

Comparative study of thermal degradation behavior of graft copolymers of polysaccharides and vinyl monomers

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Abstract The thermal degradation of graft copolymers of both polysaccharides (guar gum and xanthan gum) showed gradual decrease in mass loss. Pure guar gum degraded about 95% but pure xanthan gum degraded about 76% up to 1173.15 K, while graft copolymers of guar gum and xanthan gum degraded only 65–76% up to 1173.15 K. Acrylic acid grafted guar gum and xanthan gum showing two-step degradation with formation of anhydride and ketonic linkage during heating, same pattern of degradation was found for xanthan gum-*g*-methacrylic acid. Guar gum-*g*-acrylamide degraded in single step and xanthan gum-*g*-acrylamide started to degrade above 448.15 K and it is a two-stage process and imparts thermal stability due to the formation of imide linkage with evolution NH₃. Guar gum-*g*-methacrylamide degraded in three steps due to the loss of NH₃ and CO₂ successively. 4-vinyl pyridine grafted both polysaccharides show single step degradation due to loss of pyridine pendent. *N*-vinyl formamide grafted guar gum and xanthan gum started to degrade at about 427.15 K, showed two-stage degradation process with the evolution of CO and NH₃ molecules while guar gum-*g*-(*N*-vinyl-2-pyrrolidone) degraded into two steps by the loss of pyrrolidone nucleus. Gum-*g*-2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) showed two-step degradation processes in two successive degradation steps, while xanthan gum-*g*-

AMPS has started degradation at about 427.15 K and completed in five degradation steps. Overall, it was found that the grafted polysaccharides are thermally more stable than pure polysaccharides.

Keywords Thermal analysis · Guar gum · Xanthan gum · Graft copolymer · Vinyl monomers

Introduction

Now-a-days more emphasis is given to biodegradable and natural polymers such as polysaccharides and proteins, which have been extensively used and investigated for industrial applications from which we have selected guar gum and xanthan gum. Guar gum is a naturally occurring carbohydrate polymer consisting of straight chain monomer with single membered galactose branches and two units of mannose by β -D (1 → 4) linkages. Guar gum is a galactomannan [1] similar to locust bean gum consisting of a (1 → 4) linked α -D-mannopyranose backbone with branch points from their six positions linked to α -D-galactose (i.e., 1 → 6-linked- α -D-galactopyranose). There are between 1.5 and 2 mannose residues for every galactose residue. The ratio of D-galactose to D-mannose in guar gum is 1:2 with single D-galactopyranosyl unit side chains attached to every other D-mannopyranosyl unit [2, 3] as represented in Fig. 1. Its molecular mass has been reported as 220,000 [4]. The high thickening efficiency, hydrogen bonding properties, good compatibility, and low cost have resulted in guar gum being most extensively used gum in mining, textile, food and paper industries, explosives, petroleum recovery, and pharmaceuticals.

Xanthan gum has important role in the development of industrially useful polymers. Xanthan gum is extracellular

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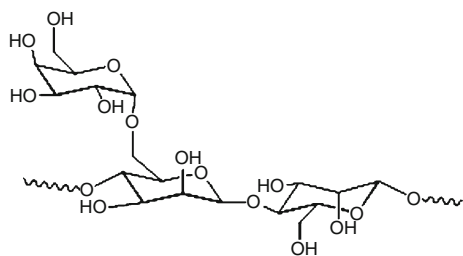


Fig. 1 Structure of guar gum

heteropolysaccharide of *Xanthomonas campestris* and was the first biopolymer product of a fermentation based on corn sugar that has attained commercial status [5–8]. The structural unit of xanthan gum consist of β -(1 \rightarrow 4)-D-glucopyranose glucan (as cellulose) backbone with side chains of $-(3 \rightarrow 1)$ - β -linked D-mannopyranose- $(2 \rightarrow 1)$ - β -D-glucuronic acid- $(4 \rightarrow 1)$ - β -D-mannopyranose on alternating residues [9, 10] (Fig. 2). The glucon backbone is protected by the side chains which lie alongside, making it relatively stable to acids, alkalis, and enzymes. Industrially, xanthan gum is used to thicken oil well drilling muds, in gelled or thickened cleaning compositions; in ceramic glazes; paints and adhesives and in textile sizing and printing agents. Xanthan gum is used widely as a compound in the preparation of cosmetic products, pharmaceutical, edible ink [11], and thickener [12]. Grafting monomer on emulsions of xanthan gum in non-aqueous liquids gives easily handled dispersions of water-soluble or sweable polymer blends [13]. The graft copolymers of xanthan gum with acrylamide [14] are used as turbulent drag reducers in sprinkler irrigation and as a flocculants in wastewater treatment, ore treatment and as coatings for slow release urea fertilizers. Methyl methacrylate [15] grafted xanthan gum is applied to absorb metal ions, such as Hg^{2+} and Cu^{2+} , while sulfonic acid and sulfomethyl [16] containing graft copolymer of xanthan gum are used in

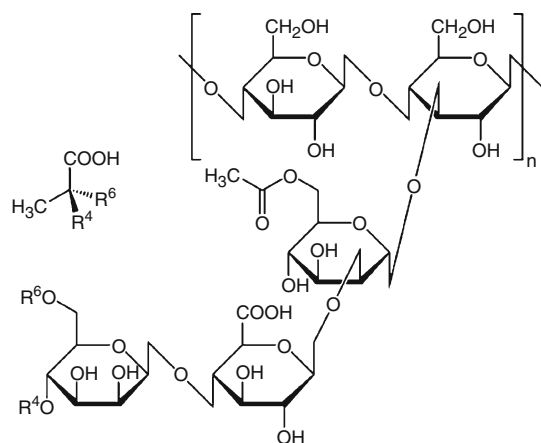


Fig. 2 Structural presentation of xanthan gum

petroleum recovery due to synergistic viscosity and as a thickener in textile and slurry explosives.

Similarly, acrylamide, methacrylamide, acrylic acid, *N*-vinyl formamide, *N*-vinyl-2-pyrrolidone, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), and 4-vinyl pyridine monomers are the synthetic vinyl monomers which have wide range of usages in industrial applications. Like other polysaccharides, xanthan gum and guar gum are also susceptible to biodegradation, which limits their applications. To overcome this, it was grafted with different vinyl monomers employing different initiators. The properties and applications of grafted xanthan gum and guar gum depend on the type of vinyl monomer grafted by the process of graft copolymerization, the physical and chemical properties of synthetic monomers are superimposed on the properties of natural polymer.

The thermal analysis of guar gum, xanthan gum, and its graft copolymers with acrylamide, methacrylamide, acrylic acid, 4-vinyl pyridine and *N*-vinyl-2-pyrrolidone, *N*-vinyl formamide, AMPS have been performed in nitrogen atmosphere. Literature survey reveals that polymer [17], copolymers [18], and graft copolymers of natural polysaccharide [19–22] shows that the thermal stabilities are varies with respect to vinyl monomers and authors failed to find out the reason of variable thermal stability. This prompted us to study the effect of graft copolymerization of various monomers on thermal stability of natural polysaccharide substrate, i.e., guar gum, xanthan gum and also to study the effect of redox pair on the thermal stability of same graft copolymers.

Experimental

Procedure for synthesis of graft copolymer

For each experiment, gum (Guar or Xanthan) solution was prepared in a reactor by adding the calculated amount of gum in required amount of triple distilled water. The calculated amount of vinyl monomer, sulfuric acid, and solution of reductant were added into the prepared solution of xanthan gum and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of de-aerated solution of oxidant was added to initiate the graft copolymerization process. The reactions were performed under a continuous flow of purified nitrogen gas. After a desired interval of time, the reaction was stopped by letting air into the reaction mixture. The grafted sample was precipitated by pouring the reaction mixture into solvent mixture (solvent composition was chosen according the nature of polysaccharide). The precipitate was dried and weighed. The homopolymer was separated by soxhlet extraction. Detailed description of synthesis and characterization of

graft copolymers of guar gum and xanthan gum have been published elsewhere [23–38].

Instrumentation

The FTIR spectra of the samples in KBr pallets were recorded on Varian Excalibur 3100 series in the range 500–4,000 cm^{-1} . The thermal analyses of xanthan gum and their grafted derivatives are carried out in nitrogen atmosphere using Perkin Elmer, Diamond TG/DTA system using with heating rate 15 K min^{-1} . The relative thermal stability of graft copolymers was determined by polymer decomposition temperature (PDT) and integral procedural decomposition temperature (IPDT) [39]. The IPDT which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus, thermal stability of pure guar gum and its graft copolymers has also been determined by calculating IPDT values using following equation [39]. The area under the curve divided by the total area is the total curve area, A^* , is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, TA^* , by following equation.

$$TA^* = (T_{\text{end}} - T_{\text{initial}})A^* + T_{\text{initial}} \quad (1)$$

TA^* represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing x axis up to TA^* and the y axis mass fraction remaining at T_{end} . K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in equation [1]. IPDT gives the start of volatilization and the TA^* gives the end of volatilization of the material.

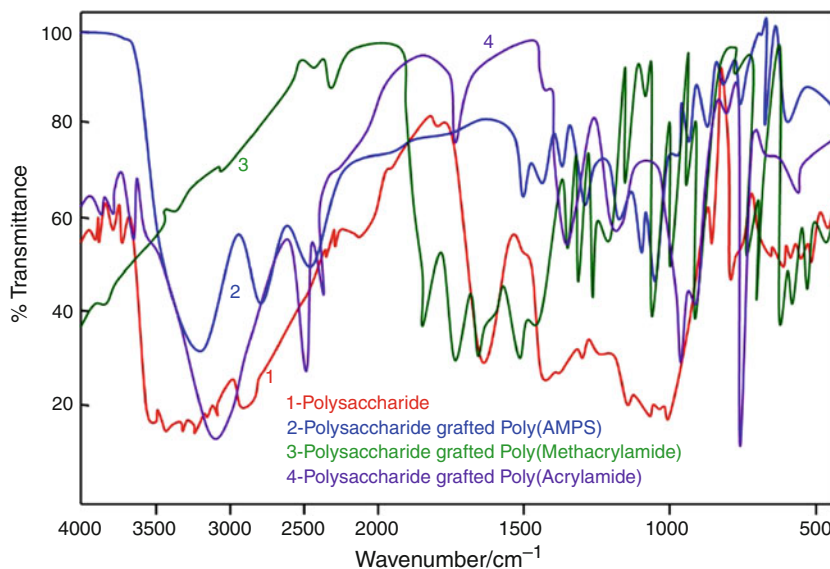
Results and discussion

Evidence of grafting: FTIR spectroscopy

Polysaccharides spectra shows band at 2,909 cm^{-1} is due to C–H stretching vibration. The bands around 1,420 and 1,300 cm^{-1} are assigned to $-\text{CH}_2$ scissoring and $-\text{OH}$ bending vibration, respectively. The band at 1,080 cm^{-1} is due to $\text{CH}-\text{O}-\text{CH}_2$ stretching. In the case of poly(acrylamide) (Fig. 3), a broad absorption band at 3,430 cm^{-1} is for the N–H stretching. Two strong bands around 1,660 and 1,620 cm^{-1} are due to amide-I ($\text{C}=\text{O}$ stretching) and amide-II (NH bending). Another band at 1,780 cm^{-1} is due to the presence of free acid groups. The bands around 1,400 and 2,970 cm^{-1} are for the C–N and C–H stretching vibrations. Other bands at 1,460 and 1,300 cm^{-1} are attributed to CH_2 scissoring and CH_2 twisting. The IR spectrum of grafted polysaccharide with acrylamide shows the presence of a broad absorption band at 3,410 cm^{-1} is due to the overlap of $-\text{OH}$ stretching band from polysaccharide and $-\text{NH}$ stretching band of poly(acrylamide). A band at 1,656 cm^{-1} is due to the amide-I band of the amide group of polyacrylamide.

The band at 1,600 cm^{-1} of polysaccharide and amide-II band of poly(acrylamide) overlap with each other and lead to a broad band at 1,640 cm^{-1} . The presence of a band at 1,780 cm^{-1} is due to free acid groups. These bands of polysaccharide-*g*-poly(acrylamide) are also present separately in polysaccharide and poly(acrylamide) spectra at different frequencies. When poly(acrylamide) was removed from the graft copolymer, the presence of above bands in the graft copolymer supports strong evidence of grafting of acrylamide onto polysaccharide (xanthan gum and guar gum).

Fig. 3 FTIR spectra of 1 polysaccharide, 2 polysaccharide grafted poly(AMPS), 3 polysaccharide grafted poly(methacrylamide), and 4 polysaccharide grafted poly(acrylamide)



It has been observed that the graft copolymer showed absorption bands of polysaccharide and also the additional bands at 1655, 1543, 1400, 1043 and 607 cm^{-1} which are attributed to C=O (amide-I band), C–N–H (amide-II band bending mode), C–N, –SO₃H (S–O) and C–S groups (stretching mode except C–N–H), respectively; these bands are characteristic of poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (Fig. 3). Amide-II bands are resulted from the interaction between N–H bending and C–N stretching of C–N–H group. Thus, the presence of these additional bands for the graft copolymer indicates the grafting has taken place on polysaccharides. The absence of O–H bending vibrations from the spectrum of polysaccharide-*g*-poly(AMPS) indicates that grafting might have taken place on the O–H sites of the polysaccharides (xanthan gum and guar gum).

On comparing the FTIR spectra of polysaccharides and polysaccharides-*g*-(4-vinyl pyridine) (Fig. 4), the following additional bands were appeared in the spectra of polysaccharides-*g*-(4-vinyl pyridine). Poly(4-vinyl pyridine) ring stretching vibration occurred in the region at 1505.8 and 1454.1 cm^{-1} . This absorption involves stretching and contraction of the entire bond in the pyridine ring (C=C, C=N) and interaction between these stretching modes. The band at 814.5 cm^{-1} was due to out of plane bending vibration of C–H of pyridine ring. Thus, the presence of these additional bands and disappearance of O–H bending vibration (1,408 cm^{-1}) from the spectra of polysaccharides-*g*-(4-vinyl pyridine) proves that the 4-vinyl pyridine has been grafted on –OH site of the polysaccharide backbone.

On comparing the spectra of polysaccharides and polysaccharides-*g*-acrylic acid the following additional peaks/bands in the spectrum of polysaccharides-*g*-acrylic acid (Fig. 4) have been observed. The broad and intense band in the region 2,730–3,050 cm^{-1} is attributed to stretching

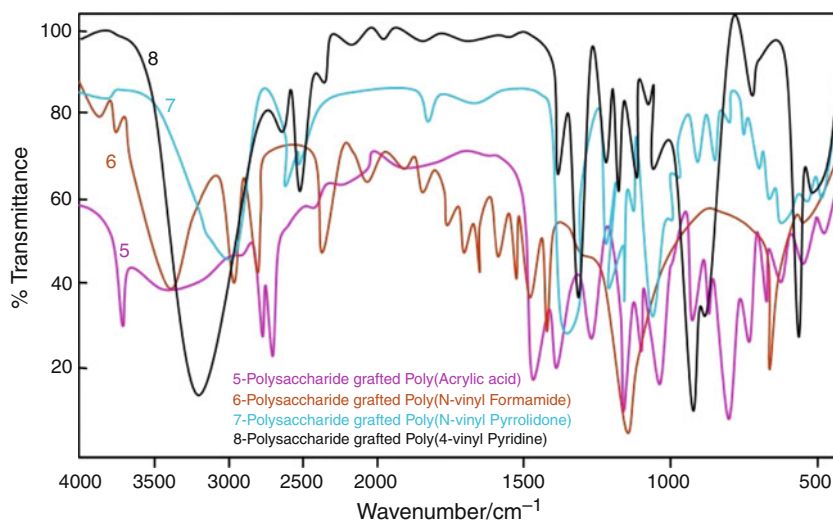
vibration of O–H bond. The peak at 1,740 cm^{-1} is attributed to stretching vibration of carbonyl group of acrylic acid. The broad and intense bands centered at 1,240 and 1,450 cm^{-1} are attributed to C–O stretching and C–O–H bending vibrations. The presence of these bands/peaks confirms the grafting of poly(acrylic acid) onto polysaccharides backbone.

FTIR spectra of graft copolymer [XOH-*g*-MAA] and xanthan gum pure's were taken, compared and found that the xanthan gum –OH broad band at 3,350 cm^{-1} was not appeared in the XOH-*g*-MAA spectra (neither broad not sharp), suggesting that grafting taken place at xanthan gum –OH sites. The band at 1,768 cm^{-1} is occurred because of –COOH, which is common in both the spectra of xanthan gum and XOH-*g*-MAA, but disappearance of broad-OH band in graft copolymer supports the formation of graft copolymer.

The IR spectra of polysaccharides and polysaccharides grafted *N*-vinyl formamide were taken in the range 400–4,000 cm^{-1} . It was found that the graft copolymer showed absorption bands of polysaccharides and also additional bands at 1649.2 and 1398.2 cm^{-1} which are attributed to amide-I band due to C=O stretching and C–N stretching vibration, respectively (Fig. 4), which are characteristics of poly(*N*-vinyl formamide). Thus, the presence of these additional bands indicates that grafting has taken place. The disappearance of O–H bending vibrations from the spectra of polysaccharides-*g*-poly(*N*-vinyl formamide) showed that the grafting might have taken place on O–H site of the polysaccharides.

In the IR spectra of guar gum-*g*-*N*-vinyl-2-pyrrolidone (Fig. 4), besides bands of the polysaccharide backbone, some additional bands are appeared like C=O stretching vibration appeared at 1,661 cm^{-1} , which is attributed to carbonyl group of *N*-vinyl-2-pyrrolidone; C–N stretching vibration occurred at 1430.2 cm^{-1} which correspond to the

Fig. 4 FTIR spectra of 5 polysaccharide grafted poly(acrylic acid), 6 polysaccharide grafted poly(*N*-vinyl formamide), 7 polysaccharide grafted poly(*N*-vinyl pyrrolidone), 8 polysaccharide grafted poly(4-vinyl pyridine)



C–N bond of pyrrolidone ring. FTIR spectral analyses of guar gum-*g-N*-vinyl-2-pyrrolidone and guar gum, it has been observed that many of bands disappeared in the spectra of guar gum-*g*-(*N*-vinyl-2-pyrrolidone) with changes. Thus, the disappearance of O–H bands (bending) in spectra of guar gum-*g-N*-vinyl-2-pyrrolidone proves that the grafting might have taken place at O–H site of the backbone.

Thermal analyses

Polysaccharide (xanthan gum (XOH) and guar gum (GOH))

The degradation of xanthan gum and guar gum started at about 505.15 and 503.15 K, respectively, and both show single step degradation process (Fig. 5). The rate of mass loss increases on increasing the temperature up to 569.15 K in the case of xanthan gum and 583.15 K for guar gum, but thereafter it decreases in both the polysaccharides. Nearly 75% of guar gum degraded up to 673.15 K (Fig. 5), while 40% mass loss was occurred between 473.15 to 583.15 K in the case of xanthan gum, 60% xanthan gum was degraded up to 873.15 K (Fig. 5); therefore, final decomposition temperature (FDT) of xanthan gum was very low, i.e., 589.15 K. PDT, temperature at which maximum degradation (T_{max}) occurred and IPDT of xanthan gum were found to be 554.15, 563.15, and 553.35 K, respectively (Table 1), while the value of PDT, T_{max} , and IPDT of guar gum is 533.15, 583.15, and 591.95 K, respectively. In both the polysaccharide case the linear relationship between $\log dw/dt$ versus $\log W$, where dw/dt is rate of mass loss and W is residual mass cannot be obtained. This is because degradation of both polysaccharide is quite complex and starts with depolymerization through random chain scission

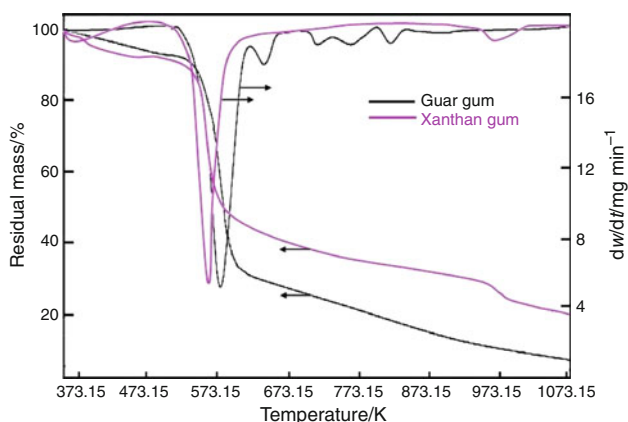


Fig. 5 TG and DTG curve of pure guar gum and pure xanthan gum

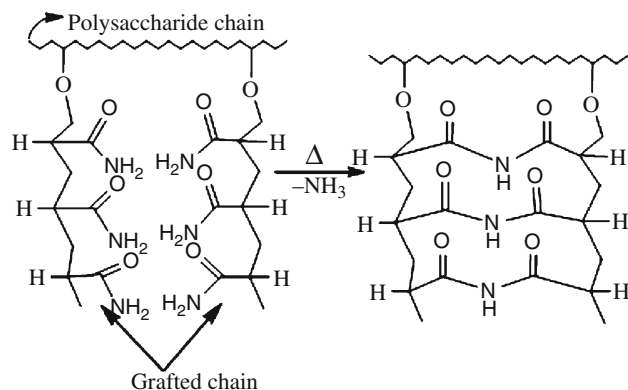
associated with degradation followed by molecular rearrangements. 24% char yield was obtained in case of xanthan gum at 1143.15 K.

Xanthan gum and guar gum grafted acrylamide

The guar gum-*g*-acrylamide was prepared by peroxy monosulfate/mercaptosuccinic acid (AM1) and vanadium/mandelic acid (AM2) redox pairs, while xanthan gum-*g*-acrylamide was synthesized by vanadium/mercaptosuccinic acid redox pair (AM3). AM1 began to degrade at about 463.15 K (Scheme 1; Fig. 6), while AM2 started to degrade at 453.15 K (Scheme 1; Fig. 6), and AM3 started to degrade above 448.15 K. However, 10% mass loss was observed at 363.15 K, which was attributed to loss of absorbed water. In AM1, the rate of mass loss increased on increasing the temperature from 423.15 to 673.15 K but gradually decreased above 673.15 K (Tables 2, 3), whereas in case of AM2 the rate of mass loss increased on increasing the temperature from 383.15 to 483.15 K but gradually decreased above this temperature (Tables 2, 3). In the case of AM1, the thermal degradation occurred in three stages, i.e., from 453.15 to 633.15 K, from 723.15 to 813.15 K, and from 813.15 to 873.15 K. The PDT, FDT, T_{max} , and IPDT of AM1 were found to be 483.15, 903.15, 563.15, and 709.05 K, respectively. While in the case of AM2, the thermal degradation occurred in two stages, i.e., from 423.15 to 450.15 K and from 450.15 to 803.15 K. The PDT, FDT, T_{max} , and IPDT of AM2 were 468.15, 833.15, 558.15, and 693.15 K, respectively. The degradation of AM3 appears to be a two-stage process, i.e., from 473.15 to 633.15 K and from 633.15 to 758.15 K (Fig. 6). The maximum mass loss in AM3 was occurred at 558.15 K (T_{max}). The PDT was found to be 525.15 K. Since the rate of mass loss decreased beyond 35%, the FDT (717.15 K) of AM3 is higher than that of pure xanthan gum (Table 1). In AM3 about 40% mass loss occurred between 493.15 to 813.15 K and 43% char yield was obtained at 1073.15 K. The value of PDT and FDT indicate that grafting of acrylamide decreases the initial decomposition temperature by 323.15 K in case of AM1 and 338.15 K in case of AM2, and 302.15 K in case of AM3, whereas, the FDT is increased by 583.15 K in case AM1, 513.15 K in the case of AM2 than guar gum and 401.15 K than xanthan gum. Thus, the grafting of acrylamide onto xanthan gum and guar gum by redox pairs lowers the initial decomposition temperature of graft copolymers which is might be due to the degradation [40] of polyacrylamide chains in the temperature range of 448.15–573.15 K by the formation of imide group via cyclization of imide group and evolution of ammonia [40] (Scheme 1). The formation of imide group imparts thermal stability to grafted polysaccharides, which was observed beyond 35% mass loss.

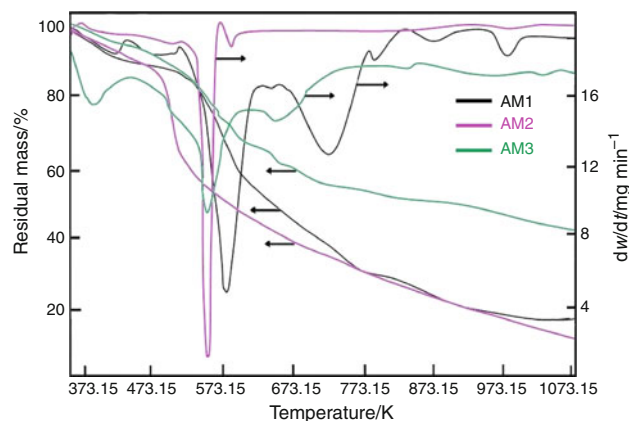
Table 1 Thermogravimetric analyses of guar gum, xanthan gum, and their graft copolymer

S. no.	Samples	PDT/K	FDT/K	IPDT/K	T_{max}/K	Char yield at 1073.15 K/%
1	Guar gum	533.15	593.15	591.15	583.15	5.0
2	Xanthan gum	554.15	589.15	553.35	563.15	27.0
3	Guar gum- <i>g</i> -acrylamide (AM1)	483.25	903.55	708.35	563.35	15.0
4	Guar gum- <i>g</i> -acrylamide (AM2)	468.15	833.15	693.15	558.15	10.0
5	Xanthan gum- <i>g</i> -acrylamide (AM3)	525.15	717.15	563.15	558.15	43.0
6	Guar gum- <i>g</i> -methacrylamide	473.35	728.55	594.75	543.15 and 663.15	28.0
7	Guar gum- <i>g</i> -acrylic acid (AA1)	473.15	1103.15	662.15	573.15 and 723.15	35.0
8	Guar gum- <i>g</i> -acrylic acid (AA2)	433.15	733.15	480.15	463.15	30.0
9	Xanthan gum- <i>g</i> -acrylic acid (AA3)	483.65	1035.15	568.15	709.15	31.0
10	Guar gum- <i>g</i> -(4-vinyl pyridine)	489.65	773.95	541.05	573.15	25.0
11	Xanthan gum- <i>g</i> -(4 vinyl pyridine)	473.15	621.55	609.05	557.15	42.0
12	Guar gum- <i>g</i> -AMPS	430.45	613.15	548.15	455.15	45.0
13	Xanthan gum- <i>g</i> -AMPS	498.15	1478.15	595.15	477.45, 835.25, 952.15, 1206.95, 1445.05	45.0
14	Guar gum- <i>g</i> - <i>N</i> -vinyl formamide	560.15	1073.15	623.15	581.15	40.0
15	Xanthan gum- <i>g</i> - <i>N</i> -vinyl formamide	540.15	1109.15	665.15	584.15, 1073.15	53.0
16	Guar gum- <i>g</i> - <i>N</i> -vinyl pyrrolidone	479.15	1073.15	618.15	517.15 and 1040.15	47.0
17	Xanthan gum- <i>g</i> -methacrylic acid	489.55	725.15	584.25	517.05, 616.65	37.0

**Scheme 1** Degradation steps of polysaccharide-*g*-acrylamide

Guar gum-*g*-methacrylamide

The degradation of guar gum-*g*-methacrylamide started at about 463.15 K (Fig. 7). The degradation occurred in two distinct stages within temperature range 443.15–823.15 K. It's PDT and FDT is 473.15 and 728.15 K, respectively. Graft copolymerization of methacrylamide on guar gum decreases the initial decomposition temperature while increases its FDT (Table 1) and IPDT is 593.91 K moreover same as that of guar gum. Two T_{max} , i.e., 543.15 and 663.15 K has been obtained in the degradation of graft

**Fig. 6** TG and DTG curve of guar gum-*g*-acrylamide by peroxymonosulfate/mercaptosuccinic acid redox pair (AM1), guar gum-*g*-acrylamide by vanadium/mandelic acid redox pair (AM2) and xanthan gum-*g*-acrylamide by vanadium/mercaptosuccinic acid redox pair (AM3)

copolymer. A char yield of 28% is obtained at 1073.15 K (Table 3). The degradation of graft copolymer is quite complex involving multistage reactions so linear relationship could not be obtained at any between $\Delta \log dw/dt$ and $\Delta \log W$ by Freeman and Carroll's method. Conclusively methacrylamide has imparted the thermal stability to the guar gum except the decrease in initial decomposition temperature.

Table 2 Decomposition temperature of guar gum, xanthan gum, and their graft copolymers

S. no.	Temperature/K	Mass loss/%							
		10	20	30	40	50	60	70	75
1	Guar gum	535.35	559.55	569.95	573.35	579.35	587.35	621.35	673.45
2	Xanthan gum	543.65	555.55	570.15	583.55	616.35	873.55	1123.65	
3	Guar gum-g-acrylamide (AM1)	423.15	485.15	494.75	528.95	577.55	734.45	808.15	–
4	Guar gum-g-acrylamide (AM2)	423.15	463.15	473.15	523.75	591.95	713.45	823.15	1063.15
5	Xanthan gum-g-acrylamide (AM3)	493.15	553.65	593.15	663.35	813.15	1123.15	–	–
6	Guar gum-g-methacrylamide	483.55	485.85	551.95	597.65	663.45	757.65	1037.65	977.15
7	Guar gum-g-acrylic acid (AA1)	488.95	553.65	613.95	683.15	733.55	913.15	1143.15	1109.65
8	Guar gum-g-acrylic acid (AA2)	393.15	453.55	463.45	523.95	613.75	713.75	963.15	
9	Xanthan gum-g-acrylic acid (AA3)	397.15	502.55	568.15	649.15	710.65	906.15	1123.15	–
10	Guar gum-g-(4-vinyl pyridine)	497.55	530.75	543.15	561.15	590.05	645.85	843.45	
11	Xanthan gum-g-(4-vinyl pyridine)	509.05	550.75	570.15	621.45	878.85	1100.15	1215.15	
12	Guar gum-g-AMPS	714.3	730.6	489.55	593.55	721.55	923.35	–	–
13	Xanthan gum-g-AMPS	715	523.15	598.15	748.15	960.65	1304.45	1448.15	–
14	Guar gum-g-N-vinyl formamide	504.65	573.85	584.25	645.65	873.15	1073.95	–	–
15	Xanthan gum-g-N-vinyl formamide	518.75	600.95	841.45	1028.05	1086.15	–	–	958.15
16	Guar gum-g-N-vinyl pyrrolidone	505.05	567.65	729.15	960.95	1042.85	–	–	
17	Xanthan gum-g-methacrylic acid	489.45	531.15	583.15	655.15	751.45	991.15	1215.15	–

Table 3 Decomposed % mass loss of guar gum, xanthan gum, and their graft copolymers

S. no.	Mass loss/%	Temperature/K								
		373.15	473.15	573.15	673.15	773.15	873.15	973.15	1073.15	1173.15
1	Guar gum	3.0	5.0	35.0	75.0	81.0	88.0	92.0	95.0	–
2	Xanthan gum	3.3	6.0	33.0	55.0	57.0	60.0	65.0	73.0	–
3	Guar gum-g-acrylamide (AM1)	3.0	17.0	47.3	49.0	54.1	69.3	75.2	86.8	–
4	Guar gum-g-acrylamide (AM2)	5.0	30.8	47.1	57.2	65.9	77.0	81.2	–	–
5	Xanthan gum-g-acrylamide (AM3)	2.8	8.3	27.0	41.0	49.0	52.0	54.0	58.0	–
6	Guar gum-g-methacrylamide	3.0	8.0	35.4	52.9	61.9	64.2	67.9	72.3	–
7	Guar gum-g-acrylic acid (AA1)	3.2	8.7	24.0	38.3	55.0	59.6	62.0	65.3	–
8	Guar gum-g-acrylic acid (AA2)	2.5	30.0	46.4	58.2	65.0	68.0	70.0	72.9	–
9	Xanthan gum-g-acrylic acid (AA3)	7.0	15.4	32.2	44.0	59.0	62.0	63.0	68.9	–
10	Guar gum-g-(4-vinyl pyridine)	3.5	7.2	45.1	63.7	68.4	70.2	73.7	75.2	–
11	Xanthan gum-g-(4-vinyl pyridine)	4.7	8.7	32.0	44.0	47.0	50.0	54.0	58.0	68.0
12	Guar gum-g-AMPS	0.6	24.0	34.2	42.4	47.2	50.0	54.5	56.1	
13	Xanthan gum-g-APMS	4.2	12.5	27.5	37.5	41.7	48.3	53.3	54.9	58.3
14	Guar gum-g-N-vinyl formamide	5.1	9.0	19.0	43.8	46.0	50.8	55.0	61.7	–
15	Xanthan gum-g-N-vinyl formamide	4.0	6.9	15.8	24.6	27.5	32.9	35.8	46.9	–
16	Gaur gum-g-N-vinyl pyrrolidone	2.0	4.2	20.4	27.9	31.6	35.0	40.4	53.3	–
17	Xanthan gum-g-methacrylic acid	4.0	8.0	29.0	42.0	52.0	54.0	58.0	63.0	66.0

Guar gum-g-poly(4-vinyl pyridine) and xanthan gum-g-poly(4-vinyl pyridine)

Both the graft copolymers began to degrade at about 383.15 K. However, 2% mass loss was observed below 373.15 K, which is attributed to the absorbed water. Single

step degradation was observed in both graft copolymers (Scheme 2; Fig. 8). The rate of mass loss increases on increasing the temperature from 453.15 to 623.15 K but gradually decreases thereafter in both the cases. The PDT is found to be 473.15 K and the temperature at which maximum degradation (T_{max}) occurred is 557.55 K

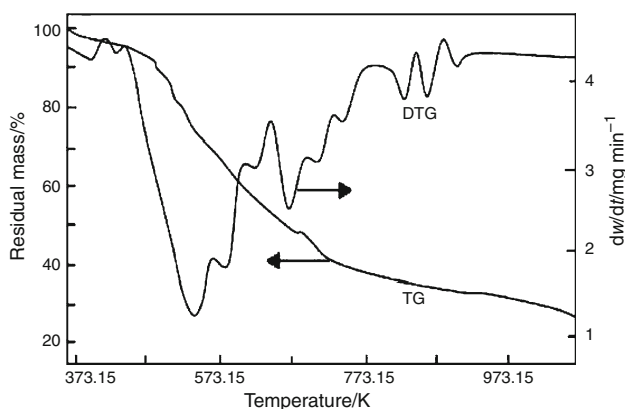
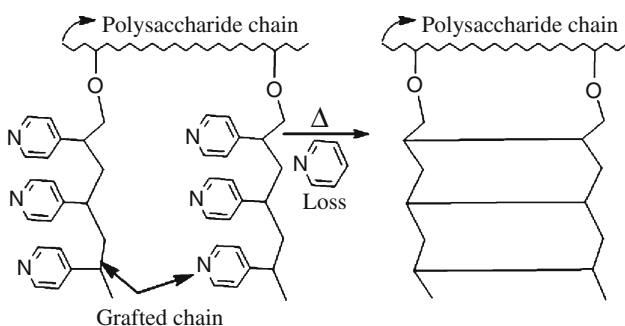


Fig. 7 TG and DTG cure of guar gum-g-poly(methacrylamide)



Scheme 2 Degradation steps of polysaccharides-g-poly(4-vinyl pyridine)

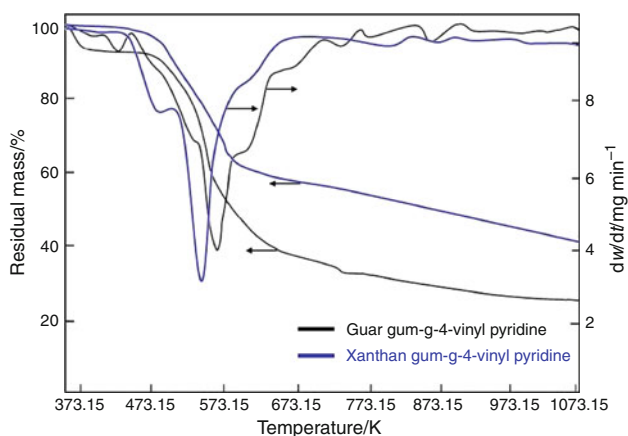


Fig. 8 TG and DTG curve of guar gum-g-poly(4-vinyl pyridine) and xanthan gum-g-poly(4-vinyl pyridine)

(Table 1) for xanthan gum grafted poly(4-vinyl pyridine) while guar gum grafted poly(4-vinyl pyridine) shows the PDT at 489.65 K and T_{\max} is 573.15 K. Maximum mass loss has been observed between 473.15 and 673.15 K (Table 1, 1–3). Thus, guar gum grafted poly(4-vinyl pyridine) initially showing more thermal stability than xanthan gum grafted poly(4-vinyl pyridine). Xanthan gum grafted poly(4-vinyl pyridine) shows about 44% mass losses between 453.15 to 673.15 K (Fig. 8). This mass loss is

lower than the mass loss in xanthan gum at the same temperature range. Guar gum grafted poly(4-vinyl pyridine) degraded about 63.7% up to this temperature range and stable than pure guar gum; up to this temperature range, xanthan gum grafted poly(4-vinyl pyridine) is thermally more stable. The IPDT of xanthan gum grafted poly(4-vinyl pyridine) is found to be 609.1 K which is higher than that of xanthan gum. The gradual decrease in the endopeak of graft copolymer also indicates that some physical and structural changes are occurring in the structure of graft copolymer which may be due to fusion. At 1073.15 K, about 42% char yield is obtained which is more than that of xanthan gum indicating that xanthan gum-g-poly(4-vinyl pyridine) is thermally more stable than xanthan gum at this temperature and it may be due to residual $-\text{CH}_2$ segment on xanthan gum-g-(4-vinyl pyridine) after leaving pyridine ring from the graft copolymer. Similar observation was also found with acrylonitrile-grafted xanthan gum [40]. The IPDT value of guar gum grafted poly(4-vinyl pyridine) is found to be 539.65 K, which is lower than the IPDT value of guar gum indicating that grafting of poly(4-vinyl pyridine) lowers the thermal stability of graft copolymer. At 1073.15 K, 25% char yield is obtained. Overall grafting of poly(4-vinyl pyridine) onto both polysaccharides imparts thermal stability more than pure substrates, and xanthan gum grafted poly(4-vinyl pyridine) is more thermally stable than guar gum grafted poly(4-vinyl pyridine). The thermal degradation of polysaccharides-g-poly(4-vinyl pyridine) may take place in the following steps.

Guar gum-g-acrylic acid and xanthan gum-g-acrylic acid

The guar gum-g-acrylic acids have been synthesized by peroxydiphosphate/Ag(I) (AA1) and vanadium/mercapto-succinic acid (AA2) redox pairs, while xanthan gum-g-acrylic acid has been synthesized by peroxomonosulfate/ferrous sulfate redox pair (AA3). AA1 began to degrade at about 453.15 K (Scheme 3; Fig. 9), AA2 began to degrade at about 423.15 K (Scheme 3; Fig. 9), while AA3 began to degrade at about 473.15 K (Scheme 3; Fig. 9). AA2 shows single step degradation process and about 4.5% mass loss was observed below 423.15 K. However, in the case of AA3, 5% mass loss was observed below 373.15 K which might be attributed to the loss of absorbed water. In the case of AA1, the rate of mass loss varies greatly with the temperature, therefore, two T_{\max} are obtained at 573.15 and 723.15 K. The PDT is 473.15 K, i.e., 333.15 K below the PDT of guar gum but FDT of the graft copolymer is higher than FDT of guar gum. In the case of AA2, the rate of mass loss increased with increase in temperature up to 483.15 K and gradually decreased thereafter, while AA3 degraded in

Scheme 3 Degradation steps of polysaccharides-g-polyacrylic acid

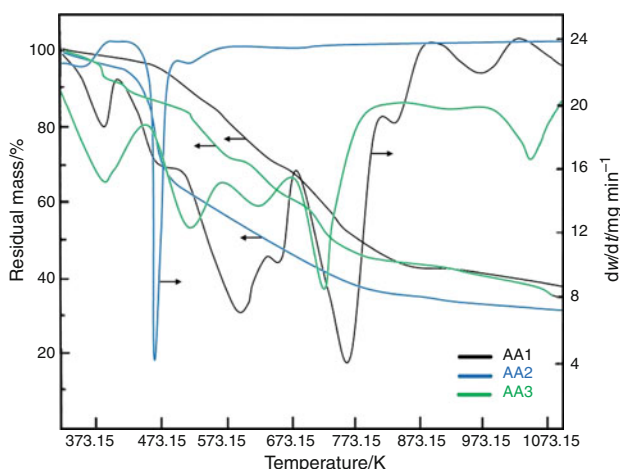
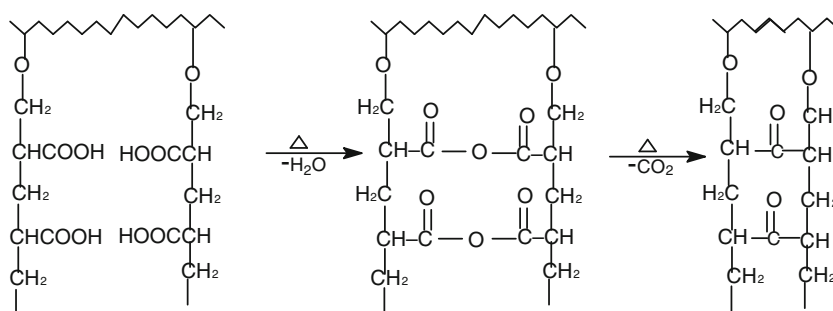


Fig. 9 TG and DTG curve of guar gum-g-polyacrylic acid (peroxydiphosphate/Ag(I)) (AA1), guar gum-g-polyacrylic acid (vanadium/mercaptosuccinic acid) (AA2), and xanthan gum-g-acrylic acid (AA3)

three stages, i.e., from 510.05 to 610.25 K, 610.25 to 709.65 K and from 709.65 to 1034.75 K. In the case of AA2, beyond 40% rate of mass loss decreased with increase in temperature, therefore, T_{max} and FDT were higher than guar gum and IPDT is 480.15 K. The mass loss in the case of AA1 at lower temperature range, i.e., 453.15–573.15 K is due to the formation of anhydride with elimination of water molecule from the two neighboring carboxylic groups of the grafted chains (Scheme 3). The second T_{max} in the case of AA1 is attributed to the decarboxylation of the anhydride formed earlier. The PDT of AA2 indicates that the grafting of acrylic acid by vanadium/mercaptosuccinic acid redox pair lowers the initial decomposition temperature because of the formation of anhydride with elimination of water molecule from the two neighboring carboxylic groups of the grafted chains as shown in Scheme 3 at lower temperature. In the case of AA3, the PDT was found to be 483.15 K which is lower than that of xanthan gum and maximum mass loss (T_{max}) occurred at 709.65 K. About 55% mass loss occurred between 373.15 and 1039.15 K. Grafting of acrylic acid onto xanthan gum lowers the PDT of the graft copolymer because of the dehydration followed by decarboxylation of

the $-COOH$ group present in the pendent chain of graft copolymer but after the formation of anhydride linkage thermal stability of the graft copolymer is greatly enhanced resulting in the overall increment of FDT, i.e., 1035.15 K and thermal stability of the grafted xanthan gum. About 30 and 17% mass loss is observed from 473.15 to 673.15 K and from 673.15 to 773.15 K in the case of AA1. At 1073.15 K, char yield of 35% is obtained in the case of AA1 while 30% in the case of AA2 and 31% in the case of AA3. IPDT value of AA1, AA2, and AA3 are 662.15, 480.15, and 568.15 K, respectively. Thus, the oxidant part of redox pair in AA1 is imparting thermal stability more to graft copolymer. The degradation of graft copolymer of acrylic acid may take place in the following way.

Xanthan gum-g-AMPS and guar gum-g-AMPS

Xanthan gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid (XOH-g-AMPS) and guar gum-g-2-acrylamido-2-methyl-1-propane sulfonic acid (GOH-g-AMPS) both graft copolymer starts to degrade at about 423.15 K (Fig. 10). However, $\approx 4\%$ mass loss has been observed at 373.15 K, which might be due to the loss of absorbed water, the rate of mass loss increased rapidly with temperature up to 473.15 K, but beyond 473.15 K the rate of mass loss was not so pronounced (Fig. 10). The TG curve of XOH-g-AMPS shows multistep degradation process, hence it is not

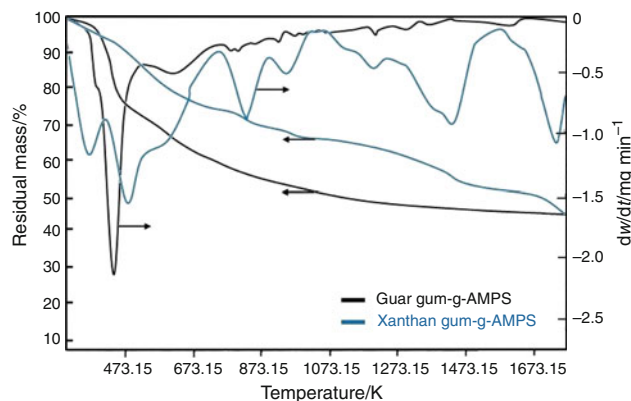


Fig. 10 Thermal behavior of guar gum-g-AMPS and xanthan gum-g-AMPS

Scheme 4 Degradation steps of polysaccharide-g-2-AMPS

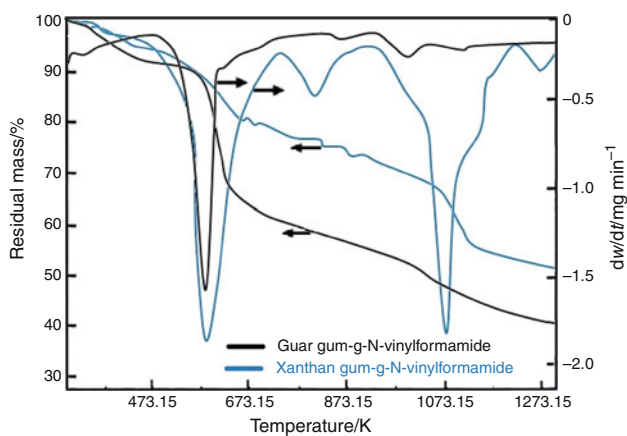
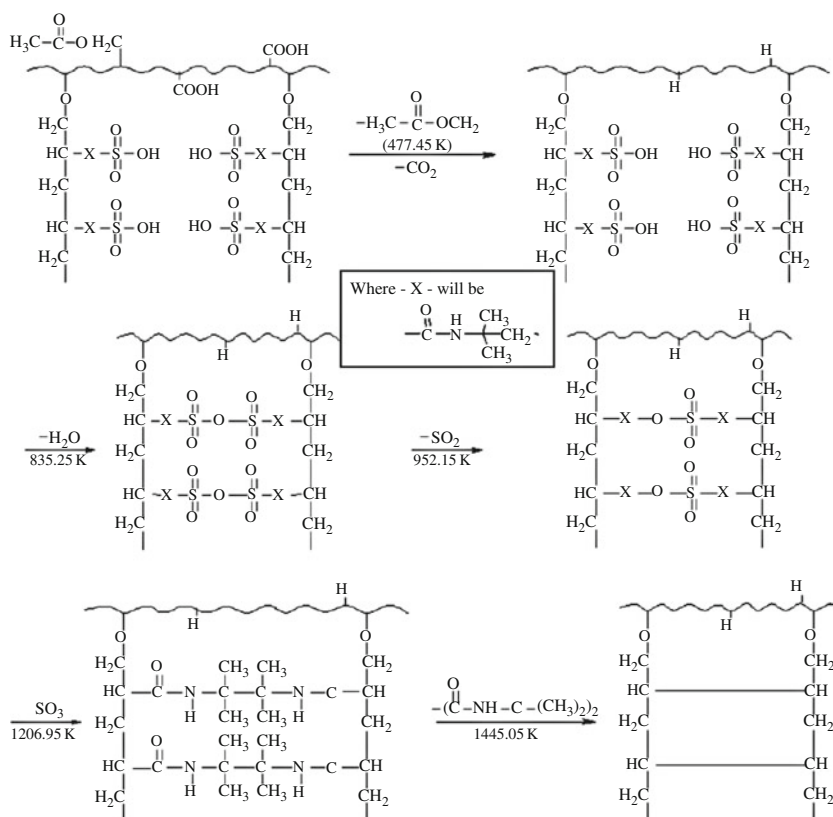


Fig. 11 TG and DTG curve of guar gum-g-poly(*N*-vinyl formamide) and xanthan gum-g-poly(4-vinyl formamide)

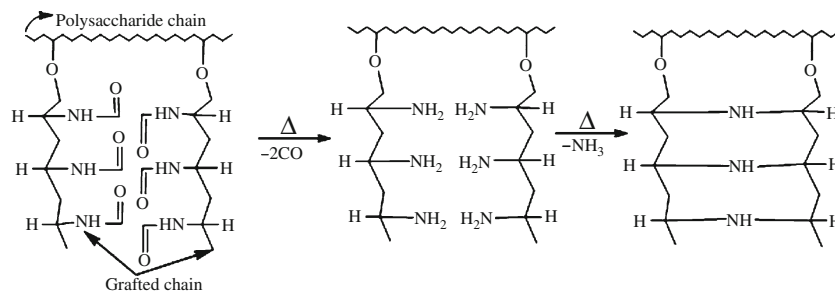
a single step degradation process, while TG curve of GOH-g-AMPS shows two-stage degradation process, i.e., from 455.15 to 613.15 K and from 613.15 to 785.15 K and about 45% mass loss was observed in the temperature range 373.15–773.15 K. The PDT of XOH-g-AMPS and GOH-g-AMPS have been found to be 498.15 and 455.15 K, respectively (Table 1), which are lower than that of polymeric backbone and this lowering might be due to the elimination of some groups from pendent polyAMPS in

both the graft copolymers. In initial stage, XOH-g-AMPS shows nearly same degradation process as of xanthan gum. Thus, first T_{\max} was observed at 477.45 K. In further degradation steps, the maximum mass loss occurred due to the elimination of H_2O , SO_2 , SO_3 and

$\left(\begin{array}{c} \text{O} \\ || \\ \text{C}-\text{NH}-\text{C}-(\text{CH}_3)_2 \end{array} \right)_2$ groups from pendent poly-

AMPS chain, respectively. Hence, on the basis of above fact there are five T_{\max} observed in thermal analysis of graft copolymer, which are shown in Table 1. In the case of GOH-g-AMPS the temperature at which maximum mass loss occurred was rather low, i.e., 455.15 K and FDT is 613.15 K which is almost same of the guar gum. The IPDT of GOH-g-AMPS has been found to be 548.15 K, which is very low than guar gum, it means grafting of AMPS onto guar gum also decreases the volatility temperature of graft copolymer. The gradual decrement in endopeak of XOH-g-AMPS indicates some physical and chemical changes in structure of graft copolymer. Sequential elimination of groups is shown in Scheme 4. About 65% of XOH-g-AMPS was lost at 1073.15 K, while 35% char yield was obtained in the case of GOH-g-AMPS up to 1073.15 K, hence FDT of graft copolymer was found at higher temperature in comparison to parent polymer, which clearly shows that the XOH-g-AMPS is thermally more stable than

Scheme 5 Scheme for degradation steps of polysaccharide-*g*-*N*-vinyl formamide



Scheme 6 Degradation step of guar gum-*g*-poly(*N*-vinyl pyrrolidone)

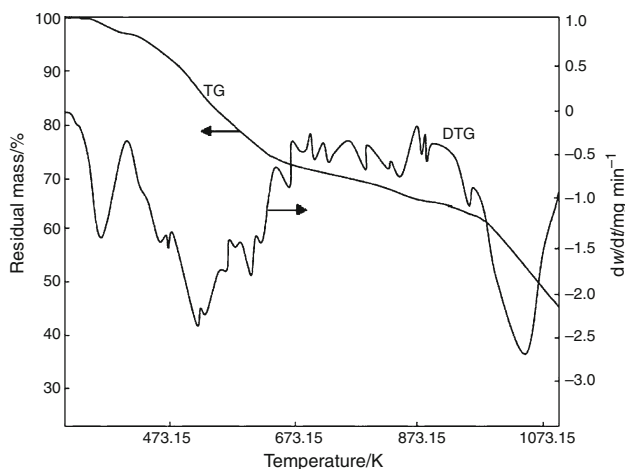
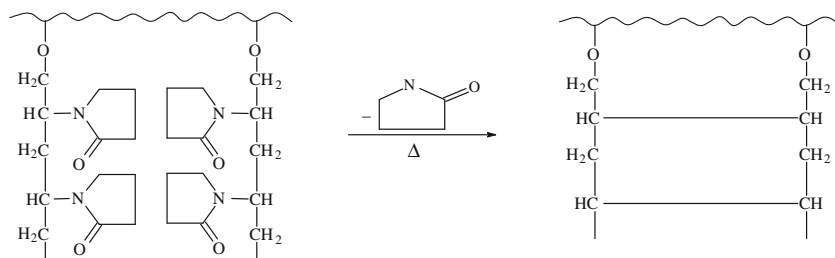


Fig. 12 TG and DTG curves of guar gum-*g*-*N*-vinyl-2-pyrrolidone

xanthan gum and this high stability was also confirmed by the high value of IPDT and high char yield of graft copolymer, which were found to be 595.15 K and 45% (at 1073.15 K), respectively.

Xanthan gum-*g*-*N*-vinyl formamide and guar gum-*g*-*N*-vinyl formamide

The degradation of xanthan-*g*-*N*-vinyl formamide and guar gum-*g*-*N*-vinyl formamide started at about 427.55 and 473.15 K, respectively (Fig. 11). However, 3.24 and 2.7% mass loss have been observed at 369.15 and 370.15 K for xanthan-*g*-*N*-vinyl formamide and guar gum-*g*-*N*-vinyl formamide, respectively, which is might be due to the loss of absorbed water. The xanthan-*g*-*N*-vinyl formamide shows

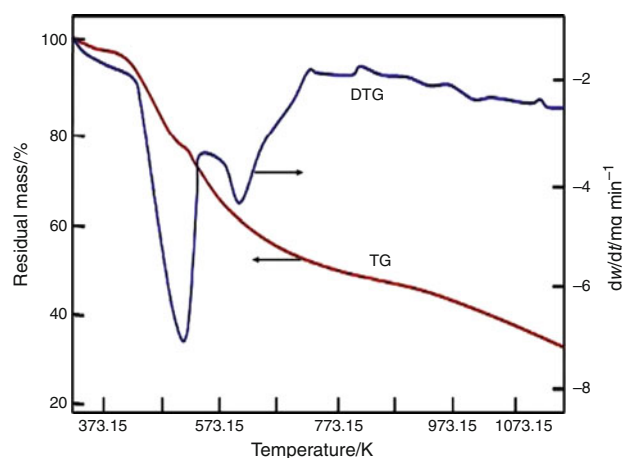
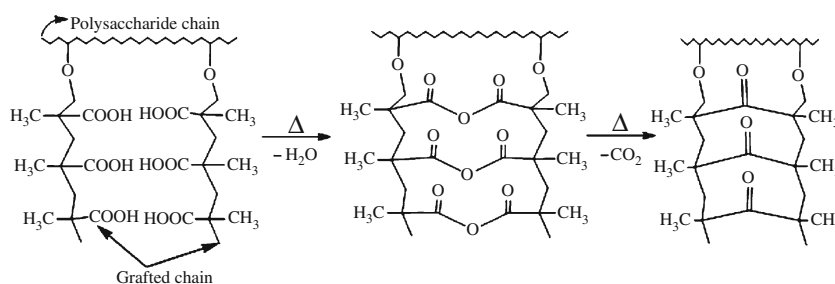


Fig. 13 TG and DTG curves of xanthan gum-*g*-methacrylic acid

two-stage degradation process, i.e., from 540.15 to 615.34 K and from 615.34 to 1073.15 K, while guar gum-*g*-*N*-vinyl formamide shows single step degradation step. Therefore, two T_{\max} has been obtained at which maximum degradation occurs, i.e., at 584.15 and at 1073.15 K in the case of xanthan-*g*-*N*-vinyl formamide. These two T_{\max} might be due to evolution of CO and NH₃ gases from pendent poly(NVF) chain at respective temperature (Scheme 5). The PDT of xanthan-*g*-*N*-vinyl formamide and guar gum-*g*-*N*-vinyl formamide has been found to be at 540.39 and 560.15 K, respectively (Table 1; Fig. 11). Only 50% guar gum-*g*-*N*-vinyl formamide has been degraded up to 873.15 K. About 50% mass loss has been observed at 1087.15 K in xanthan-*g*-*N*-vinyl formamide. Therefore, the FDT, i.e., 1109.15 K is higher in comparison to xanthan gum. A char yield of 36% has been obtained at 1105.15 K in the case of guar

Scheme 7 Scheme for degradation steps of xanthan gum-*g*-methacrylic acid



gum-*g*-*N*-vinyl formamide, while 45% char yield has been found at 1109.15 K in xanthan-*g*-*N*-vinyl formamide. Though PDT of the guar gum-*g*-*N*-vinyl formamide is lower than the guar gum but the high value of FDT, IPDT and char yield makes the guar gum-*g*-*N*-vinyl formamide thermally more stable than guar gum. IPDT of xanthan-*g*-*N*-vinyl formamide has been found to be 665.15 K. Thus, the thermal analysis data shows that xanthan-*g*-*N*-vinyl formamide is more thermally stable xanthan gum and guar gum-*g*-*N*-vinyl formamide and guar gum also.

Guar gum-*g*-*N*-vinyl-2-pyrrolidone

The graft copolymer began to degrade at 473.15 K. The mass loss of 2.22% at 373.15 K is due to desorption of absorbed water. Thermal degradation of guar-*g*-*N*-vinyl pyrrolidone (Scheme 6) has been completed in two stages. The first stage degradation has been occurred between 453.15 and 887.15 K and in this stage about 24.67% mass loss observed when temperature spans is more (Fig. 12). The second stage degradation observed from 1040.75 to 1229.35 K and in this stage maximum mass loss is 17.50%, which is due to the elimination of pyrrolidone ring from grafted polymer chain on guar gum, therefore, two T_{max} obtained at 517.75 and 1040.75 K. The PDT has been found to be at 479.40 K which is lower than guar gum about 52% guar gum-*g*-*N*-vinyl pyrrolidone was degraded up to 1073.15 K. The IPDT and FDT have been found to be at 618.57 and 1073.15 K, respectively. The maximum degradation which occurs at 1040.75 K was due to pendent chains of synthetic polymer. About 48% char yield has been obtained at 1073.15 K, which is high than guar gum. The high value of T_{max} , FDT, IPDT, and char yield makes the guar gum-*g*-*N*-vinyl-2-pyrrolidone is thermally more stable than the parent guar gum.

Xanthan gum-*g*-methacrylic acid

The graft copolymer began to degrade at about 373.15 K, 4.0% loss in the mass below this temperature is attributed due to the absorbed water. The rate of mass loss increased with increase in the temperature up to 523.15 K and gradually decreased thereafter. Again increase in the rate of mass

loss is observed from 603.15 to 773.15 K and thereafter it decreased (Fig. 13). Therefore, two T_{max} were obtained at 517.05 and 616.65 K. The PDT is found to be 489.51 K, i.e., 337.75 K below the PDT of xanthan gum, but FDT is much higher than xanthan gum (Table 1). The mass loss in the lower temperature range, i.e., 423.15–523.15 K is due to the formation of anhydride with elimination of H_2O molecule from the two neighboring carboxylic group of the grafted chains. The second T_{max} is attributed to the decarboxylation of the anhydrides formed earlier. About 34% char yield was obtained at 1173.15 K (Scheme 7).

Conclusions

From the thermal studies of guar gum and their graft copolymers grafted with different vinyl monomers reveals that the thermal degradation of graft copolymers of guar gum showed gradual decrement in mass loss while pure guar gum degraded rapidly and about 95% pure guar gum degraded up to 1073.15 K but graft copolymers degraded only 65–75% at the same temperature. On the basis of IPDT, it was found, that the guar gum-*g*-acrylamide (AM1 and AM2), guar gum-*g*-acrylic acid (AA1), guar gum-*g*-*N*-vinyl formamide, guar gum-*g*-*N*-vinyl pyrrolidone, and guar gum-*g*-methacrylamide were more thermally stable while guar gum-*g*-AMPS, guar gum-*g*-(4-vinyl pyridine), and guar gum-*g*-acrylic acid (AA2) is less thermally stable than guar gum.

From the comparative thermal study of xanthan gum and vinyl monomers grafted xanthan gum graft copolymer it was observed that the thermal degradation of graft copolymers of xanthan gum showed gradual decrement in mass loss while pure xanthan gum degraded rapidly and about 85% pure xanthan gum degraded at 1173.15 K but graft copolymers degraded only 55–75% at the same temperature. On the basis of IPDT, it was found, that the xanthan gum-*g*-*N*-vinyl formamide is thermally more stable than remaining five other graft copolymers and higher value of FDT also supports the high thermal stability than others and all the graft copolymers of xanthan gum in the present work are thermally more stable than the xanthan gum.

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