S. Uzan / Hacettepe J. Biol. & Chem., 2023, (2), 241-249

Research Article

Hacettepe Journal of Biology and Chemistry

journal homepage: www.hjbc.hacettepe.edu.tr

Thermal and Flocculation Properties of Acacia Gum Grafted with Cationic Polyacrylamide

Katyonik Poliakrilamid Aşılı Akasya Sakızının Termal ve Flokülasyon Özellikleri

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ABSTRACT

The cationic flocculants have better flocculation ability as they can work efficiently through both bridging and charge neutralization. Acacia gum, which has common advantages such as renewability, biodegradability, non-toxicity and biocompatibility, was grafted with cationic acrylamide to obtain a cationic graft copolymers. Acacia gum (AG) was grafted with polyacrylamides with different catonic ratios obtained by using different amounts of acrylamide (AM) and 2-(Acryloyloxy) ethyl]trimethylammonium chloride (DMC (cationic monomer)). Graft copolymers of acacia gum and monomers has been synthesized by free radical polymerization using an ammonium persulfate (APS)-ascorbic acid (AA) redox initiation system in an inert atmosphere. The thermal properties of these graft copolymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses. The formation of graft copolymers was confirmed by FTIR spectroscopy and thermal analysis. The effects of different cationic ratios of polyacrylamide on flocculation and their flocculation performance were evaluated in kaolin suspension. In this study, flocculation experimental results with different dosages and different graft copolymers showed that the amount of cationic monomer in graft copolymers is effective on flocculation.

Key Words

Acacia gum, graft polymer, cationic polymer, polyacrylamide, graft copolymers.

ÖZ

Katyonik flokülantlar, hem köprüleme hem de yük nötrleştirme yoluyla verimli bir şekilde çalışabildikleri için daha iyi flokülasyon yeteneğine sahiptir. Yenilenebilirlik, biyolojik olarak parçalanabilirlik, toksik olmama ve biyouyumluluk gibi ortak avantajlara sahip olan akasya sakızı, katyonik aşı kopolimerleri elde etmek için katyonik akrilamid ile aşılanmıştır. Akasya zamkı (AG), farklı miktarlarda akrilamid (AM) ve 2-(Akriloiloksi)etil]trimetilamonyum klorür (DMC (katyonik monomer)) kullanılarak elde edilen farklı katonik oranlardaki poliakrilamidlerle aşılandı. Akasya zamkı ve monomerlerin aşı kopolimerleri, inert bir atmosferde bir amonyum persülfat (APS)-askorbik asit (AA) redoks başlatma sistemi kullanılarak serbest radikal polimerizasyonuyla sentezlendi. Bu aşı kopolimerlerinin termal özellikleri, diferansiyel taramalı kalorimetri (DSC) ve termogravimetrik (TGA) analizlerle araştırıldı. Aşı kopolimerlerinin oluşumu FTIR spektroskopisi ve termal analiz ile doğrulandı. Poliakrilamidlerin farklı katyonik oranlarının flokülasyon üzerine etkileri ve flokülasyon performansları kaolin süspansiyonunda değerlendirildi. Bu çalışmada, farklı dozlarda ve farklı aşı kopolimerleri ile yapılan flokülasyon deney sonuçları, aşı kopolimerlerindeki katyonik monomer miktarının flokülasyon üzerinde etkili olduğunu göstermiştir.

Anahtar Kelimeler

Akasya zamkı, aşı polimeri, katyonik polimer, poliakrilamid, aşı kopolimerleri.

Article History: Received: Oct 31 11, 2022; Revised: Feb 7, 2023; Accepted: Feb 28, 2023; Available Online: Mar 7, 2023.

DOI: https://doi.org/10.15671/hjbc.1197157

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INTRODUCTION

The kaolin wastewater, which contains large amounts of kaolin clay, which degrades water quality, originates from the paint, rubber, paper filler, coating pigment and chemical production industries. Kaolin wastewater bring with them multiple negatives including environmental pollution, soil and air contamination, air with attendant consequences for inorganic and organic ones. Flocculation is a traditional chemical water treatment technique typically applied to separate suspended solids from water. Various chemical flocculants, such as natural polymer product, anionic/cationic polyacrylamides (PAMs), polyferric chloride, and polyaluminum chloride, are widely utilized for sewage separation. Specifically, in the flocculation process, synthetic polymer flocculants are used to form molecular bridges between the solid particles facilitating impurities to be separated from the water [1, 2]. The cationic flocculants have better flocculation ability as they can work efficiently through both bridging and charge neutralization [3]. One of the most cost-effective monomers, cationic polyacrylamides is the subject of increasing attention due to its high efficiency in the treatment of drinking water and wastewater [4] and is widely used worldwide [5]. Cationic polymers stabilize clay through electrostatic interactions with negatively charged clay surfaces. Positively charged PAM is believed to bind to negatively charged sites on mineral surfaces.Through this binding action, the PAM solution induces clay stabilization, making clay particles to stick readily to one another to form aggregates [6]. However, these synthetic polymers are not biodegradable and their degradation products are considered to be hazardous because of the release of toxic monomers, which may cause potential health hazards [7].

Acacia gum, also known as arabic gum, is a complex arabino galactan type neutral nonionic polysaccharide exuded by Acacia trees [8, 9]. Recently, a considerable attention has been paid to the production of environmentally friendly polymers due to their biodegradability and renewability [10]. Acacia gum is composed of 1,3-linked β-d-galactopyranosyl units (main chain) with two-to-five 1,3-linked β-d-galactopyranosyl units, joined to the main chain by 1,6-linkages [11]. The common advantages including renewability, biodegradability, non-toxicity and biocompatibility have enabled it to be used in many fields such as food, suspending agents and pharmaceutical and cosmetic industries [12, 13]. Natural organic flocculants also have some disadvantages such as low molecular weight, low charge density and short shelf life. Synthetic flocculants are effective even at low dosages and have long shelf life, but form fragile flocs [14]. Synthetic flocculants are available in all three forms, i.e. cationic, anionic and nonionic [15]. To overcome these shortcomings of synthetic and natural organic flocculants, grafting copolymerization is adopted, which combines the advantages of natural flocculants with the advantages of synthetic flocculants [16]. However, insight study has shown no single flocculant is capable of producing a faster settling and a low residual turbidity, simultaneously [17]. Groups or branch chains added to the backbone of natural polymer materials by graft copolymerization can change their charge, mobility, flexibility, hydrophilicity, molecular weight, viscosity and thermal stability [12, 18].

By grafting polysaccharides with synthetic polymers, grafted polymers with the advantages of both groups are obtained [14]. This is an effective technique to improve its properties and industrial applications [12, 18]. Although many materials have been developed and successfully used in removing pollutants from wastewater, there is still a need to improve their performance. The continuous increase of market needs for efficient and effective materials in wastewater treatment has induced the development of hybrid materials for coagulation–flocculation of wastewater. Hybrid materials thus have emerged as new materials that pose tremendous potential in treating wastewater due to their better performance compared to that of conventional inorganic-based coagulants, and its lower cost than that of organic-based flocculants [19].

In this study, a graft copolymer of acrylamide and 2-(Acryloyloxy)ethyl]trimethylammonium chloride was synthesized with acacia gum. The thermal properties of synthesized graft copolymers and the effects of different cationic polyacrylamide ratios on flocculation were systematically investigated. The performance of graft copolymers synthesized with $Al_2(SO_4)_3$, an important and widely applied coagulant in water treatment, was compared. The applicability of these graft copolymers as novel polymeric flocculants for treatment of wastewater (kaolin suspension) used as a model has been reported. In the existing literature, there are no studies on the effect of cationic density of graft copolymers on flocculation performance and mechanism. Therefore, this study aimed to examine the effect of the cationic percentage of grafted polymers as flocculants on the flocculation performance and mechanism, and to examine the thermal properties of these newly synthesized graft copolymers.

MATERIALS and METHODS

Materials

Acrylamide (AM, ≥ 99%), aluminum sulfate hydrate (Al2(SO4)3.xH2O, 98%), ascorbic acid (99%), acetone (≥ 99.5%) and methanol (anhydrous, 99.8%) were purchased from Sigma-Aldrich (Germany). 2-(Acryloyloxy) ethyl]trimethylammonium chloride (DMC, 80 wt. % in H2O, contains 600 ppm monomethyl ether hydroquinone as inhibitor) was purchased from Aldrich. Acacia gum (AG, branched polysaccharide, moisture content ≤ 15%, insoluble residue ≤ 0.20%), amonium persulfate (APS, ≥ 98.0%) from Sigma. Kaolin a hydrated aluminum silicate is a powder with a particle size of 0.1 to 4 microns. pH of a 20% suspension of kaolin is 3.5-5.0 and its loss on drying reported by the supplier (Sigma) is ≤ 2.0%. All chemicals were used without further purification.

Methods

Synthesis of graft copolymers

55 ml of distilled water was added to 2.0 g of AG. It was stirred at 55 oC for 15 minutes in an inert $He_{(g)}$ atmosphere. Then, 50.0 mg of ammonium persulfate (APS) as initiator and 40.0 mg of ascorbic acid (ABC) were added and mixing was continued for 30 minutes. Then, the reaction was continued under the same conditions by adding a known amount of monomers dissolved in 3 ml of distilled water to the reaction mixture. At the end of the reaction, 2/3 of the water of the reaction mixture was evaporated under vacuum. The polymer was precipitated by adding 50 ml of acetone to the reaction mixture and centrifuged. It was washed 2 times with 50 ml of acetone and then 3 times with 50 ml of distilled water/methanol (7/3 v/v) solvent mixture and centrifuged again. It was dried in an oven at 50 °C.

Thermal analysis

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyzes were used to examine thermal transitions induced by heating in an inert nitrogen ($N_{2(g)}$) atmosphere. 3-5 mg of sample was heated from room temperature to 550 ^{o}C in a sealed aluminum pan with a heating rate of 10 ^{o}C/min.

Thermogravimetry analysis

Thermogravimetric analyzes (TGA) were performed to analyze the weight loss of sample at different temperatures and their thermal stability. 8-10 mg of sample was heated from room temperature to 900 ^{o}C in a platinum pan with a heating rate of 10 ^{o}C/min.

FTIR spectroscopy

The FTIR spectra of AG and of graft copolymers were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer between 400 and 4000 cm-1.

Flocculation tests

For sedimentation tests, 2.25 g kaolin was taken into a 100 ml beaker in distilled water. After the kaolin was well suspended with a magnetic stirrer for 15 minutes, it was transferred to 100 ml measuring cylinder that was scaled in height. The flocculant/coagulant, which was prepared as 2.00 g/L, was added to this suspension in five dosages, with final concentrations of 2, 4, 6, 8 and 10 ppm. The measuring cylinder was closed quickly and shaken by turning it up and down 3 times. The descent of the solid/liquid interface (suspension line) was carefully observed and recorded as a function of settling time.

RESULTS and DISCUSSION

FTIR spectroscopy

Figure 1 shows the FTIR spectra of AG and the representative graft copolymers. AG exhibited characteristic bands at 3424 cm-1 and 2903 cm-1 representing the -OH and -CH2, -CH3 aliphatic groups. The band at 1621 cm-1 corresponds to the asymmetric and symmetric stretching of the COO- group. Also, the band at 1424 cm-1 is associated with the -OH group bending of the acid group [19]. Unlike AG, ester carbonyl (-C=O) at 1737 cm-1 and amide carbonyl (-C=O) at the range of 1646-1679 cm-1 stretching vibrations were observed in graft copolymers. As the amount of cationic monomer (DAC) in graft copolymers increased, the peak intensity of the ester carbonyl at 1737 cm-1 increased.

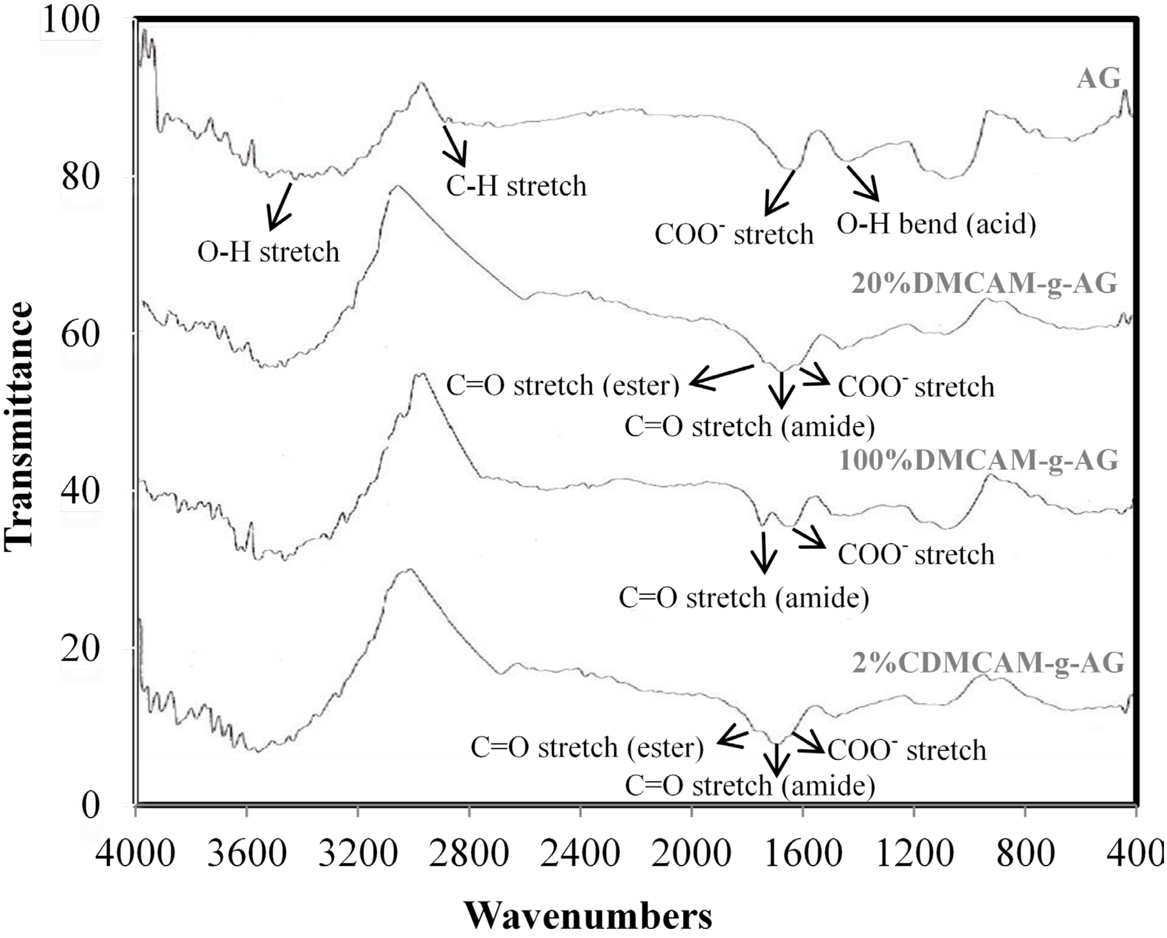

Figure 1. FT-IR spectra of AG and representative graft copolymers (20%DMCAM-g-AG, 100%DMCAM-g-AG and 2%CDMCAM-g-AG).

Thermal analysis

The thermo grams of AG and graft copolymers are presented in Figure 2 as well as the group loss and the percentage weight loss due to temperature increase at different steps are presented in Table 1. The thermal decomposition of AG occurs in three main steps, while the thermal decomposition of graft copolymers occurs in a larger number of steps. In the first stage, a weight loss of 3.08-8.96% occurs due to the presence of free water between temperature 20 and 151oC. Cross-linked graft copolymers show a weight loss of 4.35-6.21% between temperature 116 and 206 oC, unlike other graft copolymers. Due to the decomposition of the polysaccharide and the release of ammonia due to the imidization reaction between the amide

groups of acrylamide monomer units [20] occur a weight loss of 23.11-46.48% between temperature 227 and 328 oC. Unlike AG, the graft copolymers showed a weight loss of 4.73-15.85% attributable to the breakdown of the polymer backbone and the imides formed in the first decomposition region [20] between temperature 356 and 433 °C.

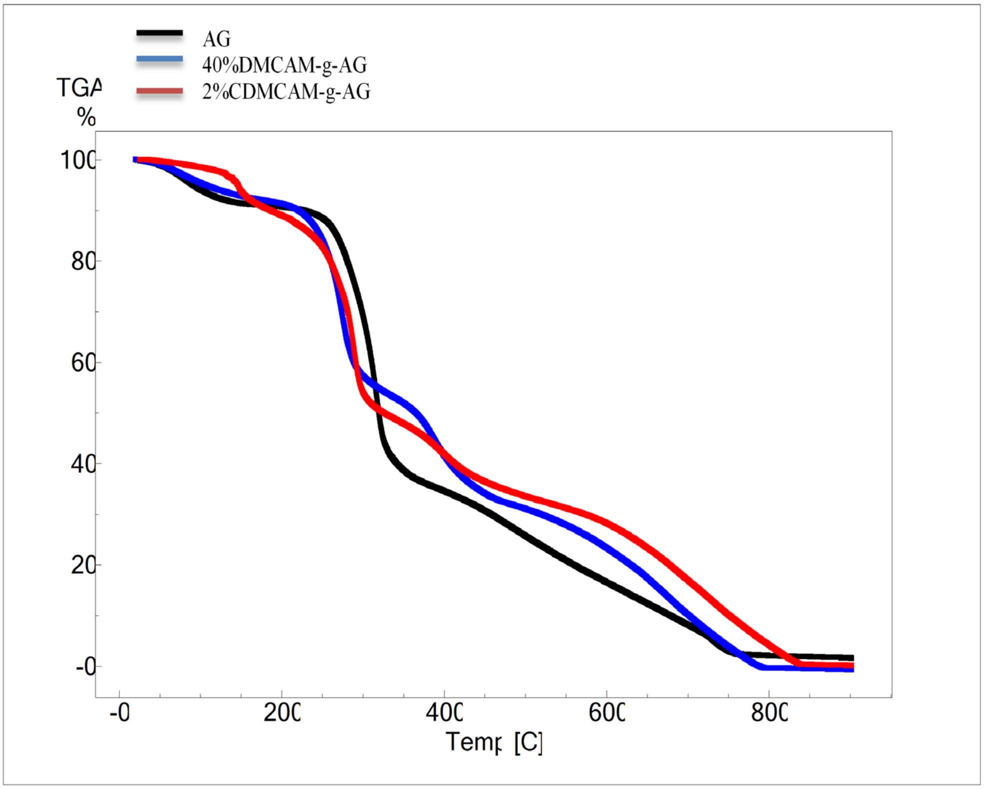

Figure 2. TGA curves AG and the respective graft copolymers.

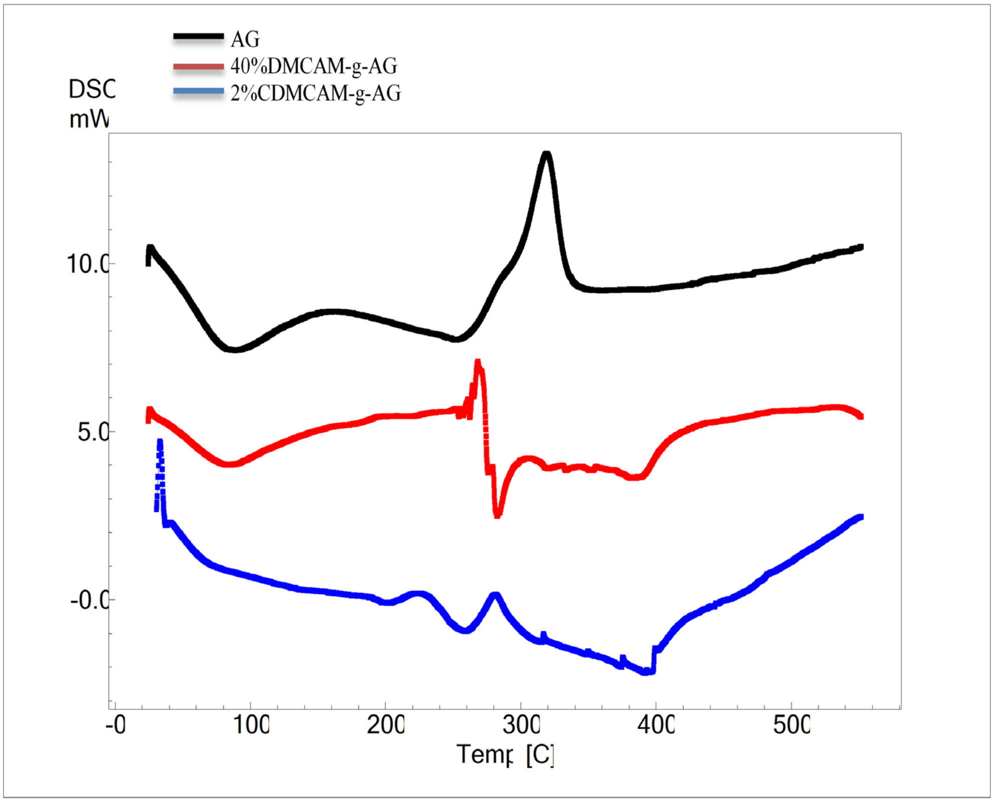

Figure 3. DSC curves of AG and the respective graft copolymers.

The DCS curves of AG, 40%DMCAM-g-AG grafted with 40% cationic acrylamide, and 2%CDMCAM-g-AG grafted with 2% crosslinked 40% cationic acrylamide are given in Figure 3 and the results are summarized in Table 2. The two main intense peaks were observed in the DSC thermograms of AG. These are an endothermic transition at 82.48 °C followed by an exothermic transition at 319.29 °C. The endothermic transition is due to the dehydration of absorbed moisture owing to the hydrophilic nature of the functional groups of the respective polysaccharide. No significant change in these endothermic peaks was observed in graft copolymers. This exothermic transition at high temperatures is due to the formation of H2O, CO and CH4 in the polymer from dehydration, depolymerization and decomposition. In 40%DMCAM-g-AG grafted with 40% cationic acrylamide, and 2%CDMCAM-g-AG grafted with 2% crosslinked 40% cationic acrylamide, these transitions were 268.34 and 282.08 oC, respectively, and shifted to lower temperatures.

Table 1. Summary of TGA results of AG and graft copolymers.

Compounds	Temperature range (°C)	Weight loss (%)
AG	20-112	6.95
	227-328	46.48
	433-755	29.53
20%DMCAM-g-AG	20-185	8.96
	244-291	21.98
	367-433	15.85
	603-837	26.90
40%DMCAM-g-AG	20-108	5.13
	246-287	24.85
	367-427	13.0
	592-787	24.13
60%DMCAM-g-AG	20-103	5.68
	238-293	32.79
	375-413	4.73
	549-769	27.07
80%DMCAM-g-AG	20-118	6.02
	242-294	31.90
	365-415	5.69
	582-841	26,28
100%DMC-g-AG	20-104	5.42
	246-289	30.42
	356-413	6.40
	534-802	26.18
1%CDMCAM-g-AG	20-116	5.45
	116-167	6.21
	241-295	27.07
	381-424	6.25
	586-782	24.70
2%CDMCAM-g-AG	20-132	3.08
	132-157	4.35
	245-299	29.41
	375-428	7.11
	611-836	26.77

Table 2. Summary of DSC results of AG and graft copolymers.

Compounds	T_{pik} (°C)	Heat (J/g)	Onset-Endset	T_{pik} (°C)	Heat (J/g)	Onset-Endset
AG	82.48	-200.89	40.86-146.43	319.29	97.32	301.12-332.86
20%DMCAM-g-AG	73.09	-130.03	26.62-135.79	219.17	46.89	190.81-247.45
40%DMCAM-g-AG	81.37	-135.02	39.89-109.10	268.34	33.22	263.01-274.05
60%DMCAM-g-AG	73.41	-100.70	30.05-147.00	288.96	35.89	273.21-304.60
80%DMCAM-g-AG	71.22	-128.88	27.32-134.99	288,72	103.31	272.69-305.43
100%DMC-g-AG	74.41	-145.66	26.97-137.44	280,37	133.55	237,78-299.74
1%CDMCAM-g-AG	108.99	-19.52	37.61-110.52	281,04	68.34	256.86-269.71
2%CDMCAM-g-AG	75.08	-207.93	35.95-230.31	290,07	95.10	276.38-302.81

Flocculation tests

The descent of the solid/liquid interface (suspension line) is given as a function of settling time in Figure 4A. Sedimentation velocity was calculated with the linear part of the curves. in Figure 4B. Sedimentation velocity comparisons made at different dosages showed that the dosage of flocculant/coagulant had an effect on the sedimentation velocity. Settling times are given as a function of dosages of AGs grafted with polyacrylamides in different cationic ratios in Figure 5A. 40%DMCAM-g-AG grafted with 40% cationic polyacryamide showed the highest sedimentation velocity in the range of 2-7 ppm dosages. The sedimentation velocity increased from 2 ppm to 8 ppm and reached the maximum at 8 ppm. It decreased after 8 ppm. In the 7-10 ppm concentration range, 20%DMCAM-g-AG grafted with 20% cationic polyacryamide showed higher sedimentation velocity than 40%DMCAM-g-AG grafted with 40% cationic polyacrylamide. The sedimentation velocity increased from 2 ppm to 8 ppm and reached the maximum at 8 ppm. It remained stable after 8 ppm. As seen in Figure 5B, sedimentation velocity of 1%CDMCAM-g-AG and 2%CDMCAM-g-AG grafted with cross-linked 40% cationic polyacryamide decreased compared to 40%DMCAM-g-AG grafted with linear 40% cationic polyacryamide. 40%DMCAM-g-AG grafted with linear 40% cationic polyacryamide was compared with AG and Al2(SO4)3 in Figure 5C. 40%DMCAM-g-AG grafted with 40% cationic polyacryamide showed better results than both AG and Al2(SO4)3 While AG, a flocculant, showed better results than Al2(SO4)3, a coagulant. The comparative study of graft copolymers with others shows the importance and superiority of the modification over AG.

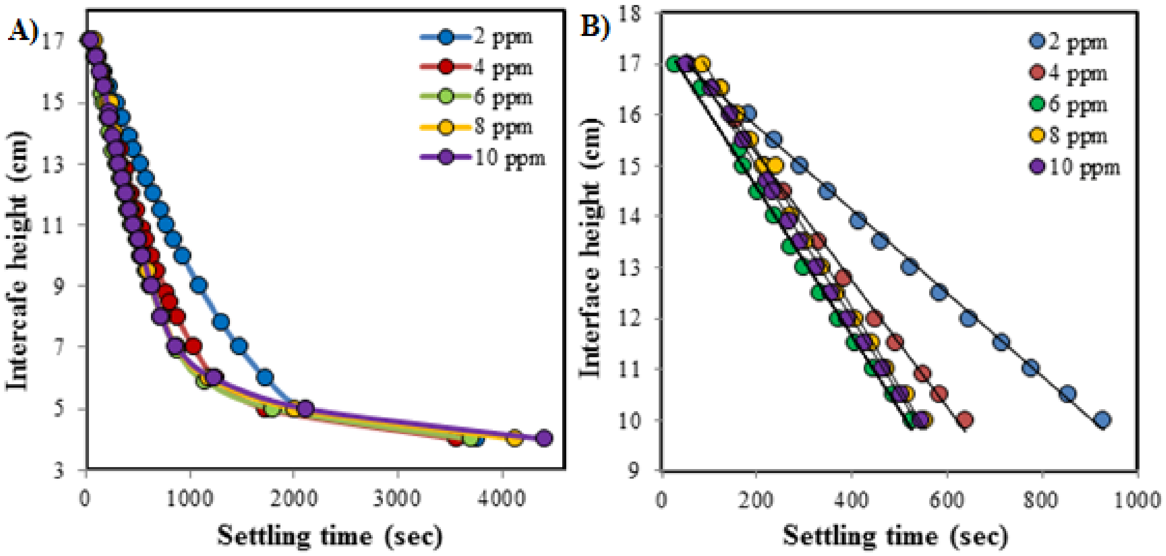

Figure 4. A) Suspension line descent at different dosages of 40%DMCAM-g-AG B) Linear region of suspension line descent at different dosages of 40%DMCAM-g-AG.

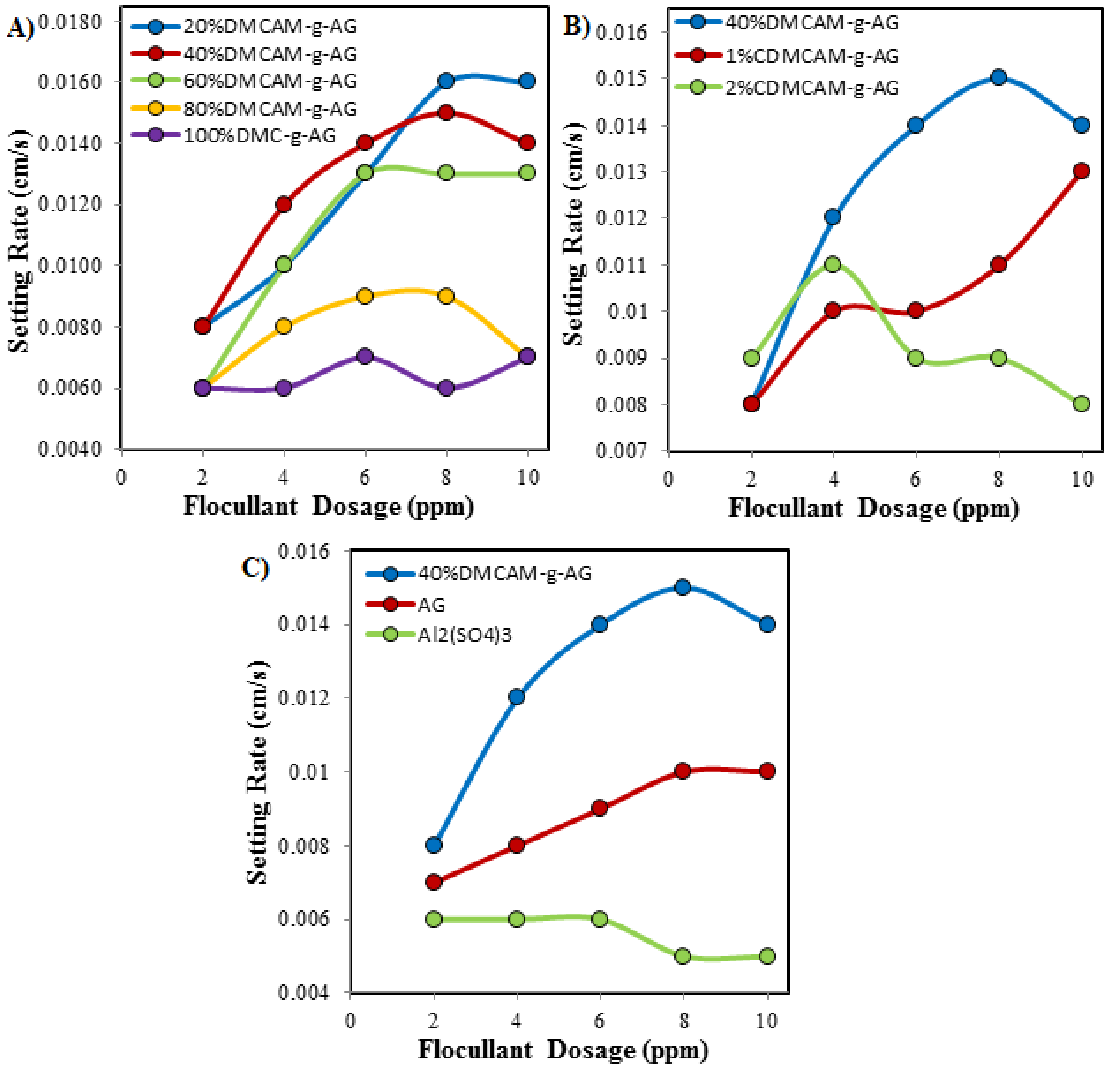

Figure 5. A) Flocculation characteristics of AGs grafted with polyacrylamides in different cationic ratios B) Effect of crosslinking on flocculation properties C) Flocculation characteristics of AG, 40%DMCAM-g-AG and Al$_2$(SO$_4$)$_3$.

CONCLUSIONS

Polyacrylamide with different cationic ratios was grafted onto acacia gum, and it was understood that grafting was achieved by FTIR and thermal analysis. Flocculation experimental results with different dosages and different graft copolymers showed that the amount of cationic monomer in graft copolymers is effective on flocculation. In addition, the crosslinker in the polymer reduced flocculation. 40%DMCAM-g-AG grafted with 40% cationic polyacryamide gave better results than both AG and Al2(SO4)3. The high sedimentation velocity was achieved by pre-neutralizing the high surface charge density through electrostatic interaction between the naturally negatively charged kaolin and the graft copolymers ions with the appropriate density of positive charge. At low dosages, 40%DMCAM-g-AG grafted with 40% cationic polyacryamide showed the highest sedimentation velocity, while 20%DMCAM-g-AG grafted with 20% cationic polyacryamide at high dosages showed the highest sedimentation velocity. By combining the active ingredients in a single grafted polymer, the performance of the grafted polymer in treating wastewater can thus be improved compared to the original ones. Natural polymer, which is readily available from the natural environment, is relatively less toxic and environmentally friendly, making the grafted polymer an attractive material for use in wastewater treatment.

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