Synthesis and Characterization of Acryloyloxy Guar Gum

Mohan A. Shenoy, Dawid John D'Melo

Polymer Engineering and Technology Division, University Institute of Chemical Technology, Nathalal Parikh Marg, Matunga (East), Mumbai, India

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ABSTRACT: Guar gum is a galactomannan commonly used as a viscosity modifier in the food, pharmaceutical, and cosmetics industry. The aim of this study was to synthesize acryloyloxy guar gum via a Schotten-Bauman reaction in aqueous media. The reaction products were characterized using FTIR, C^{13}-NMR, wide angle X-ray diffraction techniques to ascertain the effect of acrylation on the structure of guar gum. The acrylation of guar gum was found to be limited to the primary hydroxyl groups on the guar gum molecule. The maximum degree of substitution (DS) was found to be 0.56, which was observed after 3 h of reaction. Since the reaction was carried out in an aqueous medium after 3 h of reaction the DS of the derivatised guar gum was found to decrease, because of hydrolysis of the formed ester linkages. The ester content and intrinsic viscosity of the derivatised guar gums were also evaluated. Thermal analysis showed that a higher DS resulted in products with lower thermal stability and there was no evidence of reaction via the acrylate groups on heating. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 148–154, 2010

Key words: polysaccharides; biomaterials; hydrophilic polymers; modification

INTRODUCTION

Guar gum is a naturally occurring polymer extracted from the *Cyamopsis tetragonalobus* plant and is commercially cultivated in parts of the Asian subcontinent as well as in North Africa and South America. Chemically, guar gum is a galactomannan with a 1,4 – β – d - mannopyranose backbone with branch-points from their 6-positions linked to 1- α – d – galactopyranose units. However, these side chains are not evenly distributed on the mannopyranose backbone but are found in galactose rich and deficient regions.[1–3] There are various galactomannans, which are extracted from plant sources including locust bean gum, guar gum, and fenugreek gum, to name a few. These gums have varied properties, such as differing solubility in water, solution viscosity, clarity, etc. These differences arise because of the variations in their galactose to mannose ratios in the polymer i.e. 1 : 3, 1 : 2 and 1 : 1 with respect to locust bean gum, guar gum, and fenugreek gum. When the galactose content increases the polymer becomes more soluble, making fenugreek extremely water soluble and locust bean gum soluble only in hot water.

Correspondence to: M. A. Shenoy (m.a.shenoy@hotmail.com).

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Guar gum, as can be seen from Figure 1, consists of nine hydroxyl groups per repeat unit, which averages to three per pyranose ring. This is similar to other polysaccharides such as starch, a polyglucoside. There have been a limited number of studies in which gaur gum has been esterified, which have been carried out in both aqueous as well as non-aqueous media.[4–7]

The reaction of starch with acryloyl chloride and methacryloyl chlorides via a Schotten-Bauman's reaction has been reported recently and was found to result in an esterified product with a maximum DS of approximately 2, which was found to be soluble in organic solvents such as toluene.[8,9] The double bond on the acrylate was preserved making it available for further reaction such as homopolymerization and copolymerization with acrylic monomers. The reaction between guar gum and acryloyl chloride has been investigated before, which resulted in a crosslinked polymer, used as a super-absorbent polymer.[10] In this case the guar gum was esterified using acryloyl chloride and the double bond reacted with the hydroxyl groups via a Michael reaction resulting in the crosslinking of the guar gum.

This study aims at investigating the esterification of acryloyl chloride with gaur gum using a Schotten-Bauman's reaction, while preserving the double bond on the acrylate for further reaction. The acrylation of guar gum would reduce its hydrophilic nature and change the functionality from one solely consisting of hydroxyl groups to one containing terminal carbon double bonds as well as hydroxyl

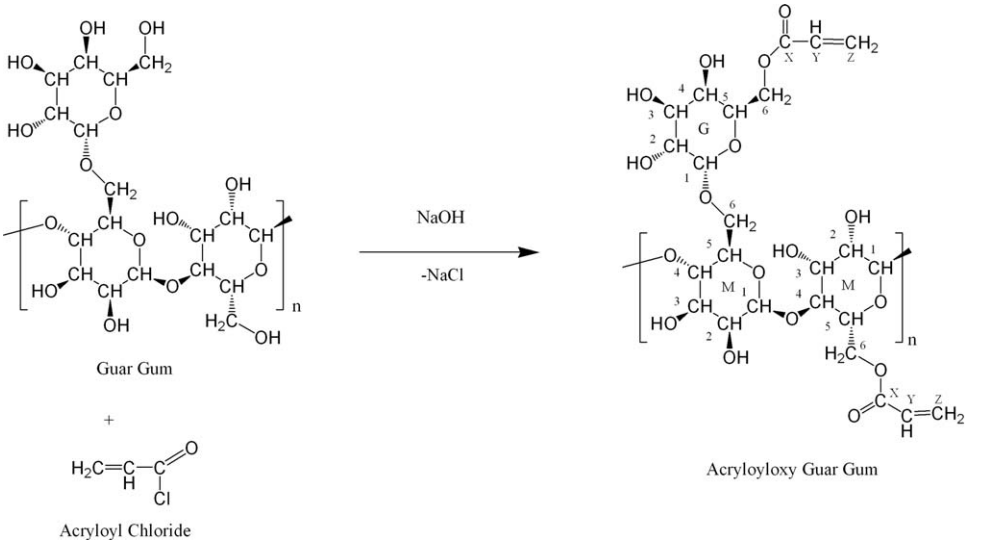

Figure 1 Schematic representation of acryloylation of guar gum.

groups, which would be the case in a partially acrylated product. The effect of reaction time on the degree of substitution was investigated. The derivatised guar gums were analyzed using FTIR and C^{13}-NMR spectroscopy. The effect of acrylation on the intrinsic viscosity, crystallinity, and thermal stability was also studied. The importance of the study lies in the potential applications of the products as cross-linking agents in coatings and castings, where the curing reaction occurs via a double bond, such as in the case of alkyd coatings and unsaturated polyesters.[11] This would allow for the use of a renewable resource in such applications.

EXPERIMENTAL

Materials

Guar gum was obtained from M/s Lucid Colloids, India and had an intrinsic viscosity of 14.6 dL/gm, moisture content of 8–9% and ash content of 2–3%. Acrylic acid and benzoyl chloride was obtained from M/s S.D. Fine Chemicals, India, was of analytical reagent grade and was used without any purification. Hydroquinone, sodium hydroxide, solvents like methyl ethyl ketone, toluene and acetone were also procured from M/s S.D. Fine Chemicals, India, were of laboratory reagent grade and were used without any further purification.

Synthesis of acryloyl chloride

Acryloyl chloride was prepared just before use by the reaction of acrylic acid and benzoyl chloride. 1.0 mole of acrylic acid was heated with 2.0 moles of benzoyl chloride in the presence of hydroquinone and the fraction distilling out between 65 and 85°C was collected in a flask containing hydroquinone. This crude acryloyl chloride was then redistilled and the fraction distilling out at 74–76°C was isolated and used for the esterification of guar gum.

Acrylation of guar gum

A solution was prepared by dissolving 5.0 g guar gum, 0.5 g hydroquinone, and sodium hydroxide in 50 mL distilled water and 50 mL methyl ethyl ketone. The solution was maintained at a temperature between 0–5°C, to which a solution of 50 mL toluene, 10 mL methyl ethyl ketone and a stiochiometric amount of acryloyl chloride was added drop wise over a time span of 10 min. The initial addition of acryloyl chloride solution to the reaction mixture was taken as the start of the reaction. The reaction was carried out at 0–5°C for varying time periods after which the derivatised product was precipitated in acetone. The precipitate was then filtered, washed with acetone and dried at 50°C under reduced pressure for 12 h to obtain a dry acryloylated guar gum. The schematic representation of the reaction is represented in Figure 1. The products obtained after varying time periods were denoted by AGG followed by the time of reaction i.e. AGG1 would refer to the product obtained after 1 h of reaction.

Estimation of DS

The DS of the derivatised products was estimated by evaluating the ester value of the samples. Weighed quantities of the derivatised guar gum and a blank, consisting of the native guar gum, were dissolved in 25 mL aqueous solution of 0.2*N* KOH and allowed to stand for 24 h at room temperature, to affect hydrolysis. The samples were then back

TABLE I
Characterization of Acryloyloxy Guar Gum

Sample Name	Time of reaction (hr)	Ester value (mg KOH/g)	DS	Intrinsic viscosity (dL/g)	% Crystallinity	Endotherm from DSC (°C)	Onset of degradation (°C)
GG	–	–	–	14.54	4.34	252	255
AGG1	1	154	0.50	0.87	13.15	222	220
AGG3	3	170	0.56	0.97	14.24	225	215
AGG5	5	122	0.39	4.03	5.13	231	223
AGG7	7	56	0.17	8.4	5.08	246	249
AGG11	11	21	0.06	14.19	4.46	251	250

titrated against a solution of 0.2*N* HCl. The ester value thus obtained was then used to calculate the DS of the samples.[12,13]

$$\text{Ester value} = \frac{56100 \times \text{functionality}}{\text{Molecular weight}} \quad (1)$$

The functionality, with reference to the ester content, in this case is the same as the DS and the molecular weight is the weight of the repeat unit of guar gum added to the weight of the added acrylate moiety. The weight of the added acrylate moiety per repeat unit will be 54 × DS, where 54 is the molecular weight of the acrylate moiety. Thus, the equation becomes

$$\text{Ester value} = \frac{56100 \times \text{D.S.}}{(162 + 54 \times \text{DS})} \quad (2)$$

Rearranging eq. (2) we get.

$$\text{D.S.} = \frac{162 \times (\text{ester value})}{56,100 - \{54 \times (\text{ester value})\}} \quad (3)$$

Thermal analysis

Differential scanning calorimetry (DSC) was performed on a MDSC Q100 from TA instruments. Samples of about 5 to 10 mg were heated from 40 to 270°C at a scan rate of 20°C/min and a modulated frequency of ± 0.5°C every 40 sec. The test was conducted under a N_2 flow of 50 mL/min.

Thermo-gravimetric analysis (TGA) of the samples was carried out on a SDT Q600 from TA instruments. The samples were measured against an alumina standard in a 90 mL/min N2 flow with a temperature ramp of 20°C/min up to 600°C.

Spectral analysis

FTIR of the samples were carried out on films of the samples. Films were cast on a Teflon sheet from an aqueous solution and dried at 80°C in an air circulating oven, followed by complete drying at 60°C in a vacuum oven. The films thus obtained were then analyzed using a Perkin Elmer 781 spectrophotometer.

The C^{13}-NMR was carried out on a Bruker DPX 250 MHz spectrometer with D_2O as solvent.

The wide angle X-ray diffraction pattern (WAXD) was analyzed using a Rigaku Miniflex+ Instrument (30 KV, 15 mA) using CuKα radiation source, NaI detector, a variable slit with a 0.05 step size and a 2 degree per minute scan rate. The powdered samples were placed on the holder and the diffraction pattern analyzed between 5 and 50°. The X-ray diffraction pattern had a standard deviation of 2Θ of 0.1°. The degree of crystallinity of the samples was estimated using a curve fitting program available with the software package of the instrument.

RESULTS AND DISCUSSION

The variation of reaction times resulted in AGG derivatives with different DS and thus different properties. Table I. enumerates the derivatives of guar gum synthesized along with their respective times of reaction and their individual properties. It was observed that the derivatives with the highest DS were obtained at 1–3 h after which the DS decreased. This observation was further evidenced by the change in viscosity of the AGG solutions, which was found to decrease as the DS increased. As the DS increased the hydrophobic nature of the derivative increased, thus reducing its interaction with water resulting in the decrease in viscosity of the solution.[14] AGG1 and AGG3 showed the lowest viscosities and had the highest DS as compared with the other samples. The reaction was carried out in an aqueous medium in the presence of an alkali and salts, which resulted in the hydrolysis of the derivatised guar gum and after 11 h the intrinsic viscosity of the solution increased to that of the native guar gum. The viscosity of solutions obtained from AGG11 closely matched that of the unmodified guar gum indicating that it was almost completely hydrolysed and that degradation of the guar gum had not taken place to a large extent. The reaction medium

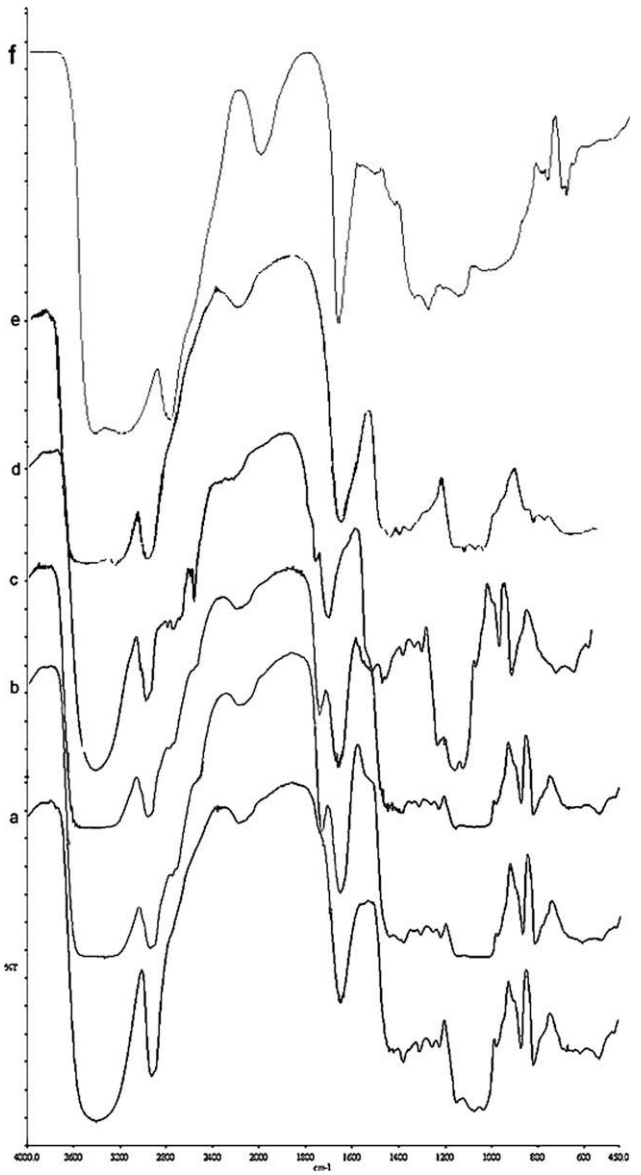

Figure 2 FTIR spectra of a-GG, b-AGG1, c-AGG3, d-AGG5, e-AGG7, and f-AGG11.

was alkaline in nature and during the course of the reaction hydrochloric acid was generated as a by-product. Acid or alkali mediated hydrolytic degradation of the guar gum would lead to a reduction in the molecular weight by the hydrolysis of the 1–4 mannopyranose ether link, leading to a reduction in the intrinsic viscosity of the resultant solutions.[15] Since the intrinsic viscosity of the solutions of AGG11 approximately matched that of native guar gum we can assume little or no degradative hydrolysis of the guar gum backbone.

The FTIR spectra of the acrylated samples showed the presence of an ester from the peak at 1727 – 1733 cm^{-1} attributed to carbonyl stretching, as seen in Figure 2. The peak observed at 1650 cm^{-1} was attributed to the hydration of guar gum.[16] The peak observed at 3300–3400 cm^{-1} be the stretching vibrations of the hydroxyl group. The presence of these peaks in the acrylated guar gum samples shows that although acrylation has taken place there were still unreacted hydroxyl groups present. It could also be observed that the carbonyl peak was the most prominent for AGG1 and AGG3 after which it decreased and AGG7 and AGG11 as could be observed in Figure 2. Because of the hydration of the AGG samples there was no observable reduction in the hydroxyl peak observed at 3300–3400 $cm^{-1.}$ This trend of the intensity of the carbonyl peak decreasing after 3 h of reaction was reflected in the ester values as well as intrinsic viscosity data obtained.

The C^{13}-NMR analysis of AGG was undertaken to confirm the esterification of GG. The NMR analysis also indicated the selectivity of the esterification, with respect to the hydroxyl group on either the galacto-anhydropyranose rings or manno-anhydropyranose rings on GG. Table II lists out the peaks obtained from the C^{13}-NMR analysis of AGG3. AGG3 was chosen for the analysis because it showed the highest DS and would give the most accurate indication of the position of the acrylation on the parent guar gum molecule. The product depicted in Figure 1 indicates the various carbon atoms which are present in the acryloxylated guar gum. The rings "M" and "G" in the figure refer to the mannopyranose and galactopyranose portions of the polysaccharide. From the presence of peaks

TABLE II
C^{13}-NMR Analysis of AGG3

Carbon atom	Peak position (ppm)	Carbon atom	Peak position (ppm)	Carbon atom	Peak position (ppm)
M1	100.14	G1	98.67	X	161.1
M2	69.77	G2	68.34	Y	129.9
M3	71.22	G3	68.34	Z	130.2
M4	74.48	G4	68.34		
M5	73.18	G5	71.22		
M6	60.44	G6	60.92		
M6-G	66.31	G6-Acrylate	61.18		
M6-Acrylate	61.18				

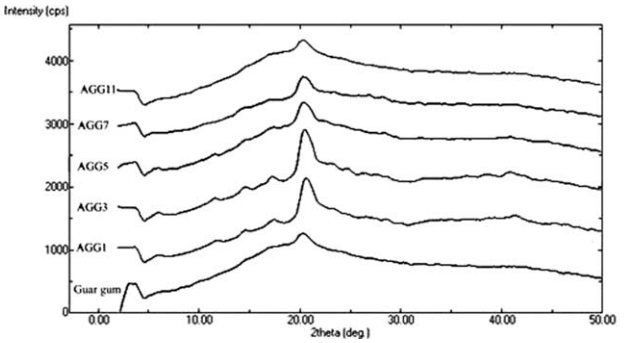

Figure 3 X-ray diffraction patterns of GG and AGGs.

attributed to carbons X, Y, and Z we positively conclude that acrylation occurred. Further, the presence of the C=C bond in the acrylate was also confirmed indicating that side reactions, such as a Michael addition reaction had not taken place, leaving the double bonds of the acrylate unreacted. It could be seen that the acrylation occurred at the G6 and M6 carbon atoms, corresponding to the primary hydroxyl groups on the galactopyranose and mannopyranose rings. The presence of the peaks attributed to nonacrylated G6 and M6 carbon atoms also showed that the acrylation was not complete with respect to the hydroxyl groups on the guar gum molecule. Thus, under the reaction conditions adopted for this study there was no apparent selectivity with reference to the type of ring i.e. manno-anhydropyranose or galacto-anhydropyranose but was restricted to the primary hydroxyl groups, because of the greater reactivity of the primary as compared with secondary hydroxyl groups. This would also explain the limitation on the DS of the AGGs observed. Figure 3 depicts the nature of the diffraction patterns observed for GG and AGG. The X-ray diffraction pattern showed a narrowing of the main peak obtained at 20.5°. For the samples AGG1 and AGG3 there was the detection of three new peaks at 2Θ values of 11.5, 14.6, and 17.4°. These minor peaks were most clear in AGG3, as seen in Figure 3. The crystallinity of the samples after acrylation increased with the DS of the derivative, this was similar to that observed in the case of acetylated starch.[17] GG has a large number of hydroxyl groups present on the molecule resulting in a large number of random hydrogen bonds being generated. The increase in the crystallinity was caused because of the reduction in random hydrogen bonding, allowing for an increase in order in the particles. The maximum DS was observed to be 0.56 and the esterification was limited to the primary hydroxyl groups located on the galactose and mannose rings. It was possible that with an increase in the DS the crystallinity would reduce, as in the case of reduction of hydrogen bonding in nylon by the replacement of amide with N-methyl amide moieties,[18] however, as a higher DS could not be achieved this could not be confirmed. As the time of reaction progressed beyond 3 h the samples obtained showed broadening of the main peak and disappearance of the minor peaks, indicating a decrease in the crystallinity of the samples as seen from Table I. This correlated with the fact that there was a decrease in the DS of the AGG after AGG3. Thus, the hydroxyl groups were regenerated resulting in an increase in the degree of random hydrogen bonding.

The thermal analysis of the derivatised guar gum products carried out through DSC and TGA indicated that their thermal stability decreased with an increase in the DS. It has already been shown that the thermal stability of guar gum decreases on esterification, with the exception of maleate esters, and this decrease has been attributed to a decrease in the hydrogen bonding on esterification.[19] The hydrogen bonding observed in the GG and AGG samples resulted in the degradation of the samples before melting. The hydrogen bonding behaves as temporary ionic bonds in the particles resulting in an increased thermal stability, since some heat is dissipated by the breaking of these bonds, requiring more heat for the cleavage of covalent bonds i.e. degradation. In the case of the AGGs the number of hydrogen bonds is lower than in the case of GG, thus resulting in the observed decrease in thermal stability. However, acrylation did not result in a sufficient decrease of hydrogen bonding to show a melting point. From Table I it could be seen that the endotherms observed from the DSC match the onset temperature of degradation as indicated from the TGA graphs. Figure 4 shows the DSC curves where an endotherm was observed above 150°C, which on comparison with the TGA results was found to coincide with the onset of thermal degradation. A comparison of the DSC curve and TGA curve of AGG1 are shown in Figure 5. From Figure 5 it could be observed that there was an endotherm observed at 85–90°C, which was reflected by a slight decrease in the weight of the sample. This was attributed to the removal of water or moisture from the sample, adsorbed by the AGG sample. The next endotherm was observed at 220°C, which coincided with the initiation of degradation of the AGG sample at 222°C. The TGA curves of GG and the AGG derivatives are shown in Figure 6. The DSC curves showed an endotherm attributed to the initiation of thermal degradation of the GG/AGG substrates. There was no evidence of reaction involving the unsaturation introduced via the acrylate moieties. Any reaction involving the unsaturation would be represented by an endotherm, and in the case of homopolymerization would be followed by an exotherm. This

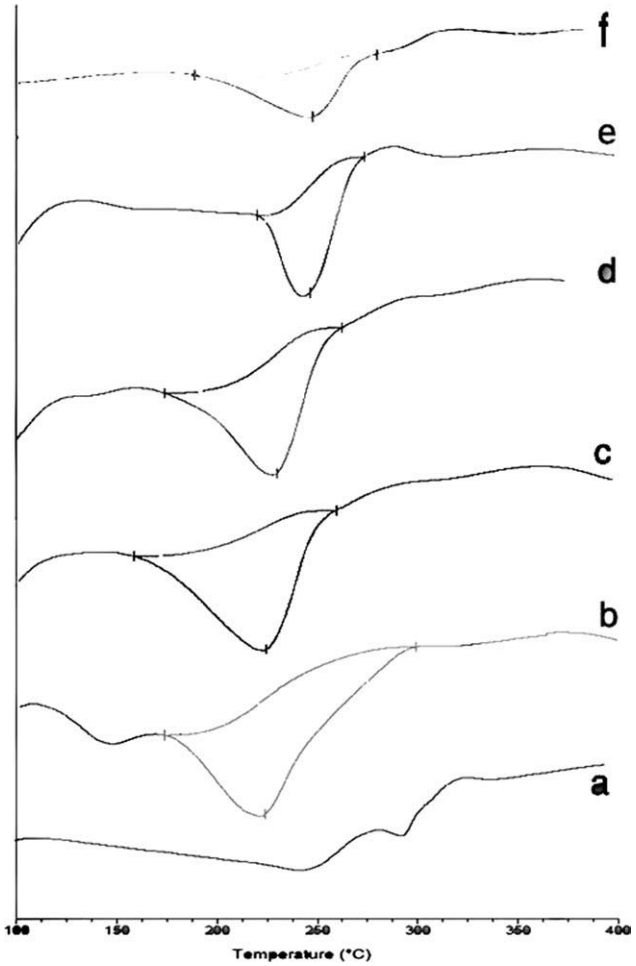

Figure 4 DSC curves of a-GG, b-AGG1, c-AGG3, d-AGG5, e-AGG7, and f-AGG11.

endotherm would further not be reflected by any change in weight of the sample in the TGA curves. However, this was not observed, the endotherm obtained in the DSC was the initiation of the degradation. The failure of the AGG substrates to undergo

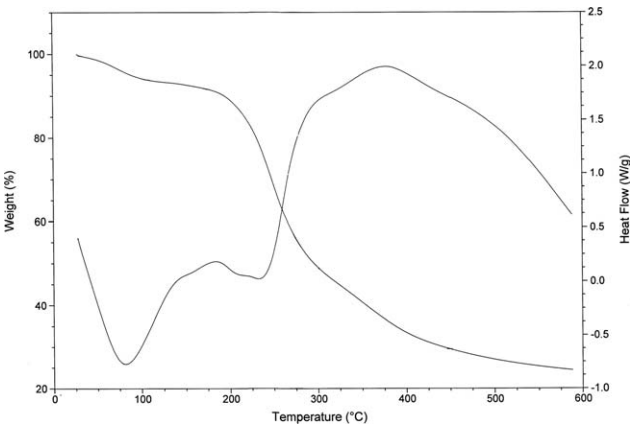

Figure 5 Comparison of DSC and TGA curves of AGG1.

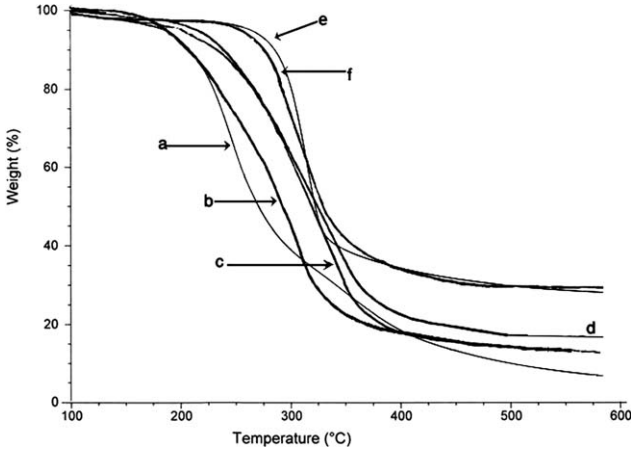

Figure 6 Comparison of TGA graphs of a-AGG1, b-AGG3, c-AGG5, d-AGG7, e-AGG11, and f-GG.

any reaction could be due to the fact that they were present as a solid, which was contrary to that observed in the case of acryloxyl starch in the presence of methyl methacrylate.[9] However, the reactivity of the double bonds present in the AGG has been studied separately.[11]

CONCLUSIONS

The acrylation of guar gum was accomplished using the Schotten-Bauman reaction leaving the acrylate double bonds unreacted. The acrylation was found to be selective with respect to the primary hydroxyl groups under the reaction conditions used and the maximum DS obtained after 3 h of reaction. The reaction was conducted in an aqueous medium and almost complete hydrolysis of the ester groups occurred after 11 h of reaction. The hydrophobic nature of the AGG increased with an increase in acrylate content, as reflected by the instrinsic viscosity as well as other properties. The crystallinity of AGG was found to increase with the DS, however, the thermal stability decreased because of the reduction in the hydrogen bonding on acrylation.

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