCL<sup>15,16</sup> is similar to that of the present investigation.

### DSC Study:

The phase transition of polymer after the structural modification is given in **Figure 2**. **Figure 2a** denotes the DSC thermogram of PAA-g-ECH system. A small peak at 86.2°C is corresponding to the removal of physisorbed water molecules or T<sub>g</sub> of PAA. The shape of the peak confirmed the dewatering temperature (T<sub>d,w</sub>) of PA-g-ECH. **Figure 2b** represents the DSC thermogram of PVA-g-ECH system with an endothermic peak at 104.9°C. This can be explained on the basis of the T<sub>d,w</sub> of PVA-g-ECH system. Gandhi *et al.*<sup>17</sup> and Parveen *et al.*<sup>18</sup> explained the T<sub>d,w</sub> of PVA. Our result is coincide with their report. In overall comparison, the PVA-g-ECH system yielded the higher T<sub>d,w</sub> and which confirmed the existence of inter and intra molecular hydrogen bonding<sup>17</sup>.

### TGA history:

The thermal stability of structurally modified polymers was determined by TGA. The TGA thermogram of ECH functionalized PAA is given in **Figure 3a** with four step degradation process. The first major weight loss around 100°C is due to the removal of moisture and physisorbed water molecules. The second major weight loss around 220°C is ascribed to the removal of chemisorbed water molecules and breaking of inter molecular hydrogen bonding. The third minor weight loss around 417°C can be explained by the breaking of linkage between AA and ECH segments. The last minor weight loss around 495°C is accounted by the degradation of

AA units with the evolution of CO<sub>2</sub>. Above 750°C the system exhibits 33% weight residue remained. **Figure 3b** represents the TGA thermogram of structurally modified PVA. Here, one can see a five step degradation process. The first and second step degradation procedure is similar to that of TGA of structurally modified PAA. The third (308°C) and fourth (463°C) minor weight loss steps are due to the breaking of interaction between PVA and ECH and PVA structural degradation respectively. The last weight loss step is due to the degradation of C=C, C=O containing PVA segments<sup>17,18</sup>. During the structural modification reaction, due to thermolytic oxidation and oxidative degradation reaction, C=O and C=C were formed on the PVA backbone<sup>15</sup>. Above 850°C, the system, exhibits 27% weight residue remained. In comparison, the PAA-g-ECH system showed somewhat higher thermal stability than the PVA-g-ECH system.

#### VSM Profile:

The presence of ferrite in the hydrogel was confirmed by VSM technique. The VSM value of the pristine ferrite is 55.5 emu/g (**Figure 4a**). The VSM value of structurally modified PAA and PVA are given in **Figure 4b** and **Figure 4c** respectively with the corresponding VSM value of 25.5 and 22.8 emu/g. After the magnetic responsive hydrogen formation the VSM value was suddenly dropped. This is due to the encapsulation of ferrite by the polymer chains (i.e) the empty or voids present in the coiled polymer chains were filled by the ferrite. During this filling process, the acid group of PAA or OH group of PVA interacted with the ferrite surface. The negative charge of carboxylic group degraded the ferrite structure to some extent. As a result, the VSM value of polymer nanocomposites was reduced. Recently, Palanikumar *et al.*<sup>19</sup> and Meenarathi *et al.*<sup>20</sup> observed this type of results after the surface functionalization of ferrite.

#### FESEM Analysis:

The surface morphology of PAA-g-ECH system is given in **Figure 5a** with a broken stone like morphology with more voids on its surface. **Figure 5b** indicates the morphology of ferrite

NP. Here one can see a sphere, square, pentagon and octahedral shaped ferrite NP. The size was varied between 50 and 484 nm. This polydispersity of ferrite was accelerated by the PAA-g-ECH chains. Palani kumar and co-workers<sup>19</sup> reported the FESEM image of ferrite with polydispersity shapes and sizes. **Figure 6a** confirms the surface morphology of PVA-g-ECH system. The surface is fully occupied by the voids and which confirmed the gel formation. **Figure 6b** represents the FESEM image of PAA-g-ECH surface, particularly ferrite NP. Here one can see a Nano sphere with the size of 80-100 nm. The FESEM study inferred that the size and shape of ferrite NP can be altered or controlled by the polymer chains through encapsulation effect.

#### Conclusions:

The following important points were derived from the above study and presented here as conclusions. The magnetic hydrogels were prepared by simple chemical grafting reaction under alkaline condition. The FTIR spectrum of PVA-g-ECH system exhibits a peak at 1734 cm<sup>-1</sup> due to the C=O stretching corresponding to the thermolytic oxidation reaction. The PVA-g-ECH hydrogel showed the highest T<sub>d,w</sub> due to the presence of inter and intra molecular hydrogen bonding. The PAA-g-ECH hydrogel exhibited the highest thermal stability with 33% weight residue remained above 750°C. Both the PVA and PAA hydrogels exhibited lower VSM value due to the encapsulation effect. The structurally modified PVA hydrogel produced spherical ferrite with the size of 80-100 nm.

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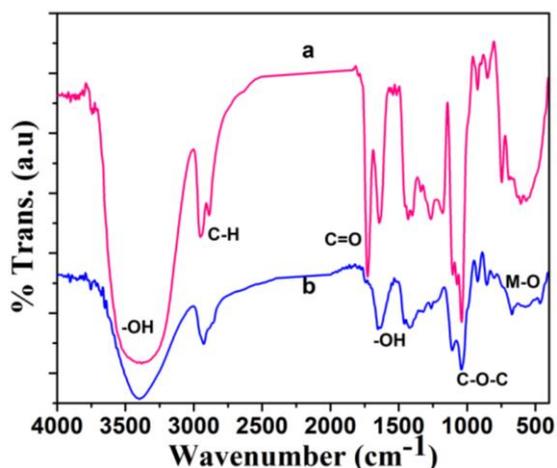


Figure 1: FTIR spectrum of (a) PAA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>, (b) PVA-g-ECH/Fe<sub>3</sub>O<sub>4</sub> systems

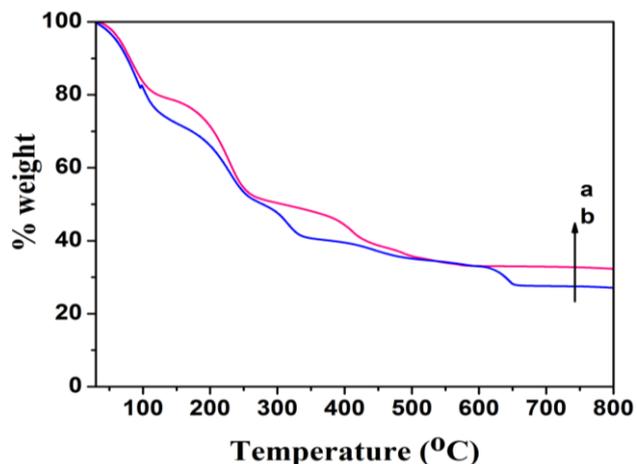


Figure 3: TGA thermogram of (a) PAA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>, (b) PVA-g-ECH/Fe<sub>3</sub>O<sub>4</sub> systems

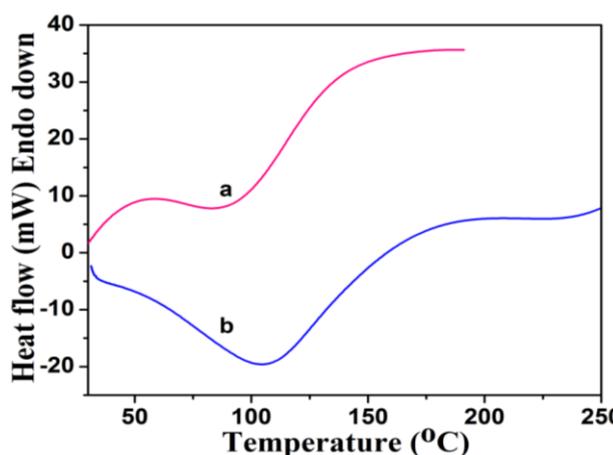


Figure 2: DSC thermogram of (a) PAA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>, (b) PVA-g-ECH/Fe<sub>3</sub>O<sub>4</sub> systems

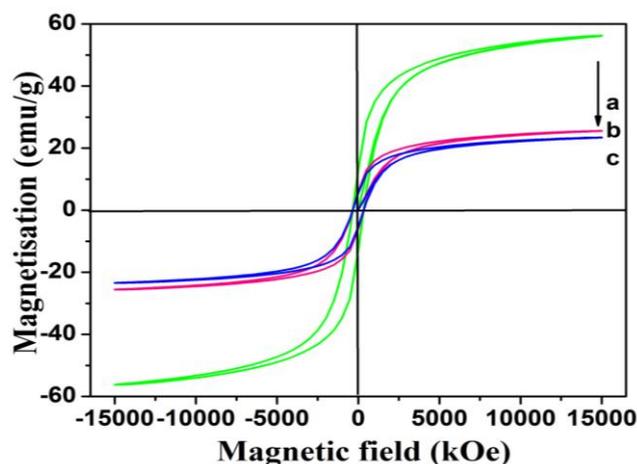


Figure 4: VSM loop of (a) pristine Fe<sub>3</sub>O<sub>4</sub>, (b) PAA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>, (c) PVA-g-ECH/Fe<sub>3</sub>O<sub>4</sub> systems

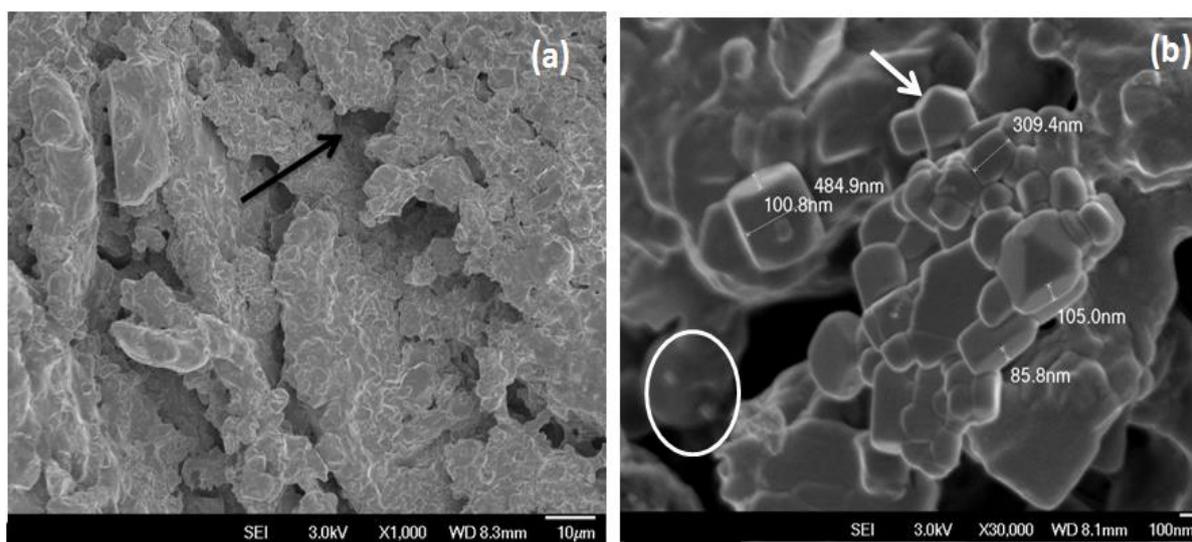


Figure 5: FESEM image of (a,b) PAA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>

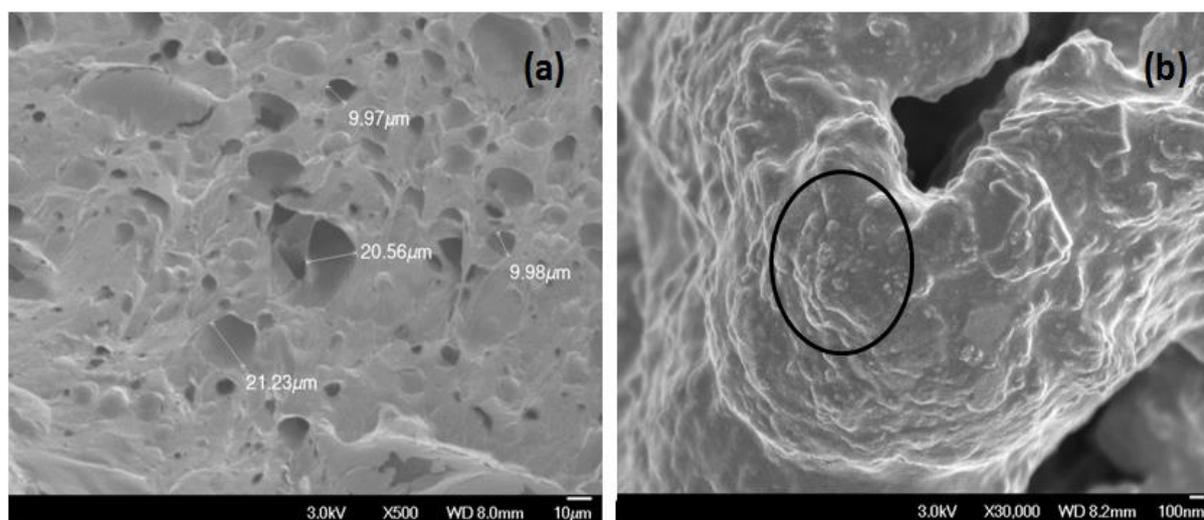


Figure 6: FESEM image of (a,b)PVA-g-ECH/Fe<sub>3</sub>O<sub>4</sub>