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Hydrogels based on mucilage of underutilized cereals: Synthesis and characterization

Ritu Sharma, Rajinder K Gupta & Archna Rani*

Department of Applied Chemistry, Delhi Technological University, Delhi, India

*E-mail: archnar8@yahoo.co.in

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Mucilage is a natural polysaccharide with a variety of physicochemical and structural properties. Plant-derived mucilage has a wide range of applications, such as binding agent, stabilizer, emulsifying agent, thickening agent, and gelling agent. This study investigated the potential of underutilized cereals' mucilage and further explored their application by synthesizing mucilage-based hydrogels. For this purpose, we have explored four new sources of mucilage, namely adzuki beans (A_b), amaranth (A_m), proso millet (P_r), and little millet (L_m). The underutilized cereals' mucilage application has been examined by developing hydrogels through the free radical co-polymerization technique. Mucilages are confirmed to be a natural thickening and a substitute for synthetic polymers after being evaluated physically and phytochemically. Structural analysis of mucilages and their hydrogels (A_bH, A_mH, P_rH & L_mH) were characterized by using FTIR-ATR, XRD, ^1H & ^{13}C NMR techniques. It confirms that all four mucilages are rich in polysaccharide residues and grafting of sodium acrylate has been successfully done on mucilages. Thermal gravimetric analyses represent the better thermal stability of the synthesized hydrogels than their respective mucilages. SEM confirms the porous structure of the mucilages and their hydrogels. All of these studies demonstrated that the underutilized mucilage from cereals might be a good feedstock for a hydrogel-forming agent, which can be explored in the food, cosmetics, and pharmaceutical industries.

Keywords: Co-polymerization, Hydrogel, Mucilage, Natural polysaccharide, Structural characterization

In recent years, there is a lot of interest in plant-derived mucilage owing to their non-toxicity, eco-friendliness, cost-effectiveness, and biodegradable nature. To meet the growing need, new sources are being investigated on a regular basis. Chemically, mucilage is a natural polysaccharide composed of highly branched structures of carbohydrates such as L-arabinose, D-xylose, and D-galactose monomer units[1]. They can be obtained from different parts of the plant like seeds, leaves, roots, and stems. The process of producing mucilage from the plant part is known as Myxospermy. Mucilage is partially soluble when it comes in contact with water[2]. These polysaccharides are composed of ten or more monosaccharide units. Mucilages obtained from different sources exhibit varied functional properties due to differences in the monosaccharide units, type of glycosidic bond, and conformation of the chains[3]. Due to their hydrophilic nature, these polysaccharides swell in water and form a gel-like solution, which has excellent and diverse use as a binding agent, stabilizing agent, emulsifying agent, thickening agent, etc.

Mucilage isolated from different plant materials has been extensively used in pharmaceutical and food industries. Recently, the isolation and characterization of new sources of plant-derived mucilage (chia mucilage, okra seed mucilage, marshmallow mucilage, and Chinese yam mucilage) and their applications have been investigated. Herein, we report four newer sources of mucilage, these are underutilized cereals of India i.e., Adzuki beans (A_b), Amaranth (A_m), Proso millet (P_r), and Little millet (L_m).

Adzuki bean (*Vigna angularis*) is a legume belonging to Fabaceae (Leguminosae) family. It is widely cultivated in countries like China, Japan, and Korea. It is widely utilized as an ingredient in desserts[4]. Amaranth (*Amaranthus*) belongs to the family Amaranthaceae. It is commonly known as Ramdana or Rajgira in India and is a nutritious pseudo-cereal. It is widely cultivated in different countries as a cereal, vegetable, weed, or crop. Proso millet (*Panicum miliaceum*) belongs to the Poaceae family. It is cultivated in India, China, Nepal, Africa, Turkey, Romania, and Russia. It is gluten-free and rich in proteins, vitamins, and minerals[5]. Little millet (*Panicum sumatrense*) belongs to the family Poaceae. It is widely cultivated across India, China, and Africa.

It is considered as "cool food" in light of its cooling impact on the human body when consumed in summers[6].

According to Deore et al., mucilage possesses swelling property because of the presence of distinct functional and polar groups that exhibit their hydro-gelling potential[7]. This swelling ability of mucilage can be further enhanced by synthesizing hydrogels based on mucilage. Hydrogels are three-dimensional polymeric networks that contain hydrophilic or polar functional groups to hold water in them. They are known for their high absorption capacity. Hydrogels are typically crosslinked with physical or chemical crosslinking, preventing them from dissolving in water[8]. They are suitable for various biomedical, agricultural, food, and cosmetic applications due to their biocompatibility and harmless nature. As natural polymers show several advantages over synthetic polymers, hence they have gained the interest of researchers as a potential source for hydrogel formation[9].

The aim of the current study is for the isolation of mucilage from four underutilized cereals of India, namely Adzuki bean (*Vigna angularis*), Amaranth (*Amaranthus*), Proso millet (*Panicum miliaceum*), and Little millet (*Panicum sumatrense*) and to develop mucilage-co-Acrylic acid (M-co-AAc) graft copolymeric hydrogels by free radical polymerization. The study also focused on their physicochemical, morphological, and structural characterization by various instrumental analysis. This is the first report on the isolation of mucilage from these underutilized cereals and their hydrogel synthesis to the best of our knowledge.

Experimental Section

Materials

Adzuki beans (A_b) were purchased from Himjoli Products, Delhi, India. Proso millet (P_r), and Little millet (L_m) were gifted from ICAR, Hyderabad, India. Amaranth (A_m) was purchased online from Amazon, India. The grain samples were authenticated by CSIR-NIScPR, Raw Materials Herbarium, and Museum, Delhi (RHMD), India. All samples were prepared in Milli-Q grade water. All the reagents and chemicals used in the experiments were of analytical grade.

Extraction of mucilage

The extraction was done following the method given by Nuria et al. with slight modifications[10]. Each cereal sample was sieved to remove any foreign particles and then sun-dried. 50 g of each dried and powdered sample were mixed with deionized water in a separate Erlenmeyer flask. The pH was maintained at 8 with 0.1 M sodium hydroxide (NaOH) solution. The temperature of the solution was kept at 70 ± 2ºC under constant stirring until a viscous solution was obtained. The solution was cooled at an ambient temperature and then passed through a muslin cloth to separate the mucilage from the cereals. Then the solution was centrifuged at 10,000 rpm, 25ºC for 20 min. The supernatant obtained after centrifugation was collected and used for further purification. A pictorial representation of the extraction method of mucilage is shown in Fig. 1.

Purification of mucilage

Isolated mucilage was purified, according to the method described by Morales-Tovar et al. with slight changes[11]. The supernatant obtained in the previous step was mixed with acetone in 1:3 (sample: acetone) ratio and left undisturbed for 3 h. The precipitated mucilage was then filtered and dried in an oven below 50ºC overnight. The dried mucilage was powdered using mortar and pestle and stored in a desiccator for further use. The percentage yield of pure mucilage isolated from 50 g powdered cereals was recorded and calculated using the formula (Eq. 1)[12].

$$\%\, Yield = \frac{Weight\ of\ dried\ mucilage\ obtained}{Weight\ of\ powdered\ cereal\ material\ used} \times 100 \quad ...(1)$$

Physicochemical characterization

pH and solubility

To measure the pH of the isolated mucilage, 1% (w/v) aqueous solution was prepared and stirred for

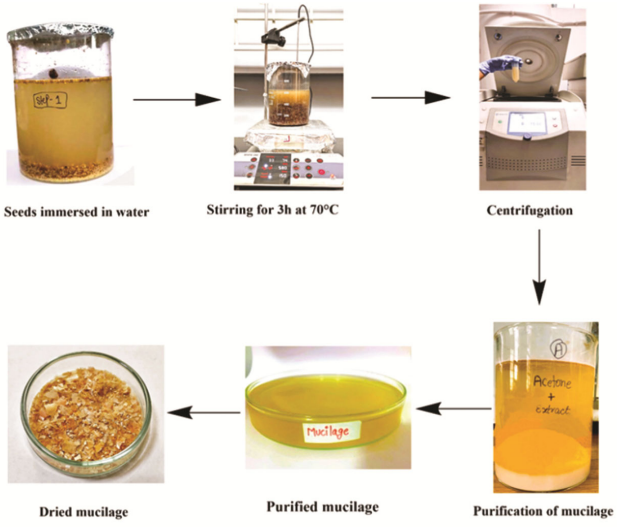

Fig. 1 — Pictorial representation of extraction of mucilage

30 min. The pH was measured using a calibrated digital pH meter.

The solubility of the extracted mucilage was studied using different solvents like deionized water, acetone, ethanol, methanol, and chloroform[13].

Swelling index

Swelling index (SI) was obtained by the method reported by Archana et al. with slight modifications[14]. 1 g dried mucilage was taken in a stopper graduated cylinder. 2 mL ethanol (95%) was added for better dispersion, and then 10 mL deionized water was added. After a gentle shaking, it was kept at room temperature till constant weight was observed. The volume raised was observed and recorded. SI was calculated according to the formula (Eq. 2).

$$\%S = \frac{V_f - V_i}{V_i} \times 100 \quad ...(2)$$

where, V_f is the final volume after hydration (mL); V_i is the initial volume before hydration (mL).

Organoleptic characterization

For organoleptic characterization, the mucilage was analyzed for various parameters like odour, colour, appearance, fracture and taste[14].

Phytochemical investigation

To confirm the chemical nature of the isolated mucilage, various identification tests like Molisch's test (carbohydrates), Ninhydrin test (proteins and amino acids), Ruthenium Red test (mucilage), Iodine test (starch), Ferric chloride test (tannins), and Wagner's test (alkaloids) were performed[13].

Exploration of cereal-based mucilage as hydrogel

The polysaccharide material isolated had the ability to form a viscous solution with an increase in concentration. The mucilage derived from all four cereals showed the hydrophilic nature, and suitable swelling property. Hence, it was planned to prepare hydrogels (A_bH, A_mH, P_rH & L_mH) based on isolated mucilages.

Synthesis of M-co-AAc hydrogels

The hydrogels were synthesized following the method described by Hussain et al. with slight modifications[8]. The hydrogels were synthesized using a free radical co-polymerization mechanism by taking potassium persulphate (KPS) and N,N'-methylenebisacrylamide (MBA) as an initiator and a crosslinker, respectively. For this, a desirable amount of each dried mucilages was first dissolved in 10 mL of hot deionized water. To this, AAc, NaOH, MBA, and KPS were mixed in desired ratios and continuously stirred for 2 h at room temperature using a magnetic stirrer. Each mixture was sonicated for 5 min to remove any air bubbles. The solutions were poured into the test tube and placed in a water bath for an hour. Prepared hydrogels were cut into small discs. The hydrogels were then air-dried, followed by drying in an oven at 60°C until the constant weight was observed. Formulations of all four M-co-AAc hydrogels are given in Table 1.

Swelling index

Swelling studies were conducted using deionized water at an ambient temperature. The dried hydrogels were weighed with the help of weighing balance. The dried hydrogels were weighed and then immersed in deionized water till constant weight was observed[15]. Periodically, the swollen hydrogels were taken out, and excess water was wiped off using tissue paper. The SI for each hydrogel was calculated according to the given formula (Eq. 3).

$$\%SI = \frac{W_{SH} - W_{DH}}{W_{SH}} \times 100 \quad ...(3)$$

where, W_{SH} is the weight of the swollen hydrogel and W_{DH} is the initial weight of the dried hydrogel.

Characterizations

All the mucilages and their respective hydrogels were characterized by FTIR (Perkin Elmer, spectrum version two) in ATR mode, thermogravimetric analysis (Perkin Elmer, TGA 4000) in N_2 atmosphere with a heating rate of 10 °C/min from 25 to 800°C, X-ray diffraction analysis (Bruker D8 Avance) with an angle ranging from 10° to 80° with a scan speed of 0.5 sec/step, scanning electron microscopy (Carl Zeiss, EVO 18) with 30 kV accelerating voltage and 2.519 A beam current, ^{1}H-NMR (Bruker Avance-III)

Table 1 — Formulations of all four M-co-AAc hydrogels

S. No.	Formulation	Mucilage (g)	Monomer (AAc) (mL)	NaOH (g)	Initiator (KPS/Distilled water) (g/mL)	Crosslinker (MBA) (mg)
1.	A_bH	0.05	7.1	4.2	0.09/10	60
2.	A_mH	0.05	7.1	4.2	0.09/10	60
3.	P_rH	0.05	7.1	4.2	0.09/10	60
4.	L_mH	0.05	7.1	4.2	0.09/10	60

and ^{13}C-NMR (JEOL Resonance ECX-400) at an operating frequency of 500 MHz.

Results and Discussion

Isolation of mucilage

Mucilage from all four underutilized cereals was isolated effectively. The extraction method and species variation can affect the percentage yield of the polysaccharide obtained. The percentage yield of all four mucilages is shown in Table 2. Among all, A_m showed the highest yield of 27.61%. A_b, A_m, P_r, and L_m were observed as light brown, white, creamy white, and light green mucilage powder, respectively, as shown in Fig. 2(A).

Physicochemical characterization

The solubilities of all four mucilages were studied using different solvents like water, acetone, ethanol, methanol, and chloroform. They were partially soluble in cold water, soluble in hot water and insoluble in acetone, methanol, and chloroform. From the data mentioned in Table 3, it is observed that mucilage is insoluble in all organic solvents. However, due to the presence of hydrophilic moieties, it forms a viscous solution when combined with water[16].

The pH of the mucilage is one of the important factors in determining its suitability as an excipient in various pharmaceutical industries. The results shown in Table 4, indicates that all four mucilaginous polysaccharides are nearly neutral. This suggests that it will be less irritating to the gastrointestinal tract. Hence, they can be used as an excipient in various pharmaceutical preparations[17].

The swelling index of the mucilage is shown in Table 4. The data indicates that all four mucilages have a hydrophilic character and hence swells when it absorbs water due to the hydroxyl groups present in it. Among all, L_m has the highest value of swelling index which may confirms that it has more hydroxyl groups than others[18].

Organoleptic characterization

The dried and powdered mucilages are shown in Fig. 2(A) and the organoleptic characterization are tabulated in Table 5. The quality of mucilage depends on the method of extraction. A_b, P_r, and L_m mucilage

Table 2 — The percentage yield of mucilage extracted from four underutilized cereals

Mucilage samples	% Yield
Adzuki beans (A_b)	12.86 %
Amaranth (A_m)	27.61 %
Proso millet (P_r)	20.01 %
Little millet (L_m)	7.24 %

Table 3 — Solubility of isolated mucilage in different solvents

Solvents	Solubility			
	A_b	A_m	P_r	L_m
Cold water (2°C)	Partially Soluble	Partially Soluble	Partially Soluble	Partially Soluble
Hot water (90°C)	Soluble	Soluble	Soluble	Soluble
Methanol	Insoluble	Insoluble	Insoluble	Insoluble
Acetone	Insoluble	Insoluble	Insoluble	Insoluble
Benzene	Insoluble	Insoluble	Insoluble	Insoluble
Chloroform	Insoluble	Insoluble	Insoluble	Insoluble
Dimethylsulphoxide	Insoluble	Insoluble	Insoluble	Insoluble

Table 4 — Swelling index and pH of the isolated mucilage

S. No.	Property	Mucilage			
		A_b	A_m	P_r	L_m
1.	pH	6.80	6.68	6.98	7.46
2.	% Swelling index	125	137.5	100	150

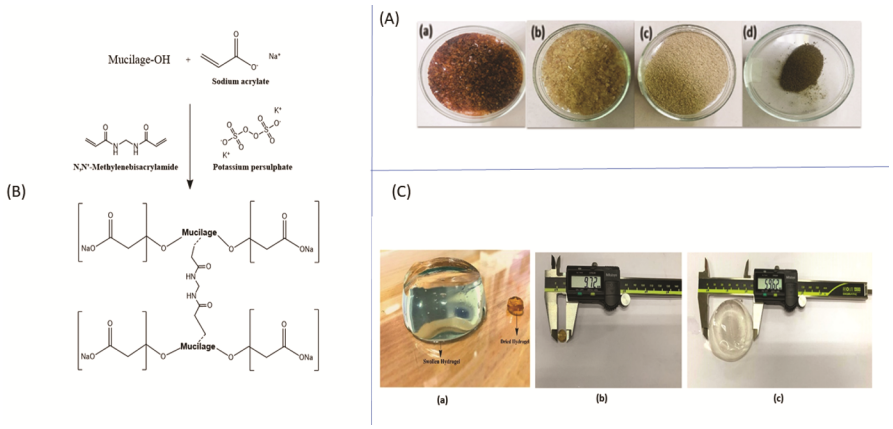

Fig. 2 — (A)-Dried and powdered mucilage [of (a) A_b (b) A_m (c) P_r (d) L_m], (B) schematic diagram for the formation of M-co-AAc graft copolymeric hydrogels and (C) images of hydrogels [(a) dried and swollen hydrogel (b) diameter of dried hydrogel (c) diameter of swollen hydrogel]

Table 5 — Organoleptic characterization of extracted mucilage

Property	A_b	A_m	P_r	L_m
Appearance	Amorphous powder	Lustrous crystalline flakes	Amorphous powder	Amorphous powder
Odour	Odourless	Odourless	Odourless	Odourless
Colour	Light brown	White	Creamy white	Light green
Taste	Tasteless	Tasteless	Tasteless	Tasteless
Fracture	Rough	Smooth	Rough	Smooth

Table 6 — Phytochemical screening of the isolated mucilage

Active constituent	Identification Test	Inference			
		A_b	A_m	P_r	L_m
Carbohydrate	Molisch's test	+	+	+	+
Protein	Ninhydrin test	-	-	-	-
Tannin	Ferric chloride test	-	-	-	-
Mucilage	Ruthenium Red test	+	+	+	+
Starch	Iodine test	-	-	-	-
Alkaloids	Wagner's test	-	-	-	-

powder was rough, while A_m mucilage powder was shiny and flaky in nature. All four mucilages were coloured and tasteless.

Phytochemical characterization

The qualitative identification tests were done for the phytochemical investigation of the mucilages. The results obtained are shown in Table 6. The phytochemical analysis confirmed the presence of mucilage and carbohydrates by performing Ruthenium Red test and Molisch's test, respectively. The results also indicate the absence of starch, tannin, proteins, and alkaloids in all the mucilages. Therefore, it can be concluded that mucilages were pure and free from any impurities and other phytoconstituents of the seeds.

Instrumental analysis of mucilages

FTIR-ATR spectroscopy

FTIR-ATR is used to study the molecular structure of the mucilages. This technique helps in identifying the functional groups attached in the polymeric structure. The mucilage isolated from the different underutilized cereals shows characteristic peaks in the range 4000-400 cm^{-1} that correspond to different stretching and bending vibrations. The spectra in Fig. 3(A) show typical bands and peaks corresponding to the polysaccharide. The broad absorption band at 3272 cm^{-1} corresponds to the presence of hydroxyl groups. The peak obtained at 2916 cm^{-1} corresponds to the C-H stretching vibration[19]. The band near 2109 cm^{-1} corresponds to C-C stretching bonds[20]. The peak at 1627 cm^{-1} is due to the deformation of amide I / C=O asymmetric stretching mode[14]. The sharp peak at 1032 cm^{-1} and 1000 cm^{-1} are attributed to C-O-C and C-O-H vibrations of glycosidic bond in the polysaccharide[13]. All mucilages showed characteristic absorption bands between 1200-800 cm^{-1} in the fingerprint region for carbohydrates. From the IR characteristic peaks, we can say that the isolated mucilages contains carbohydrate moiety.

Thermogravimetric analysis (TGA)

Thermal stability is a significant factor in determining whether a polysaccharide is suitable for use in the pharmaceutical industry. TGA gives the information regarding the decomposition pattern and thermal stability of the polysaccharide. Fig. 3(B) represents the stability profile of all four isolated mucilage's which shows majorly three weight loss events. The initial phase of weight loss was obtained below 200°C in all the mucilage samples. This may be associated due to desorption of moisture present in the mucilage. The second weight loss was obtained in the range of 200-500°C in each polysaccharide. According to Silveira et al., this is due to the decomposition of the mucilage, which leads to the breaking of the polysaccharide branches. The final phase is in the range of 500-800°C. This is because of the degradation of the polysaccharide backbone[21]. From the decomposition pattern of all four mucilages, L_m is thermally more stable as it has 24% of residual weight at 800°C than the others. The observed thermal stability order of mucilages is $L_m > A_b > A_m > P_r$.

Powder X-ray diffraction analysis (XRD)

XRD is done to analyze the spatial arrangement of the atoms and molecules within the sample. It enables us whether the sample is amorphous or crystalline in nature. The powder XRD analysis data of different mucilages are shown in Fig. 3(C). In the XRD diffractogram, there was no sharp peak obtained in all the mucilage samples. This indicated the amorphous nature of all the mucilage. According to Ujwaldip et al., the absence of any intense peak indicates that mucilage is completely amorphous[13]. The broad peaks were obtained in the same region in all four mucilages indicated the similarity in the structure. Ma et al.

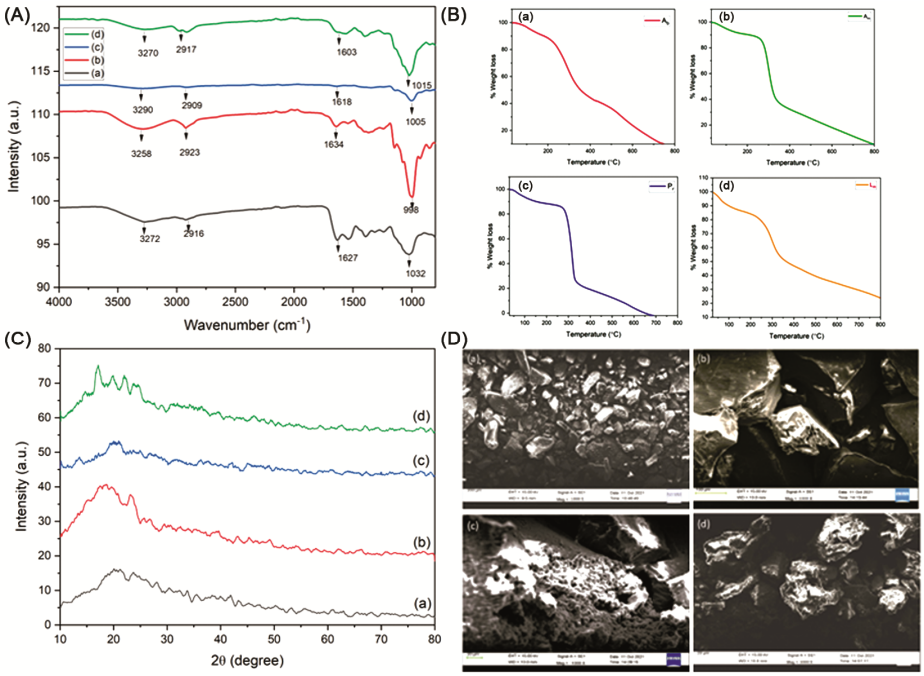

Fig. 3 — (A) FTIR-ATR spectra, (B) thermograms, (C) XRD plots and (D) SEM micrographs (at 1000 magnification) of the mucilage (a) A_b (b) A_m (c) P_r (d) L_m

obtained the X-Ray diffractogram for Chinese yam mucilage and observed the amorphous nature similar to this study[22]. The broad peaks spanning 2θ values ranging from 15° to 25° indicate the amorphous nature of all four mucilages.

Scanning electron microscopy (SEM)

To study the surface morphology of the polysaccharide obtained and to confirm the microstructure, SEM analysis was done and is represented in Fig. 3(D). The data revealed that the mucilage material is amorphous in nature. In the micro photograms, there is a high degree of irregularity with the dimensions and shapes of all the samples and the surface looks rough. According to Silva et al., choosing the right method for extraction and purification of the mucilage is very important, as it can change the structure, shape and topography of the mucilage obtained[23]. Singh et al. obtained the SEM data for *Diospyros melonoxylon Roxb.* where they obtained the same micrographs indicating the amorphous nature of the mucilage[24]. They reported that rough surface and irregular particle size can affect the hydration behaviour of the mucilage.

1D Nuclear magnetic resonance studies (NMR)

NMR spectroscopy is one of the essential technique used for the structural determination of the polysaccharide. The liquid state ^{1}H and ^{13}C-NMR of all the mucilage isolated from the different underutilized cereals were recorded and is shown in Fig. 4. From the ^{1}H-NMR it was confirmed that the protons in the up-field region that may be present in the mucilage might be attributed to the aliphatic protons. The peak around δ1.32 ppm is due to the methyl groups. The spectra of all the mucilage show the crowded region near δ3.1-5.3 ppm, indicating the polysaccharide region and the presence of various similar sugars units[25]. According to Kaushik et al., the peaks in the range of δ3-4.3 ppm are due to non-anomeric protons and δ4.5-5.5 ppm are due to anomeric protons[26]. The ^{1}H signals observed near δ3.35-3.58 ppm was due to the -CH_2 and -OH group of arabinose. The signal between δ3.43-3.69 ppm was due to -CH and -OH group of mannose. The presence of anomeric protons has been assigned to α-sugar residue (δ5-6 ppm) and β-sugar residues (δ4-5 ppm) as reported earlier by Singh et al.[24]. So, the signals in the range of δ5.0- 5.3 ppm can be assigned due to α-anomeric protons and from δ4.30-4.96 ppm was assigned due to β-anomeric protons. The overall study of ^{1}H NMR of different mucilages revealed that mucilage may contain arabinose, mannose and various sugar units. In the ^{13}C-NMR of mucilages, the data revealed that the peak near δ72.37 ppm indicates the presence of -CH group of

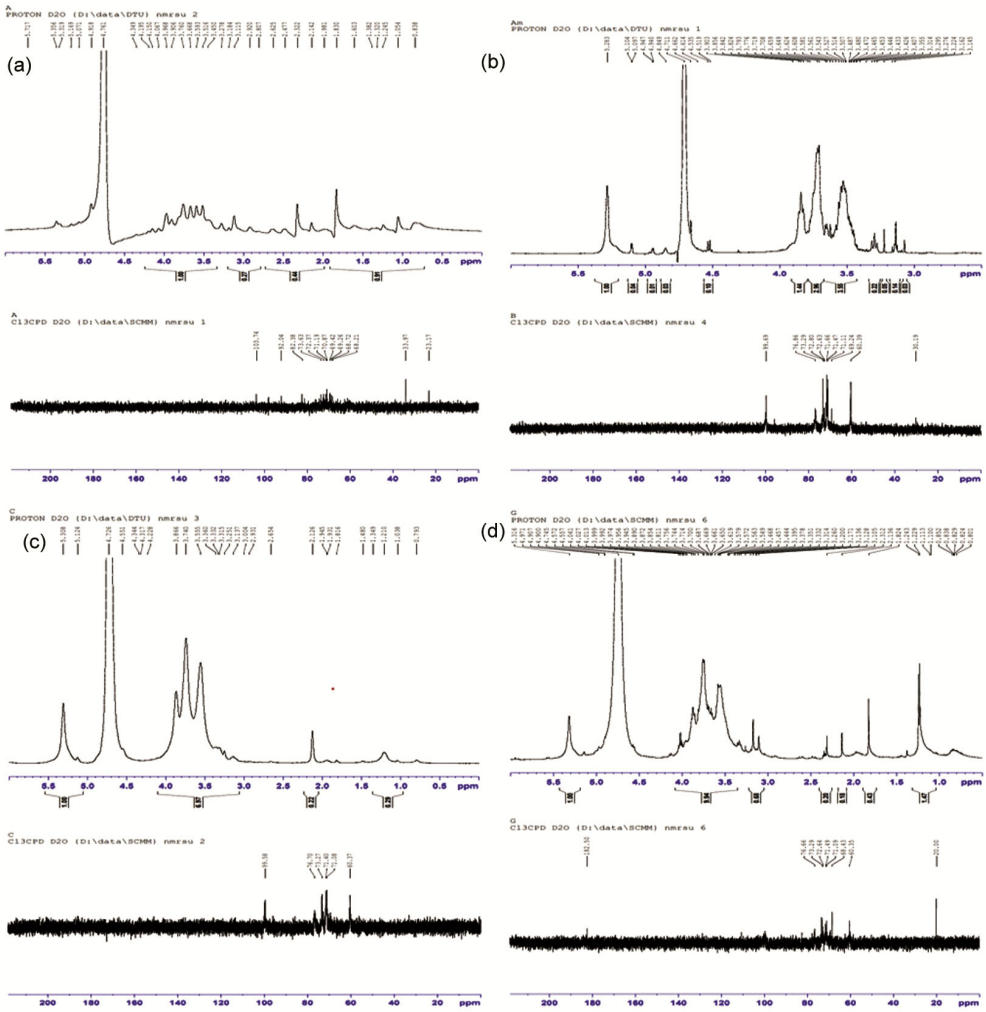

Fig. 4 — ^{1}H and ^{13}C-NMR spectra of (a) A_b (b) A_m (c) P_r (d) L_m

mannose and δ70- 71.66 ppm indicates the presence of -CH of arabinose.

Exploration of mucilage as hydrogel

Synthesisof M-co-AAc hydrogels

The hydrogels were successfully synthesized by free radical polymerization and is mentioned in Table 1. The proposed mechanism for the formation of M-co-AAc graft copolymeric hydrogels is shown in Fig. 2(B). According to Sennakesavan et al., first, KPS turns into persulfate radical by thermal decomposition[27]. The radicals formed attacks the hydrophilic groups present in the mucilage and makes it a reactive species. The sodium acrylate makes a covalent bond with the hydroxyl groups of the mucilage and hence makes poly(sodium acrylate). Then, termination of the polymerization is carried out using MBA by the formation of cross-linking junctions. This results in the formation of 3D polymeric structure of the hydrogels.

Table 7 — Swelling index of the formulated hydrogels

S. No.	Hydrogel formulation	% Swelling index
1.	A_bH	26854
2.	A_mH	28134
3.	P_rH	14794
4.	L_mH	35199

Swelling index

Swelling studies of the hydrogels in deionized water at 25°C is shown in Table 7. It is well known fact that hydrogels when immersed in water, tends to absorb it and swelling ratio increases with time until equilibrium is attained. The interaction between the hydrophilic groups of the polysaccharide hydrogel and water molecules led to an increase in swelling. As the hydrophilicity of the

hydrogel is increased, the swelling index increases. Thus, M-co-AAc hydrogels show significantly higher swelling index than the mucilage itself. According to the swelling studies, L_mH was observed to have shown maximum swelling index in deionized water hence it can be predicted that it is more hydrophilic in nature as compared to others[28]. The dried and swollen hydrogel is shown in Fig. 2(C).

Instrumental analysis of hydrogels

FTIR-ATR

FTIR-ATR analysis was done to confirm the AAc grafting on mucilage isolated from all four cereals. FTIR-ATR data of all the hydrogels is shown in Table 8 and the spectra is shown in Fig. 5(A). The stretching band at 3305 cm^{-1} indicated the presence of -OH group present in the polysaccharide. The observed wavenumber near 2904 cm^{-1} was due to aliphatic C-H stretching vibration. The absorption peak at 1722 cm^{-1} showed C=O stretching vibration, which is attributed to absorption shown due to the linking of poly(sodium acrylate) to the mucilage depicting (C=O) functional group[29]. Asymmetric stretching vibration of carboxylate ion at 1579 cm^{-1}. The confirmation of hydrogel formation is also evaluated by absorption bands near 1340-900 cm^{-1} which shows C-N stretching due to crosslinking of MBA, and poly(sodium acrylate). The appearance of wavenumber at 1041 cm^{-1} indicated the presence of C-O-C stretching vibration[30].

Table 8 — FTIR-ATR data of all four hydrogels

S. No.	Functional group	Vibration	A_bH (cm^{-1})	A_mH (cm^{-1})	P_rH (cm^{-1})	L_mH (cm^{-1})
1.	O-H group	Stretching	3305	3300	3282	3295
2.	C-H group	Stretching	2904	2942	2925	2931
3.	C=O group	Stretching	1722	1717	1718	1717
4.	COO^- group	Asymmetric stretching	1579	1557	1556	1560
5.	C-N group	Stretching	1402	1406	1402	1401
6.	C-O-C group	Stretching	1041	1050	1048	1040

SEM analysis

To evaluate the morphological features of the prepared hydrogels, scanning electron microscopy was done. The SEM images of dried hydrogels are shown in Fig. 6. The SEM images showed the porous morphology and rough surface of the super absorbent hydrogels. The pores in the hydrogel allow more liquid to seep into the voids. The large number of pore is responsible for the swelling behaviour of synthesized hydrogels. From the SEM data, it is evident that L_mH showed a greater number of pores as compared to other hydrogels, which supports its highest swelling index[31].

TGA analysis

The stability profiles of hydrogels were studied by TGA, as shown in Fig. 5(B). All four thermograms showed four phase degradation 30-200°C, 200-360°C, 360-570°C, and 570-700°C. The first phase degradation is due to moisture removal, second phase represents the decomposition of the polysaccharide chains and the latter two phases represents the

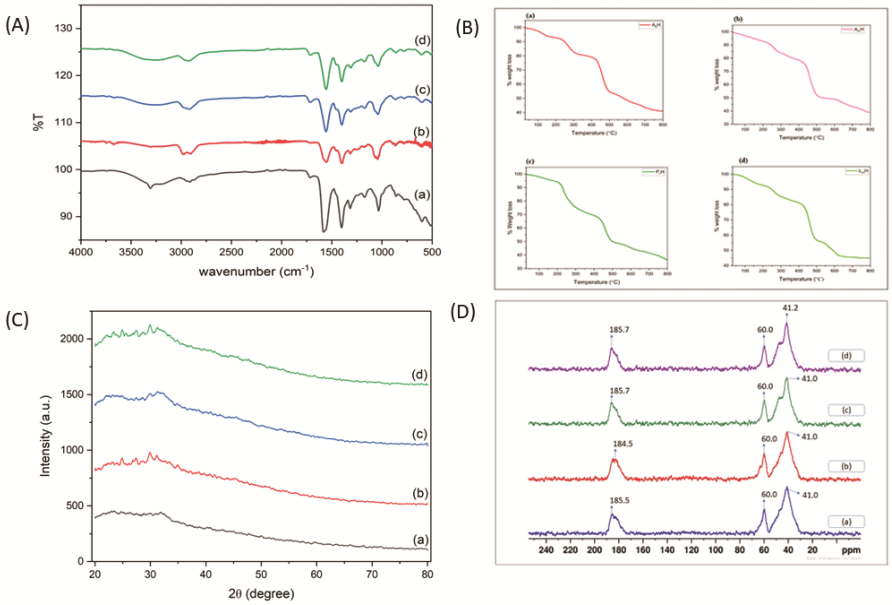

Fig. 5 — (A)-FTIR spectra, (B) TGA plots, (C)-XRD plots and (D) ^{13}C-NMR spectra of the hydrogels (a) A_bH (b) A_mH (c) P_rH (d) L_mH

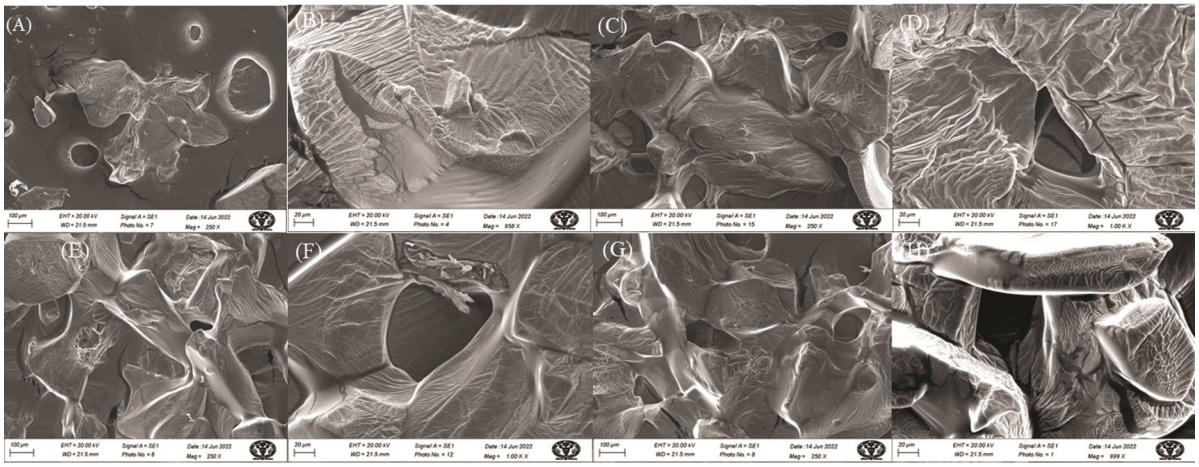

Fig. 6 — SEM micrographs of the hydrogels (a) A_bH sample at approx.250 X, (b) A_bH sample at approx. approx.1000 X, (c) A_mH sample at 250 X, (d) A_mH sample at approx.1000 X, (e) P_rH sample at approx.250 X, (f) P_rH sample at approx.1000 X, (g) L_mH sample at approx.250 X and (h) L_mH sample at approx.1000 X

complete breakdown of the polysaccharide backbone and sodium acrylate chain, respectively[29]. Among all the hydrogels, L_mH is thermally more stable as it has 45% of residual weight at 800°C. The thermal stability order of hydrogels is $L_mH > A_bH > A_mH > P_rH$. The TGA data clearly proved that thermal stability has increased in the case of all hydrogels as compared with their native mucilaginous polysaccharides.

XRD

Fig. 5(C) represents the diffractograms of all four hydrogels obtained from XRD. The XRD diffractogram data revealed that there was no sharp peak obtained in all the hydrogel samples. This indicates the amorphous nature of all four hydrogels[33].

^{13}C-NMR

The solid state ^{13}C NMR spectra of all four hydrogels are shown in Fig. 5(D). The ^{13}C-NMR peaks are nearly similar in the case of all four hydrogels. The broad peak at δ185.7 ppm can be attributed to the carboxylate group of poly(sodium acrylate), δ60.0 ppm depicted the -CH_2OH group present in the mucilage, and δ41.0 ppm represented the methylene carbon (-CH_2-) which is due to the introduction of MBA crosslinker in the formation of hydrogels[34]. The peaks observed in all four spectra confirmed the synthesis of hydrogels by chemical crosslinking of poly(sodium acrylate) on the mucilage with the help of MBA as a crosslinking agent. Hence, ^{13}C-NMR data confirmed that all four mucilaginous polysaccharides have been crosslinked to form hydrogels.

Conclusion

The present study concludes that mucilage isolated from the seeds of underutilized cereals of Adzuki beans (*Vigna angularis*), Amaranth (*Amaranthus*), Proso millet (*Panicum miliaceum*), and little millet (*Panicum sumatrense*) would be useful in pharmaceutical and bio-medical applications. Spectroscopic analysis (FTIR-ATR and ^{1}H & ^{13}CNMR) shows the presence of polysaccharides as carbohydrate residues in the mucilage which confirms the mucilage's' excipient property. The mucilages characteristics and applicability in advanced technical fields are enhanced by the modification of mucilages by graft copolymerization with sodium acrylate. The prepared hydrogels exhibited porous structure and a remarkable swelling index along with enhanced thermal properties with respect to their mucilages. So, from a technical perspective, these functionalized polymers are capable of playing a significant role in various fields.

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