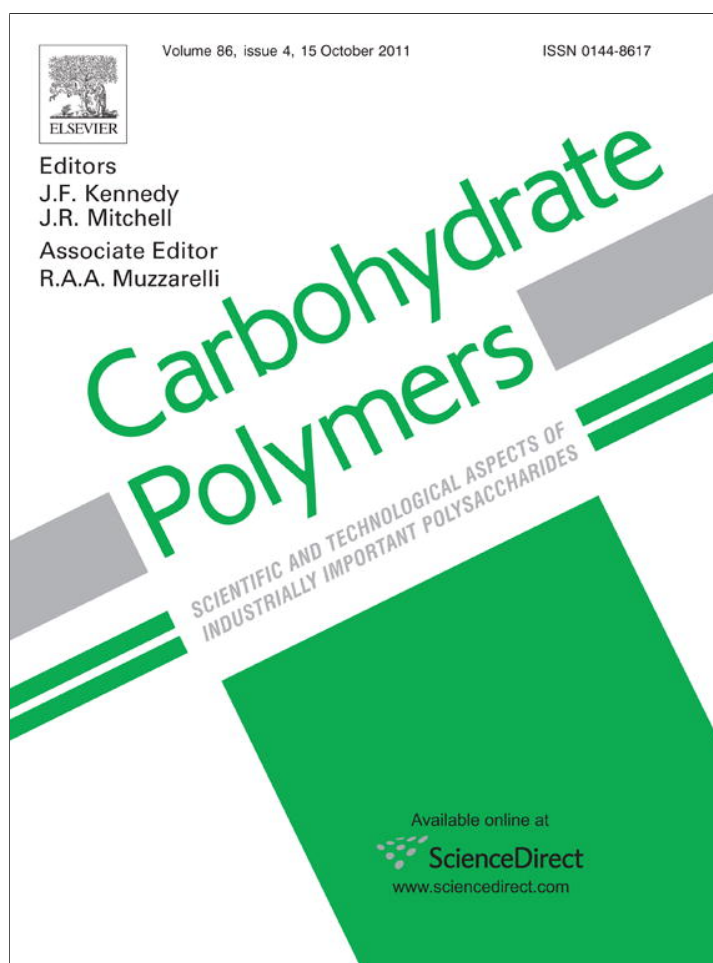


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Thermal studies of plant carbohydrate polymer hydrogels

Mohammad S. Iqbal^{a,*}, Jamshed Akbar^b, Shazia Saghir^c, Abdul Karim^b, Andreas Koschella^d, Thomas Heinze^{d,1}, Muhammad Sher^e

^a Department of Chemistry, Forman Christian College, Lahore 54600, Pakistan^b Department of Chemistry, University of Sargodha, Sargodha 40100, Pakistan^c Department of Chemistry, Government Post-graduate College for Women, Wahdat Road, Lahore, Pakistan^d Friedrich Schiller University of Jena, Institute for Organic Chemistry, Centre of Excellence for Polysaccharide Research, Humboldtstrasse 10, D-07743 Jena, Germany^e Department of Pharmacy, University of Sargodha, Sargodha 40100, Pakistan

ARTICLE INFO

Article history:

Received 31 May 2011

Received in revised form 1 July 2011

Accepted 9 July 2011

Available online 19 July 2011

Keywords:

Natural hydrogels

Modified arabinoxylans

Thermal analysis

Pyrolytic GC–MS

Thermal parameters of hydrogels

ABSTRACT

Isolation and thermal analysis of hydrogels from *Plantago ovata* (PO), *Salvia aegyptiaca* (SA), *Ocimum basilicum* (OB) and *Mimosa pudica* (MP) are reported. The hydrogel obtained from PO was modified by cross-linking, carboxymethylation and ethylation as a model to see the effect of modification on thermal behavior. Activation energy, enthalpy, entropy, free energy change, pre-exponential factor, comprehensive index of intrinsic thermal stability (ITS) were determined from the thermograms. The ITS values indicated good thermal stabilities of the hydrogels. Hydrogels isolated from SA, OB and MP did not show significant differences in their thermal behavior, whereas significant differences in thermal profiles of PO gel and its modified forms were observed. The modified gels exhibited improved thermal stability. Formation of water, 2-hydroxybutanedial, 3-hydroxypropanal and 2-furfuryl alcohol as degradation products was detected in the GC–MS analysis of some of the materials. The possible implications of these results are discussed.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogels are three-dimensional, hydrophilic, polymeric networks that absorb large quantities of water and swell producing a gel like material. They can be derived from natural or synthetic sources. They have a number of applications in medical and pharmaceutical preparations, food technology, tissue engineering, etc. (Barbucci, 2009; Davis & Anseth, 2002). Some of these materials are well characterized and well recognized industrial chemicals, e.g., hydroxypropylmethyl cellulose (HPMC) is widely used as a drug carrier and carboxymethyl cellulose is used as a thickener in food items. Hydrogels are being extensively explored for their potential in tissue engineering, biosensors and drug delivery devices (Peppas, Bures, Leobandung, & Ichikawa, 2000). Although synthetic polymers have well established structures suitable for such applications but natural hydrogels may be preferable for being biocompatible (Lin & Metters, 2006). Among the natural hydrogels, polysaccharide-based materials have gained much attention due to their low cost and high biocompatibility (Coviello, Matricardi, Marianecchi,

& Alhaique, 2007; Dumitriu, 1998; Munarin, Petrini, Farè, & Tanzi, 2010).

It has been reported that seeds of PO, SA, OB and MP all contain swellable polysaccharides. PO is best known for its production of ispaghula husk, obtained from the dried seeds by mechanical milling/grinding of the outer layer of the seed. It is a white fibrous hydrophilic material. Ispaghula husk is a medicinally active polysaccharide (Singh, 2007). Hot water-extracted arabinoxylans from seeds of PO have recently been reported as good drug carriers (Iqbal, Akbar, Hussain, Saghir, & Sher, 2011). Seeds of PO, SA, OB and MP have been used in traditional medicines since long time for the treatment of different diseases (Duke, 2002; Hammiche & Maiza, 2006; Rahman, Mossa, Al-Said, & Al-Yahya, 2004). The chemical nature of these hemicellulosic polysaccharides has been studied by many workers (Azuma & Sakamoto, 2003; Chatterjee & Mukherjee, 1958; Farooqi, Kapoor, & Khan, 1977; Fischer, Yu, Gray, Ralph, Anderson, & Marlett, 2004; Saghir, Iqbal, Hussain, Koschella, & Heinze, 2008; Tharanathan & Anjaneyalu, 1972, 1975). Thermal stability of hemicelluloses generally decreases with decrease in molar mass (Jin et al., 2009). The differential scanning calorimetry curves of some hemicelluloses show an endothermic peak from 85 to 110 °C due to the loss of moisture as hydrogen-bonded water to the hemicellulosic structure.

Comprehensive studies on the physicochemical properties of polysaccharides from various sources are required to find their rational application in food, pharmaceuticals and manufacture of

* Corresponding author. Tel.: +92 42 37058841.

E-mail address: saeediq50@hotmail.com (M.S. Iqbal).¹ Member of the European Polysaccharide Network of Excellence (EPNOE), <http://www.epnoe.eu>.

other products (Khomutov, Ptichkina, Sheenson, Lashek, & Panina, 1994). Thermal stability of prospective materials is a key factor in determining their potential in various applications (Villette et al., 2002; Zohuriaan & Shokrolahi, 2004). Therefore, it was thought worthwhile to study the thermal behavior of some of the important hydrogels prepared from PO, SA, OB and MP.

2. Materials and methods

2.1. Materials

The materials used in this study were: PO husk and seeds, seeds of SA, OB and MP were obtained from local market; acetone; acetic acid; methanol; carboxyamidediimidazole (CDI); dimethylsulphoxide (DMSO); ethanol; sodium bicarbonate (all from E. Merck, Germany). The chemicals were used without further purification. Double-distilled water was used throughout this study.

2.2. Extraction of hydrogels from ispaghula seeds and husks

The hot water-extract of ispaghula seeds was obtained as per reported method (Iqbal et al., 2011). Isolation of the hydrogel from husk by use of acetic acid as coagulating solvent was carried out as reported earlier (Saghir et al., 2008). Other fractions were isolated by using acetone, methanol and ethanol instead of acetic acid. Briefly, ispaghula husk (15 g) was transferred to a 2-L beaker containing distilled water (500 cm³) and kept overnight. The mixture was then treated with the appropriate solvent in order to coagulate the hydrogel completely; the gel was filtered out, washed and air-dried. The hydrogel fractions thus obtained were characterized, as previously (Saghir et al., 2008), to be arabinoxylans (AXs) and coded as AXH (hot water process), AXE (ethanol process), AXM (methanol process) and AXA (acetone process).

2.3. Extraction of gel from seeds of OB, SA and MP

The seeds (15 g) were washed with distilled water (50 cm³) and transferred to a 2-L beaker containing distilled water (500 cm³). After soaking for 6 h, the mixture was blended with blunt blades vigorously using kitchen blender. The mucilage was separated from seeds by filtration through muslin cloth. The mucilage was divided into three portions. One portion was air-dried as such for 1 week; the second and third portions were treated, respectively, with acetone and methanol. The coagulated material was filtered out, air-dried and powdered by use of kitchen grinder. The materials from SA, OB, MP and their yields were: SAD (direct dried), 12%; SAA (acetone process), 9%; SAM (methanol process), 9%; OBD (direct dried), 11%; OBA (acetone process), 9%; OBM (methanol process), 8%; MPD (direct dried), 12%; MPA (acetone process), 9%; and MPM (methanol process), 9%.

2.4. Modification of arabinoxylans

Keeping in view the importance of AXs isolated from ispaghula (Iqbal et al., 2011; Niño-Medina et al., 2010) thermal behavior of chemically modified fractions, including carboxymethylarabinoxylans (CMAXs), ethyl arabinoxylans (EAXs) and cross-linked arabinoxylans (CLAXs), was studied in detail to see the effect of modification on various thermal parameters. The carboxymethylation and ethylation were carried out as described earlier (Saghir et al., 2008; Saghir, Iqbal, Koschella, & Heinze, 2009) and cross-linking was achieved as follows. The isolated AX (0.5 g, 3.75 mmol) was dissolved in DMSO (30 cm³) at 80 °C by stirring. To this CDI (0.087 g, 0.536 mmol) was added and the mixture was further stirred for 20 h with heating at 60 °C. After this time the product was filtered out, washed with ethanol, neutralized to pH 7 with

Table 1

Reaction conditions for the synthesis of CLAXs 1–4 (in DMSO as slurry medium at 60 °C), WRV and elemental analysis data.

Sample code	Molar ratio ASU:CDI	Time (h)	WRV (%)	C (%)	H (%)
AX	–	–	8100	40.4	6.1
CLAX-1	1:0.2	16	455	39.9	6.3
CLAX-2	1: 0.14	20	188	39.8	5.9
CLAX-3	1:0.33	20	128	40.6	5.9
CLAX-4	1:1	20	72	41.6	5.5

dilute NaHCO₃ solution, washed again with water to remove salts and freeze-dried.

Cross-linked arabinoxylans (CLAXs) from samples 1 to 4, with different degrees of cross-linkage, were obtained by use of different molar ratios of anhydrous sugar unit (ASU) to CDI, and different reaction time (Table 1). Percentage yields of CLAXs could not be determined due to lack of information about exact degree of cross-linking.

The water retention values (WRV) of AX and CLAXs were determined by centrifugation method (Saghir, 2009). Accurately weighed sample (approximately 0.5 g) was mixed with water (100 cm³). It was kept at 30 °C for 2 h for complete swelling. The swollen material was transferred to four glass tubes equipped with permeable bottom (fritted glass) and centrifuged at 4000 rpm for 15 min. Water was removed by centrifugation. During centrifugation process the gel blocked the sintered pores; hence, excess water was decanted off the gel after centrifugation. The samples were dried at 105 °C in an oven until constant weight. The mass difference before and after drying was used for calculation.

$$\text{WRV}(\%) = \left[\frac{W_w - W_d}{W_d} \right] \times 100 \quad (1)$$

where W_w and W_d are the weights of samples in wet state and after drying, respectively. The average ($n=6$) WRV (%) of AX and CLAXs were determined. However, WRV of EAXs was difficult to determine by this method because EAXs blocked the sintered pores of glass tube during centrifugation resulting variation in WRV. The WRV of CMAXs was not determined because of their solubility in water.

2.5. Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with a simultaneous thermal analyzer SDT, Q-600 (TA instruments, USA), under nitrogen atmosphere at a flow rate of 100 cm³ min⁻¹ with 10 °C min⁻¹ heating rate in the temperature range ambient (20 °C) to 600 °C using platinum crucible. Activation energy (E_a) and pre-exponential factor (A) for a major stage of decomposition were determined by Broido's method (Broido, 1969) using Eq. (2).

$$\ln\{\ln(1/y)\} = -\frac{E_a}{RT} + \ln \frac{ART_m^2}{\theta E_a} \quad (2)$$

where $y = (w_t - w_\infty)/(w_0 - w_\infty)$, w_t is the weight of the sample at any time t , w_0 the initial weight and w_∞ the final weight; R the general gas constant; θ the heating rate and T_m the temperature for maximum reaction rate. A plot of $\ln\{\ln(1/y)\}$ against $1/T$ gives a straight line, the slope of which gives E_a and intercept gives A . Although kinetic parameters are better estimated by use of multiple heating rate methods such as isoconversional methods, however, single heating rate methods are being used by several researchers (Adel, El-Wahab, Ibrahim, & Al-Shemy, 2010; Anandalakshmi, Parthiban, Parvathi, Thanikachalam, & Mojumdar, 2011; Ghaemy & Amini Nasab, 2010; Madani, 2011; Nam, Park, Ihm, & Hudson, 2010; Spencer & Kohl, 2011).

Table 2
GC–MS data.

Experimental conditions of GC–MS analysis		
GC	Carrier gas = helium; flow rate = 1.2 cm ³ min ⁻¹ ; injection temperature = 200 °C; ion source temperature = 200 °C; interface temperature = 250 °C; temperature program = injection at 50 °C and hold for 2 min, temperature increase of 2 °C min ⁻¹ to 150 °C followed by an isothermal hold for 15 min, temperature increase of 5 °C min ⁻¹ to 300 °C, followed by an isothermal hold at 300 °C for 15 min.	
MS	Mode = electron impact; ionization energy = 70 eV	
Mass spectral data of identified compounds		
Compound	Mol. mass	Mass fragments
Water	18	18, 17
2-Hydroxybutanedial	102	102, 84, 74, 44, 69, 55, 45, 43, 42, 39
3-Hydroxypropanal	74	74, 73, 60, 56, 45, 44, 42, 41
2-Furfuryl alcohol	98	98, 97, 81, 70, 69, 53, 42, 41, 39

The enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) were determined by use of standard equations (Adel et al., 2010; Ghaemy & Amini Nasab, 2010; Mallakpour & Dinari, 2010). Thermal stabilities of the hydrogels were determined by integral procedural decomposition temperature (IPDT) and comprehensive index of intrinsic thermal stability (ITS) by Doyle's method (Doyle, 1961). The data were analyzed by the use of Universal Analysis 2000 software, version 4.2E (TA Instruments, USA), and MS Excel[®] 2010. Thermograms were compared by difference (f_1) and similarity (f_2) factors (Eqs. (3) and (4), respectively) calculated by a reported method (Moore & Flanner, 1996).

$$f_1 = \frac{\sum_{t=1}^n |R_t - T_t|}{\sum_{t=1}^n |R_t|} \times 100 \quad (3)$$

$$f_2 = 50 \times \log \left\{ \left[1 + \left(\frac{1}{n} \right) \sum_{t=1}^n |R_t - T_t|^2 \right]^{-0.5} \times 100 \right\} \quad (4)$$

where R_t is the remaining weight at a particular temperature of the reference TGA curve (unmodified material) and T_t is the remaining weight at a particular temperature of the test TGA curve (modified material). The summation was done over all the points, n , taken at 5 °C interval. The closer the f_1 value to zero and f_2 value to 100, the greater the similarity among the curves. Generally, f_1 value in the range 0–15 and f_2 value greater than 50 are sufficient to establish the equivalence of two curves. Hierarchical cluster analysis (HCA) was performed to classify the materials with similar thermal properties by use of STATISTICA 8 and dendrogram were drawn using weighted pair-group average and Euclidean distance.

2.5.1. Pyrolytic GC–MS analysis

Volatile fractions from thermal degradation in the ranges 80–120 °C and 300–320 °C of some of the representative samples were collected from the headspace and analyzed by GC–MS technique using 1 μ L aliquots of the solutions of the fractions dissolved in acetone (10 cm³). The GC–MS system consisted of a GC2010 gas chromatograph interfaced with a GCMSQP2010 mass selective detector. The capillary column used was DB5–MS with dimensions 30 m \times 0.25 mm I.D. and film thickness of 0.25 μ m (Schimadzu, Japan). The chromatographic and mass spectrometric conditions are given in Table 2. Data were acquired and processed with the Lab Solution[®] software (Schimadzu, Japan). Compound identification was performed by comparison with the chromatographic retention characteristics, reported mass spectra (Faix, Fortmann, Bremer, & Meier, 1991a, 1991b; Müller-Hagedorn, Bockhorn, Krebs, & Müller, 2003) and the mass spectral library of the GC–MS data system.

3. Results and discussion

3.1. Isolation of materials

The hydrogels were isolated in good yield (8–12%). The dried hydrogels were white, off-white or light brown in color. Both natural and modified hydrogels showed good swelling characteristics in water. Solvent separated hydrogels were more neat and whiter than others.

3.2. Modification of arabinoxylans

Carboxymethylation, ethylation and cross-linking of AX were achieved successfully according to the experimental procedures adopted. Schematic representation for the synthesis of cross-linked AX, CLAX, is given in Scheme 1. In order to ensure complete conversion of the CDI, the reaction was carried out for 16–20 h at 60 °C (Heinze, Liebert, & Koschella, 2006). Cross-linking of polymers may influence the physical characteristics such as solubility, swelling ability, viscosity and elasticity. In the CLAXs samples 1–4, it was observed that with an increase in reaction time, rate of cross-linking increased even at lower CDI to ASU molar ratios (CLAX-2) as indicated by the decrease in WRV (Table 1). The WRV decreased with increase in cross-linking. For example the WRV of non-cross-linked AX was 8100%, which reduced to 455–72% after cross-linking.

AX is soluble in DMSO at 80 °C as well as aqueous NaOH solution at room temperature. In contrast, the cross-linked samples CLAXs 1–4 were insoluble in DMSO, aqueous NaOH solution, water, ethanol, methanol, 2-propanol, diethyl ether, chloroform, acetone, tetrahydrofuran, and *N,N*-dimethylformamide. The products were characterized by elemental analysis, FT-IR spectroscopy, and thermal analysis. Elemental analysis showed slight decrease in percentages of carbon and hydrogen (Table 2) as compared with unmodified AX. The authenticity of these results was ensured by repeating elemental analysis several times. This indicates cross-linking with CDI results in increase in percentage of oxygen and decrease in percentage of carbon and hydrogen. Absence of nitrogen indicated that CDI and by-product imidazole has been removed completely.

FT-IR spectra of CLAXs 1–4 are shown in Fig. 1. The assignments of the FT-IR absorption bands observed in the spectra of CLAXs are: 3496 cm⁻¹ (ν OH), 2979 cm⁻¹, 2939 cm⁻¹ (ν CH), 1760 cm⁻¹ (ν C=O), 1635 cm⁻¹ (ν COO) 1475 cm⁻¹, 1399 cm⁻¹, 1254 cm⁻¹, 1167 cm⁻¹, 1051 cm⁻¹, (ν C–H or ν C–O) 1005 cm⁻¹, 784 cm⁻¹,

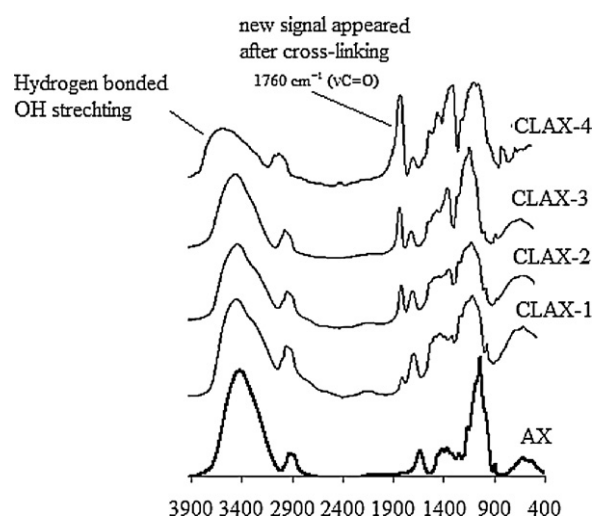
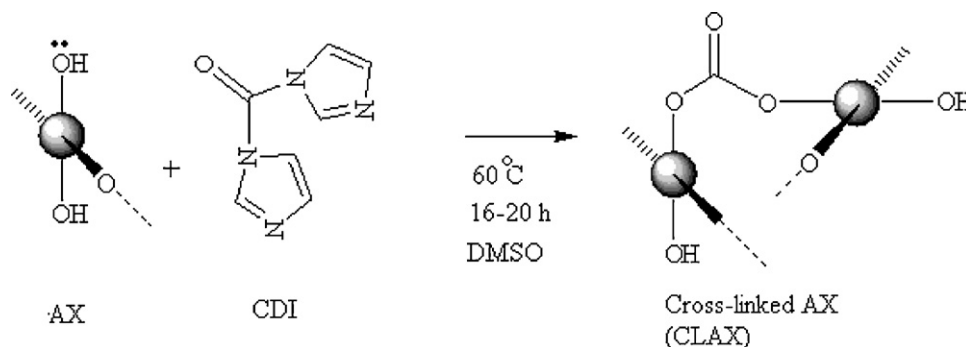


Fig. 1. FT-IR spectra of CLAXs 1–4.



Scheme 1. Schematic representation for the synthesis of CLAX with CDI.

761 cm^{-1} , 649 cm^{-1} , 596 cm^{-1} , and 519 cm^{-1} (polymer backbone bendings). It can be seen that intensity of the peak at 1760 cm^{-1} ($\nu\text{C}=\text{O}$) increases with the increase of CDI molar ratio used for cross-linking. The intensity of the $\nu\text{C}=\text{O}$ peak also increased with increase in reaction time. This is evident from the example of CLAX-1, which was synthesized with a higher CDI molar ratio and 16 h reaction time resulting in low cross-linking as compared to that in CLAX-2 synthesized with lower CDI molar ratio and 20 h reaction time.

3.3. Thermal studies

DSC and TGA studies of hydrogels and modified AXs were carried out to get qualitative and quantitative information about thermal transitions. The results are discussed as follows.

3.3.1. Natural hydrogels

TGA of natural hydrogels isolated from the plant materials under investigation by different methods mainly showed a two-

stage decomposition behavior (Fig. 2agr1). An early endothermic weight loss (8–12%) in the range 80–120 °C was also observed in all the samples. This was assigned to the loss of absorbed moisture as supported by GC–MS analysis of the fractions collected in this range (Table 2) and also by some earlier studies (Peng & Wu, 2010; Popescu, Popescu, Lisa, & Sakata, 2011; Yang, Yan, Chen, Lee, & Zheng, 2007). The first major stage of decomposition is characterized by the initial decomposition temperature (IDT) in the range 220–270 °C and final decomposition temperature (FDT) in the range 310–375 °C. This stage resulted in 39–56% weight loss with a small exothermic enthalpy change (ca. Fig. 3a). GC–MS analysis of the fractions collected in this range revealed the expulsion of 2-hydroxybutanedial, 3-hydroxypropanal and 2-furfuryl alcohol as the main pyrolytic products (Table 2). These results suggest that the hydrogels undergo a low energy chain scission producing high mass volatiles. These pyrolytic products have also been reported previously (Fagerston, 1969; Faix et al., 1991a; Müller-Hagedorn et al., 2003). For the second major decomposition stage, the IDT

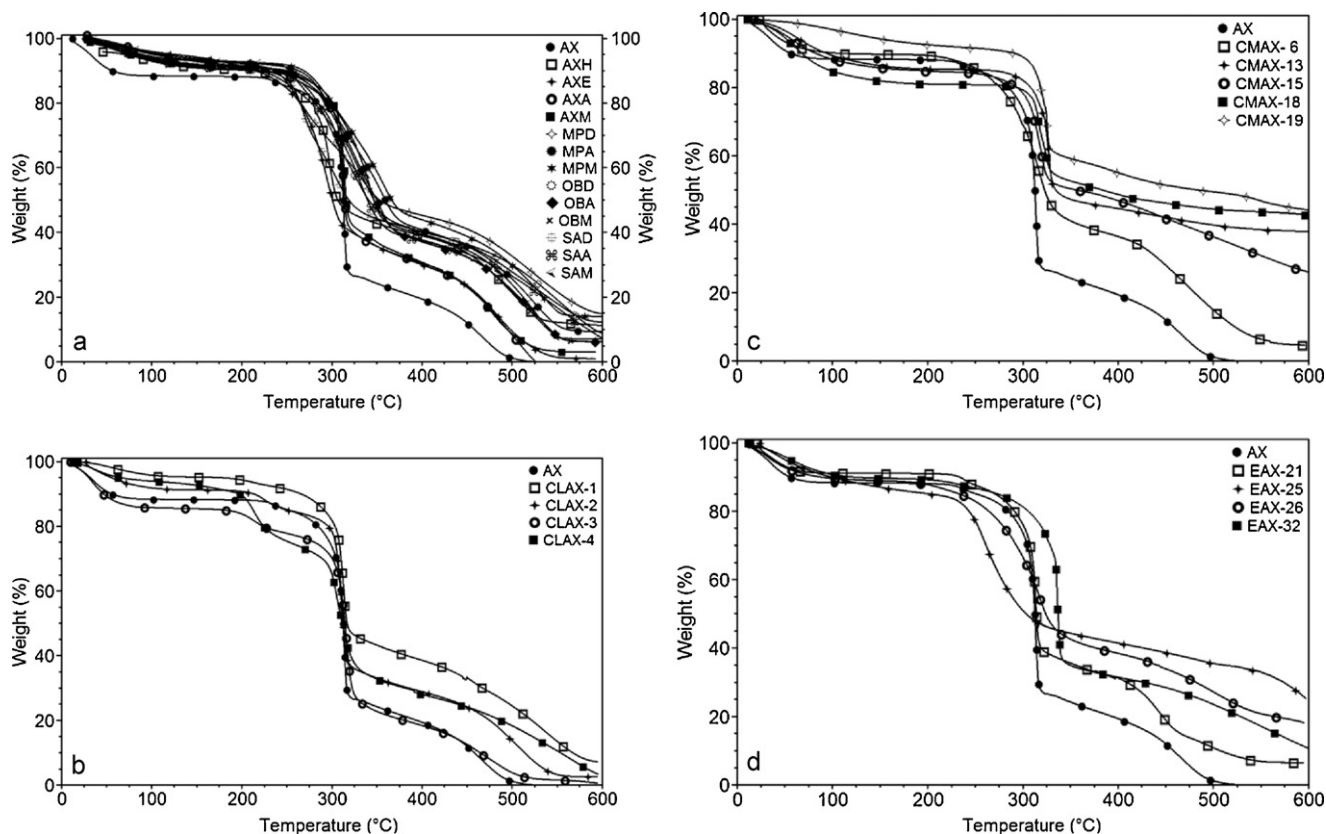


Fig. 2. TGA curves (a) natural hydrogels, (b) AX and CLAXs (samples 1–4) synthesized under different reaction conditions, (c) AX and CMAXs of different DS values synthesized under different reaction conditions, and (d) AX and EAXs of different DS values synthesized under different reaction conditions.

Table 3
Thermal analysis data of natural hydrogels.

Sample code	Temp. range ^a (°C)	Mass loss (%)	E_a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (J K ⁻¹ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	lnA	IPDT (°C)	ITS	Mass at 600°C (%)
AX	240–315	56.79	139.61	134.74	-74.06	178.07	21.22	269.42	0.44	0.40
AXH	220–310	41.46	141.43	138.70	-54.78	169.87	23.51	308.44	0.47	11.20
AXE	220–315	48.10	143.57	138.84	-52.32	168.56	23.81	287.21	0.47	0.99
AXA	245–315	45.60	136.53	131.67	-78.34	177.50	20.71	302.27	0.49	0.53
AXM	230–320	47.18	148.77	143.90	-56.79	177.18	23.30	300.99	0.49	14.59
MPD	240–355	39.67	108.68	104.22	-118.12	167.54	15.84	311.81	0.51	14.88
MPA	265–370	44.81	128.65	123.41	-99.08	185.83	18.29	325.78	0.54	9.34
MPM	265–375	43.51	123.76	118.51	-108.57	187.02	17.15	330.56	0.54	13.95
OBD	260–355	41.60	146.00	141.26	-60.80	175.91	22.79	312.07	0.51	8.79
OBA	270–365	46.31	146.57	141.60	-66.55	181.33	22.15	315.48	0.52	6.10
OBM	265–365	45.64	144.25	139.30	-69.64	180.80	21.77	310.99	0.51	6.09
SAD	250–325	39.22	148.57	144.07	-44.10	167.93	24.75	294.77	0.48	12.33
SA	250–360	47.80	120.86	115.83	-107.57	180.91	17.23	311.26	0.51	7.30
SAM	245–355	46.76	118.38	113.26	-114.14	183.57	16.45	321.94	0.53	7.14

^a Temperature range for the main stage of decomposition. lnA, E_a , ΔH^* , ΔS^* and ΔG^* were calculated for this stage. IPDT and ITS were calculated for the entire thermogram.

range was 415–450 °C and FDT range was 490–550 °C. The weight loss was around 20% accompanied by a wide exothermic enthalpy change (ca. Fig. 3a), which was attributed to the complete degradation of hydrogels forming gaseous molecules like CO, CO₂, H₂O, etc. and eventually leaving a carbon rich residue. The char yield at 600 °C varied from 0.4 to 14.88%. Glass transition temperature (T_g) could not be observed in the experimental temperature range. Thermal parameters, calculated from Broido plots (Fig. 3b shows a typical plot for AX) and standard equations, are presented in Table 3. The E_a values ranged from 108 to 148 kJ mol⁻¹ as observed for some other polysaccharides (Zohuriaan & Shokrolahi, 2004). The E_a depends on the conditions applied for thermal analysis, e.g. the E_a is lower when thermal degradation occurs in air than that in nitrogen atmosphere (Aggarwal, Dollimore, & Heon, 1997). E_a is also

related to the structural variations, e.g. conformational changes on the polysaccharides (Dumitriu, 1998). An overall thermal stability of the hydrogels was assessed by IPDT and ITS values. The IPDT and ITS ranges were 269–330 °C and 0.44–0.54, respectively. These values suggest a good thermal stability of the isolated hydrogels, which are comparable with those of other commercially available polysaccharides (Zohuriaan & Shokrolahi, 2004). In case of OB, the stability of hydrogels was almost extraction-method independent. However, in cases of SA and MP (ITS 0.48 and 0.51, respectively),

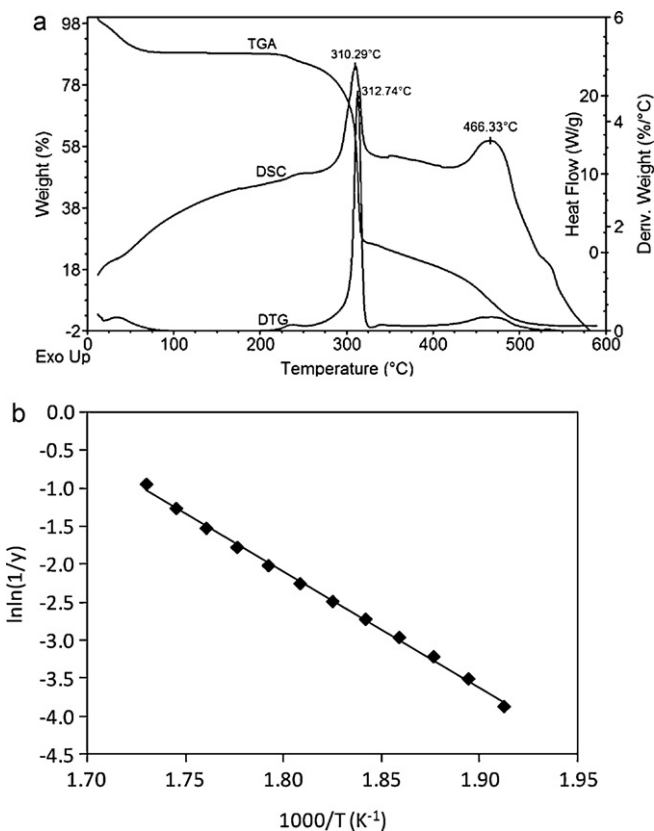


Fig. 3. (a) Representative TGA, DTG and DSC curves for AX, and (b) representative Broido plot for AX used for calculation of E_a and A.

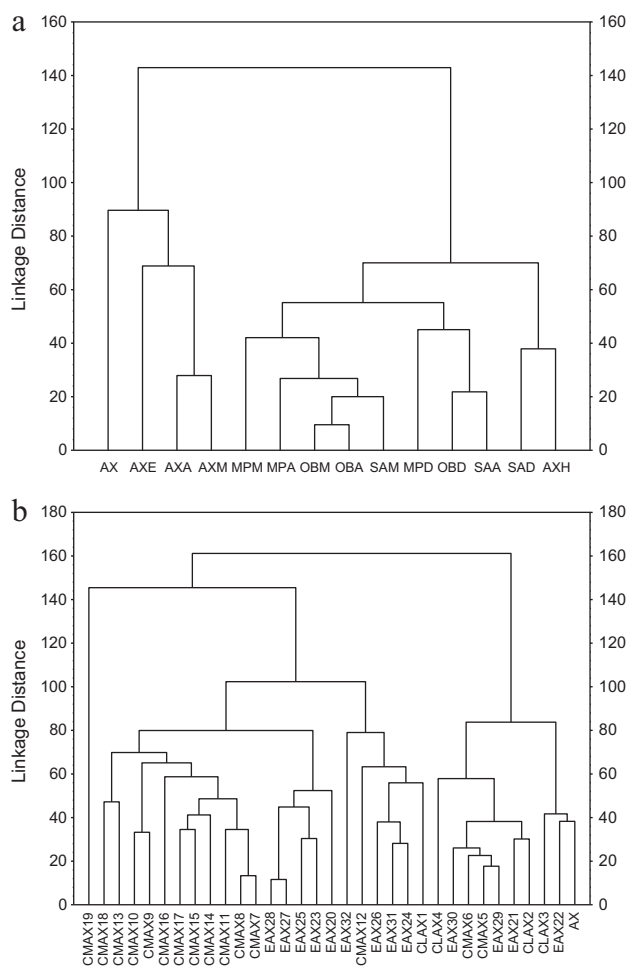
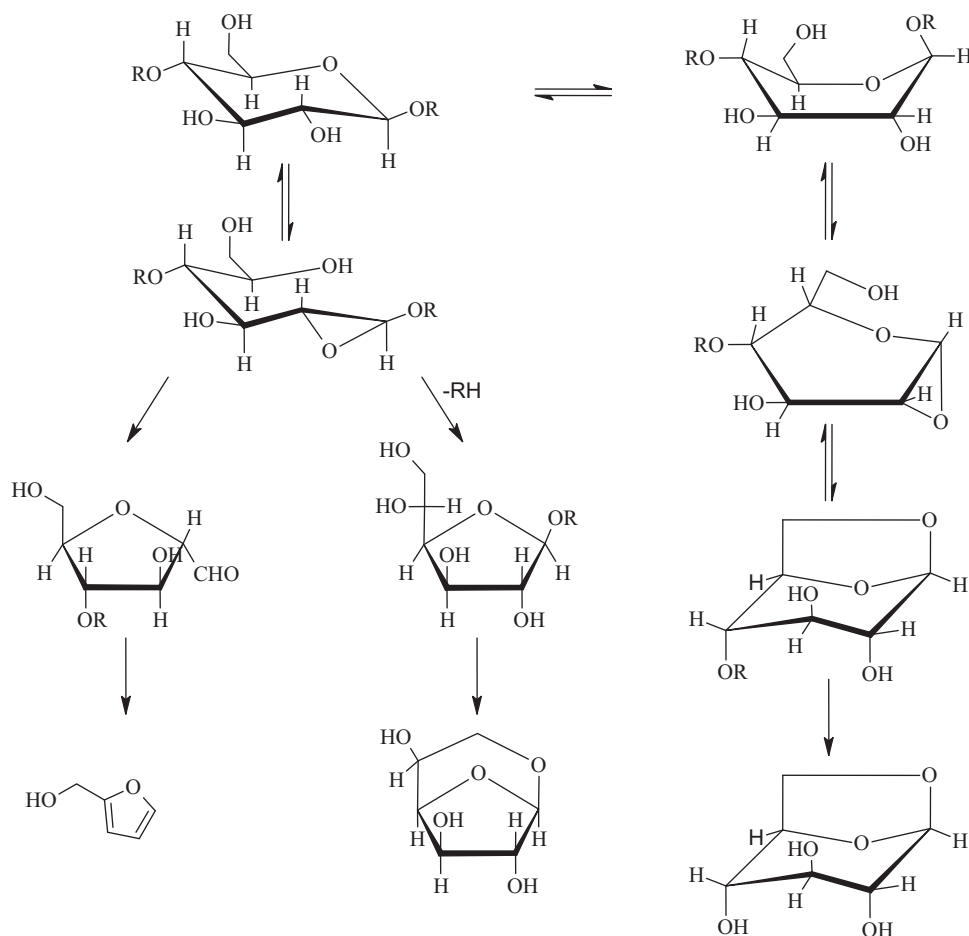


Fig. 4. Thermal classification of hydrogels: dendrogram showing similarity levels of thermograms for (a) natural hydrogels, and (b) AX and modified AXs.

Table 4
Thermal analysis data of modified hydrogels.

Sample code	DS	Temp. range ^a (°C)	Mass loss (%)	E_a (kJ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	ΔS^* (JK ⁻¹ mol ⁻¹)	ΔG^* (kJ mol ⁻¹)	lnA	IPDT (°C)	ITS	f_2	f_1	Mass at 600 °C (%)
AX	-	240–315	56.79	139.61	134.74	-74.06	178.07	21.22	269.42	0.44	-	-	0.40
CLAX-1	-	290–325	39.30	503.87	499.00	562.11	170.17	97.74	317.26	0.52	42.81	24.23	7.02
CLAX-2	-	295–320	43.34	736.80	731.95	965.96	168.80	146.31	288.88	0.47	57.81	11.12	2.65
CLAX-3	-	295–330	46.41	500.53	495.64	550.25	172.09	96.32	252.70	0.41	71.80	5.34	0.59
CLAX-4	-	295–330	33.18	373.93	369.12	336.62	174.22	70.61	280.97	0.46	51.80	16.28	2.90
EAX-20	0.13	235–335	39.74	127.63	122.84	-85.40	171.95	19.84	261.34	0.43	38.59	26.66	27.80
EAX-21	0.25	285–320	42.23	394.17	389.30	372.93	171.14	74.99	289.17	0.47	57.95	11.60	6.60
EAX-22	0.30	285–320	40.40	399.63	394.77	384.42	170.27	76.37	270.75	0.44	72.14	5.01	0.50
EAX-23	0.36	235–305	31.70	169.25	164.80	3.75	162.80	30.49	274.01	0.45	35.41	31.75	21.70
EAX-24	0.36	285–320	31.80	400.40	395.55	385.89	170.19	76.55	289.99	0.47	42.78	19.47	5.60
EAX-25	0.37	235–310	33.95	152.21	147.78	-29.53	163.52	26.49	260.60	0.42	34.75	31.96	25.20
EAX-26	0.40	245–335	38.29	144.63	139.72	-59.46	174.80	22.99	281.19	0.46	41.09	22.55	18.00
EAX-27	0.41	240–315	33.30	159.78	155.30	-18.79	165.43	27.79	242.68	0.39	32.55	34.33	37.40
EAX-28	0.44	235–325	34.80	130.17	125.72	-74.77	165.72	21.05	242.29	0.39	33.28	32.97	36.50
EAX-29	0.47	280–320	37.58	266.55	261.66	150.16	173.36	48.20	288.89	0.47	54.17	12.09	3.40
EAX-30	0.48	290–320	37.50	557.34	552.50	658.09	168.83	109.28	285.57	0.47	53.33	12.09	4.40
EAX-31	0.53	275–320	35.00	268.19	263.32	156.34	171.86	48.94	296.01	0.48	43.61	20.39	11.90
EAX-32	0.61	310–345	43.15	464.24	459.18	462.13	177.74	85.76	303.79	0.50	42.30	20.31	10.70
CMAX-5	0.08	250–330	42.30	169.58	164.69	-15.83	174.00	28.23	286.02	0.47	51.86	12.91	1.80
CMAX-6	0.12	260–340	41.00	180.91	176.01	2.26	174.67	30.41	289.20	0.47	49.29	15.00	4.70
CMAX-7	0.17	255–335	37.70	177.75	172.90	-0.94	173.45	30.02	279.59	0.46	34.53	30.22	33.00
CMAX-8	0.27	255–335	37.40	174.24	169.43	-5.84	172.81	29.42	271.20	0.44	34.08	30.58	35.00
CMAX-9	0.33	285–350	41.05	260.60	255.65	130.83	177.81	45.88	299.46	0.49	36.79	28.61	26.03
CMAX-10	0.43	280–340	38.30	260.19	255.24	132.83	176.07	46.13	298.28	0.49	34.19	32.36	31.51
CMAX-11	0.48	265–330	34.30	238.09	233.31	107.86	171.29	43.09	252.46	0.41	33.66	31.33	36.20
CMAX-12	0.61	270–320	29.40	258.21	253.45	147.75	168.94	47.88	295.47	0.48	37.50	28.31	16.98
CMAX-13	0.73	290–345	35.70	347.34	342.36	277.60	176.07	63.55	274.14	0.45	31.58	34.62	37.00
CMAX-14	1.07	275–320	29.10	354.49	349.72	315.46	168.96	68.05	274.72	0.45	35.88	28.71	21.90
CMAX-15	1.18	290–335	29.10	378.47	373.57	339.57	173.22	70.98	288.19	0.47	33.92	31.39	26.10
CMAX-16	1.37	280–310	27.40	566.39	561.63	692.40	164.88	113.39	243.95	0.40	31.05	36.42	38.10
CMAX-17	1.47	280–305	26.10	595.93	591.19	746.33	165.03	119.88	282.60	0.46	34.23	30.53	27.81
CMAX-18	1.72	305–335	24.00	546.64	541.74	620.59	175.59	104.78	248.98	0.41	29.10	40.16	42.60
CMAX-19	1.81	305–335	27.15	571.50	566.53	659.97	172.53	109.53	316.03	0.52	26.13	48.02	44.10

^a Temperature range for the main stage of decomposition. lnA, E_a , ΔH^* , ΔS^* and ΔG^* were calculated for this stage. IPDT, ITS, f_2 and f_1 were calculated for the entire thermogram.



Scheme 2. Mechanism of formation of anhydroglucoses and furfurals during thermal analysis (Fagerson, 1969).

for the hydrogels separated without use of any coagulating solvent, somewhat lower stability was observed. The positive ΔG^* values indicate a non-spontaneous degradation and negative ΔS^* values indicate the formation of a more ordered activated complex for all hydrogels. The cluster analysis indicated a good similarity of thermal behavior of hydrogels separated from MP, OB and SA by use of acetone and methanol except SAA (Fig. 4a). All AXs exhibited distinct thermal behavior than others except AXH, which is more close to SAD. However, the IPDT and ITS values for all AXs were lower than others (Table 3). TGA of AX rapidly went down to a very low char residue (0.4%) at the second major stage of decomposition. On the basis of overall thermal behavior, the natural hydrogels used in this study can be broadly divided into two groups; one consisting of AXs isolated from PO by various methods and the other group consisting of hydrogels from SA, MP and OB (Fig. 4a, Table 3).

3.3.2. AX and its modified forms

The thermal behavior of AX was found to be similar to that of other hydrogels under investigation as the thermograms consisted of removal of water around 100 °C, followed by the major decomposition stage due to chain scission and degradation. In the degradation products 2-furfuryl alcohol was detected by GC–MS. Thus the degradation can be represented by Scheme 2 (Fagerson, 1969). The decomposition products of the final stage were CO, H₂O and CO₂ in the range 415–495 °C. The AXs separated by use of different solvents showed no significant changes in the thermograms and the thermal parameters (Fig. 4a, Table 3).

The effect of cross-linking on thermal properties of AX was examined in the temperature range ambient to 600 °C (Fig. 2b).

A new decomposition step occurred between 195 and 245 °C. The features observed in the thermogram suggest that after passing through the decomposition stage between 195 and 245 °C the material returns to normal thermal behavior. In this range decross-linking appears to take place. After examining the WRVs and ITSs (Tables 1 and 3) of the natural and cross-linked materials it can be concluded that WRV is controlled by cross-linking without significant change in thermal stability of the material. This presents a distinct behavior of the arabinoxylans under investigation in contrast to the other polymers where normally cross-linking of polymers renders them thermally more stable (Wang, Jiang, McKinney, & Wilkie, 1999). No correlation of E_a and ITS values was found with CDI-ASU molar ratios used in cross-linking procedure.

The thermograms of AX and CMAXs (Fig. 2c) showed that the amount of char residue of the later was higher than that of the former. This was found to be due to high sodium content as verified by flame photometry of the residue. The mass loss in the main decomposition step decreased with increase in DS (Table 3). E_a was found to correlate linearly ($R^2 = 0.9204$) with DS in the series (Table 3) except in cases of CMAXs 18 and 19, which may be due to some experimental error.

In case of EAXs (Fig. 2d), mass loss during the main decomposition stage was in the range 31–43% at temperature range 235–345 °C for different EAX samples. Significant changes in thermal parameters were observed, however, no correlation was found among these (Table 4). These changes need to be studied in detail by investigating the conformational and morphological changes after ethylation. CLAXs have high positive ΔS^* suggesting a more disordered activated complex than the reactants, however, the increased

ΔH^* contribution put the ΔG^* in the same range as that of unmodified hydrogels. Most of EAXs and CMAXs also have high positive entropy contributions.

The f_2 and f_1 determination and cluster analysis were performed to determine the thermal similarity levels of AX and modified AXs. Most of the modified products showed distinct thermal behavior than the AX (Fig. 4b, Table 3). In this study, no mathematical relation could be found between the degree of crosslinking or degree of substitution and thermal stability as indicated by ITS. The derivatization of the arabinoxylan, however, improved the thermal stability for most of the modified arabinoxylans (Table 4). The chemically modified AX indicated an overall mixed clustering. However, some grouping can be recognized as most of the CMAXs form one group while CLAXs and EAXs are scattered in the other group (Fig. 4b).

4. Conclusion

Thermal studies revealed that decomposition of natural hydrogels and modified AX polymer chain was an exothermic process. Natural hydrogels from SA, OB and MP showed good thermal similarity with each other but different from AXs possibly due to presence of different sugars. Hydrogel obtained from AX exhibited relatively lower thermal stability than that from SA, MP and OB which showed similar thermal behavior. On the basis of thermal stability parameter (ITS) and cluster analysis, the natural hydrogels can be divided into two groups, the one consisting of AXs from PO and the other consisting of hydrogels from SA, MP and OB. The chemically modified AXs indicated an overall mixed clustering with most of the CMAXs forming one group and CLAXs and EAXs are scattered in the other group. Cross-linking of the AX decreases the water retention value with little change in thermal stability. Most of the modified products exhibited improved thermal stability over the parent material. Carboxymethylation with higher degree of substitution furnishes thermally more stable products. It was observed that values of E_a increase with increase in DS for CMAX samples but in case of EAX samples no such relationship was found. The ITS values of all materials under investigation were in the range 0.44–0.54 which correspond to a comparable thermal stability with commercially available materials like HPMC.

Acknowledgement

Shazia Saghir thanks to Higher Education Commission (HEC) of Pakistan for a PhD fellowship.

References

- Adel, A. M., El-Wahab, Z. H. A., Ibrahim, A. A., & Al-Shemy, M. T. (2010). Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis. *Bioresource Technology*, *101*(12), 4446–4455.
- Aggarwal, P., Dollimore, D., & Heon, K. (1997). Comparative thermal analysis study of two biopolymers, starch and cellulose. *Journal of Thermal Analysis and Calorimetry*, *50*(1), 7–17.
- Anandalakshmi, H., Parthiban, S., Parvathi, V., Thanikachalam, V., & Mojumdar, S. (2011). Thermal and optical properties of Cu(II)-doped magnesium rubidium sulfate hexahydrate crystals. *Journal of Thermal Analysis and Calorimetry*, *104*(3), 963–967.
- Azuma, J., & Sakamoto, M. (2003). Cellulosic hydrocolloid system present in seed of plants. *Trends in Glycoscience Glycotechnology*, *15*(81), 1–14.
- Barbucci, P. (Ed.). (2009). *Hydrogels: Biological properties and applications*. Milan, Italia: Springer-Verlag.
- Broido, A. (1969). A simple, sensitive graphical method of treating thermogravimetric analysis data. *Journal of Polymer Science Part A-2: Polymer Physics*, *7*(10), 1761–1773.
- Chatterjee, A. K., & Mukherjee, S. (1958). The structure of Tuhmalanga (*Salvia aegyptica*) Mucilage. Part I. Nature of sugars present and the structure of the aldobiouronic acid. *Journal of the American Chemical Society*, *80*(10), 2538–2540.
- Coviello, T., Matricardi, P., Marianecchi, C., & Alhaique, F. (2007). Polysaccharide hydrogels for modified release formulations. *Journal of Controlled Release*, *119*(1), 5–24.
- Davis, K. A., & Anseth, K. S. (2002). Controlled release from crosslinked degradable networks. *Critical Reviews in Therapeutic Drug Carrier Systems*, *19*(4–5), 385–423.
- Doyle, C. D. (1961). Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. *Analytical Chemistry*, *33*(1), 77–79.
- Duke, J. A. (2002). *Handbook of medicinal herbs*. Boca Raton, USA: CRC Press LLC.
- Dumitriu, S. (1998). *Polysaccharides structural diversity and functional versatility*. New York, USA: Marcel Dekker Inc.
- Fagerson, I. S. (1969). Thermal degradation of carbohydrates: A review. *Journal of Agricultural and Food Chemistry*, *17*(4), 747–750.
- Faix, O., Fortmann, I., Bremer, J., & Meier, D. (1991a). Thermal degradation products of wood. Gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products. *European Journal of Wood and Wood Products*, *49*(5), 213–219.
- Faix, O., Fortmann, I., Bremer, J., & Meier, D. (1991b). Thermal degradation products of wood. A collection of electron-impact (EI) mass spectra of polysaccharide derived products. *European Journal of Wood and Wood Products*, *49*(7), 299–304.
- Farooqi, M. I. H., Kapoor, V. P., & Khan, P. S. H. (1977). Chemical investigation on the mucilage of lajwanti seeds from *Mimosa pudica* Linn. *Indian Drugs*, *15*, 39.
- Fischer, M. H., Yu, N., Gray, G. R., Ralph, J., Anderson, L., & Marlett, J. A. (2004). The gel-forming polysaccharide of psyllium husk (*Plantago ovata* Forsk.). *Carbohydrate Research*, *339*(11), 2009–2017.
- Ghaemy, M., & Amini Nasab, S. M. (2010). Synthesis and identification of organosoluble polyamides bearing a triaryl imidazole pendent: Thermal, photophysical, chemiluminescent, and electrochemical characterization with a modified carbon nanotube electrode. *Reactive and Functional Polymers*, *70*(5), 306–313.
- Hamliche, V., & Maiza, K. (2006). Traditional medicine in Central Sahara: Pharmacopoeia of Tassili N'ajjer. *Journal of Ethnopharmacology*, *105*(3), 358–367.
- Heinze, T., Liebert, T., & Koschella, A. (2006). *Esterification of polysaccharides*. Berlin, Heidelberg, New York: Springer.
- Iqbal, M. S., Akbar, J., Hussain, M. A., Saghir, S., & Sher, M. (2011). Evaluation of hot-water extracted arabinoxylans from ispaghula seeds as drug carriers. *Carbohydrate Polymers*, *83*(3), 1218–1225.
- Jin, A. X., Ren, J. L., Peng, F., Xu, F., Zhou, G. Y., Sun, R. C., et al. (2009). Comparative characterization of degraded and non-degradative hemicelluloses from barley straw and maize stems. Composition, structure, and thermal properties. *Carbohydrate Polymers*, *78*(3), 609–619.
- Khomutov, L. I., Ptichkina, N. M., Sheenson, V. A., Lashek, N. A., & Panina, N. I. (1994). Thermal degradation of polysaccharides. *Russian Journal of Applied Chemistry*, *67*, 574–577.
- Lin, C., & Metters, A. T. (2006). Hydrogels in controlled release formulations: Network design and mathematical modeling. *Advanced Drug Delivery Reviews*, *58*(12–13), 1379–1408.
- Madani, M. (2011). Structure, optical and thermal decomposition characters of LDPE graft copolymers synthesized by gamma irradiation. *Current Applied Physics*, *11*(1), 70–76.
- Mallakpour, S., & Dinari, M. (2010). Eco-friendly fast synthesis and thermal degradation of optically active polyamides under microwave accelerating conditions. *Chinese Journal of Polymer Science*, *28*(5), 685–694.
- Moore, J. W., & Flanner, H. H. (1996). Mathematical comparison of dissolution profiles. *Pharmaceutical Technology*, *20*(6), 64–74.
- Müller-Hagedorn, M., Bockhorn, H., Krebs, L., & Müller, U. (2003). A comparative kinetic study on the pyrolysis of three different wood species. *Journal of Analytical and Applied Pyrolysis*, *68–69*, 231–249.
- Munarin, F., Petrini, P., Farè, S., & Tanzi, M. (2010). Structural properties of polysaccharide-based microcapsules for soft tissue regeneration. *Journal of Materials Science: Materials in Medicine*, *21*(1), 365–375.
- Nam, Y. S., Park, W. H., Ihm, D., & Hudson, S. M. (2010). Effect of the degree of deacetylation on the thermal decomposition of chitin and chitosan nanofibers. *Carbohydrate Polymers*, *80*(1), 291–295.
- Niño-Medina, G., Carvajal-Millán, E., Rascón-Chu, A., Márquez-Escalante, J. A., Guerrero, V., & Salas-Muñoz, E. (2010). Feruloylated arabinoxylans and arabinoxylan gels: Structure, sources and applications. *Phytochemistry Reviews*, *9*(1), 111–120.
- Peng, Y., & Wu, S. (2010). The structural and thermal characteristics of wheat straw hemicellulose. *Journal of Analytical and Applied Pyrolysis*, *88*(2), 134–139.
- Peppas, N. A., Bures, P., Leobandung, W., & Ichikawa, H. (2000). Hydrogels in pharmaceutical formulations. *European Journal of Pharmaceutics and Biopharmaceutics*, *50*(1), 27–46.
- Popescu, M.-C., Popescu, C.-M., Lisa, G., & Sakata, Y. (2011). Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods. *Journal of Molecular Structure*, *988*(1–3), 65–72.
- Rahman, M. A., Mossa, J. S., Al-Said, M. S., & Al-Yahya, M. A. (2004). Medicinal plant diversity in the flora of Saudi Arabia 1: A report on seven plant families. *Fitoterapia*, *75*(2), 149–161.
- Saghir, S. (2009). Isolation, modification, characterization and pharmacological evaluation of gellable material from ispaghula husk. Ph.D. Thesis. Department of Chemistry, University of Sargodha, Sargodha.
- Saghir, S., Iqbal, M. S., Hussain, M. A., Koschella, A., & Heinze, T. (2008). Structural characterization and carboxymethylation of arabinoxylan isolated from ispaghula (*Plantago ovata*) seed husk. *Carbohydrate Polymers*, *74*(2), 309–317.
- Saghir, S., Iqbal, M. S., Koschella, A., & Heinze, T. (2009). Ethylation of arabinoxylan from (*Plantago ovata*) seed husk. *Carbohydrate Polymers*, *77*(1), 125–130.
- Singh, B. (2007). Psyllium as therapeutic and drug delivery agent. *International Journal of Pharmaceutics*, *334*(1–2), 1–14.
- Spencer, T. J., & Kohl, P. A. (2011). Decomposition of poly(propylene carbonate) with UV sensitive iodonium salts. *Polymer Degradation and Stability*, *96*(4), 686–702.

- Tharanathan, R. N., & Anjaneyalu, Y. V. (1972). Polysaccharides from the seed mucilage of *Ocimum basilicum* Linn. *Current Science*, 41, 214.
- Tharanathan, R. N., & Anjaneyalu, Y. V. (1975). Structure of the acid-stable core-polysaccharide derived from the seed mucilage of *Ocimum basilicum*. *Australian Journal of Chemistry*, 28(6), 1345–1350.
- Villetti, M. A., Crespo, J. S., Soldi, M. S., Pires, A. T. N., Borsali, R., & Soldi, V. (2002). Thermal degradation of natural polymers. *Journal of Thermal Analysis and Calorimetry*, 67(2), 295–303.
- Wang, Z., Jiang, D. D., McKinney, M. A., & Wilkie, C. A. (1999). Cross-linking of polystyrene by Friedel–Crafts chemistry to improve thermal stability. *Polymer Degradation and Stability*, 64(3), 387–395.
- Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 86(12–13), 1781–1788.
- Zohuriaan, M. J., & Shokrolahi, F. (2004). Thermal studies on natural and modified gums. *Polymer testing*, 23(5), 575–579.