Synthesis, characterization and kinetic studies of PEMA grafted acacia gum

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Graft polymerization of ethyl methacrylate (EMA) onto acacia gum (AG) has been studied. The grafting was found to be optimal under the following reaction conditions: gum 0.4 g/dL, monomer 0.066 mol/dL, H_2SO_4 0.037 mol/dL, ceric ammonium sulphate 0.0009 mol/dL, temperature 50°C and time 3.5 h. FTIR spectroscopy was used for the confirmation of grafting. Thermal, physical and biodegradation properties of the copolymer were studied. A probable mechanism of polymerization has been suggested based on reaction kinetics.

Keywords: Acacia gum, Graft polymerization, Reaction kinetics, FTIR, Biodegradation

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In recent years, chemical modification of natural polymers by grafting has received considerable attention because grafted polymers have improved physicochemical properties and industrial applications. Grafting of vinyl monomers onto natural polymers like starch[1,2], cellulose[3,4], guar gum[5,6], cassia tora gum[7] by ceric ion has been studied. Jana *et al.*[8,9] studied the effect of plant gums on the ceric ion initiation of graft polymerization. However, there are few reports on the modification of acacia gum (AG) through redox driven graft polymerization[10-12].

Acacia gum is obtained from acacia tree. It consists of a mixture of high molecular weight polysaccharide (major component) and hydroxyproline-rich glycoprotein (minor component). The basic structural units of the gum are L-arabinose, D-galactose, L-rhamnose and D-glucuronic acid[13,14]. The proportion of the structural units varies significantly with source and the exact molecular structures are still uncertain[15]. Structurally and chemically, AG is different from other gums including guar gum[7]. AG enjoys a wide range of applications in industries[15,16] such as paper, textile, pharmaceutical, etc, due to its water binding capacity and high thickening efficiency[16]. AG is hydrophilic and susceptible to easy biodegradation[16]. It has poor thermal and mechanical properties[15]. The easy biodegradation weakens its drag reduction property[6]. The addition of small amount of high molecular weight polymers to solvents in turbulent pipe flow reduces the pressure drop at a given flow rate. This phenomenon of pressure drop reduction by polymer additives is known as drag reduction and was originally coined by Toms[17]. The high biodegradability along with poor physical properties of AG limits its application as an effective drag reducer. The grafting of poly ethyl methacrylate (PEMA) onto AG has been done to control the easy biodegradation of AG and to improve its thermal and mechanical properties. Poly ethyl methacrylate (PEMA) is a non-biodegradable and hydrophobic polymer[18]. The monomer ethyl methacrylate has been successfully used in graft co-polymerization of polyvinyl alcohol to improve its physico-chemical properties[18]. The effect of poly methyl methacrylate (PMMA) grafting onto AG was reported earlier[19]. About 35% methyl methacrylate (MMA) was lost due to homo-polymerization during grafting. Ethyl methacrylate (EMA) is comparatively less reactive towards homo-polymerization[18]. The less reactivity towards homo-polymerization makes EMA to be a suitable monomer for grafting.

With a view that grafted AG may find better applications as an effective drag reducer in comparison to virgin polymers, the graft co-polymerization of ethyl methacrylate (EMA) onto AG has been studied here. The 'grafting form' technique[20,21] using ceric ammonium sulphate (CAS) as an initiator has been followed. A reaction scheme has been proposed to elucidate the grafting process. A comparison of the properties of PMMA-g-AG and

PEMA-g-AG has been made to observe the effect of increasing chain length from methyl to ethyl group of the monomer.

Experimental Procedure

Materials

Acacia gum (AG) was procured from National India Chemical Co, Calcutta. Ethyl methacrylate (EMA, Merck, Germany) monomer was purified before use[21]. Ceric ammonium sulfate (CAS, Himedia Laboratories Pvt. Ltd, India) was used as an initiator.

Graft polymerization

Graft polymerization was carried out following the procedure described elsewhere[20-24] within the temperature range 30-70[0]C. A definite amount of AG (0.1-0.8 g) was soaked with requisite quantity (0.016-0.082 mol) of monomer, EMA for 15 min. The volume of the reaction mixture was made to 100 mL after adding initiator, CAS (0.0002-0.0022 mol) and H_2SO_4 (0-0.074 mol). Nitrogen atmosphere was maintained throughout the reaction period. After a certain time interval (1-5 h), the reaction was arrested by quenching with 0.1 g hydroquinone. In order to remove homopolymers, the samples were extracted with acetone by a soxhlet apparatus for 6 h to remove all the homopolymers. The colorless product was dried under the vacuum at 60°C for 24 h to a constant weight.

Characterization

Grafting ratio (GR), grafting efficiency (GE), percentage of homopolymerization (H) and rate of grafting were used to evaluate the graft polymerization according to the following relation[20-24]

GR = Weight of PEMA grafted/weight of AG.

GE(%) = (Weight of PEMA grafted/weight of EMA)
$$\times\ 100$$

H(%) = (Weight of PEMA homopolymer/
weight of EMA) × 100.

Rg = (Weight of PEMA grafted/M.t.v.)

where M = molecular weight of the monomer, t = reaction time in second and v = volume of the reaction mixture in m^3 (100 mL).

FTIR spectra of the samples (using KBr pellets) were recorded on a Shimadzu (Model No. 84005) FTIR system in the range of 4000-400 cm^{-1}. Thermogravimetric analysis (TGA) was conducted using a Stantum Redcraft Thermal Analyzer (STA-780) in air at a rate of 10°C/min. The *p*H of the system was measured by a *p*H meter (Elico, India, Model 11120). A universal testing machine (Instron 4411, USA) and Durometer were used to measure the tensile strength and hardness respectively. Swelling co-efficient (*q*) was determined by swelling the sample in acetone and water at room temperature for 72 h according to the following relation[20-24].

$$q = (m - m_0)/m_0.d$$

where *m, m*$_0$ and *d* are the weight of the swelled sample and weight of the original sample and density of the solvent, respectively.

Preparation of film

A 15% solution of PEMA-g-AG was prepared using a solvent mixture (acetone: methyl alcohol = 1:1 by volume). The solution was stirred vigorously with a magnetic stirrer for homogeneous mixing. Then, the film was cast by pouring solution onto a clear and dry glass plate. The glass plate was shaken back and forth to spread the solution uniformly and then it was dried for about an hour in an oven maintained within the temperature range of 30-40°C.

Biodegradability test

PEMA-g-AG films of various graft yields were taken to test the biodegradability of the films. The biodegradability test was carried out by soil burial test[25,26].

The soil for the soil-burial test was obtained from a fertile land. The soil was made free from large clumps, plants debris, etc, and was kept in several earthen pots. In the entire study, the films were not maintained uniform in size but were of uniform thickness of about 0.5 mm. The thin film samples of known weight were buried in these pots at a depth of about 10 cm. The soil containing the samples was watered daily. The samples were removed periodically after a fixed time interval, washed thoroughly with water, and then the samples were dried within the temperature range of 40-45°C in a vacuum oven for 24 h. The weight of the film was recorded and used to calculate the extent of biodegradation of the samples. The percentage of

biodegradation was calculated using the formula as given below.

Biodegradation (%) = 100 × (wt loss of film after

specified days)/original wt of film

Results and Discussion

FTIR spectra analysis

Figure 1 shows the FTIR spectra of the native polymer (AG) and a representative graft copolymer (PEMA-g-AG). The spectrum of the grafted polymer contains all the characteristic peaks for AG except the one at 1610 cm^{-1}. The band at 1610 cm^{-1} may be assigned to the stretching frequency of carboxylate ions[23,27]. The absence of peak at 1610 cm^{-1} in the spectra of grafted polymer indicates that the carboxylate group of the AG takes part in the grafting reaction. The appearance of new peak at 1725 cm^{-1} in the spectrum of grafted polymer clearly indicates the presence of ester group (a characteristic peak of PEMA[19,27-29]). The presence of ester group (COOCH$_3$) in the grafted polymer unambiguously indicated the grafting of PEMA onto AG at the carboxylate group center.

Thermal analysis

Figure 2 shows that the raw gum (AG) undergoes three stages degradation (11% weight loss between 80 to 260°C, 70% loss between 261 to 394°C and 14% between 395 to 775°C). The initial weight loss is due to absorbed moisture and the major weight loss may be attributed to burning of the gum itself. The last stage weight loss is due to decomposition of the impurities present in the raw gum. However, the grafted gum (GR=14.1) shows four steps degradation (4% weight loss between 150 to 270°C, 55% between 271 to 380°C, 26% between 381 to 500°C and 10% between 501 to 770°C). The first step is due to removal of moisture while the second, third and fourth steps are due to decomposition of gum, PEMA branch, and impurities present in the system, respectively. The TGA curve reveals that water absorption capacity of the grafted gum is decreased while thermal stability of the copolymer is increased with respect to native gum.

Physicochemical properties

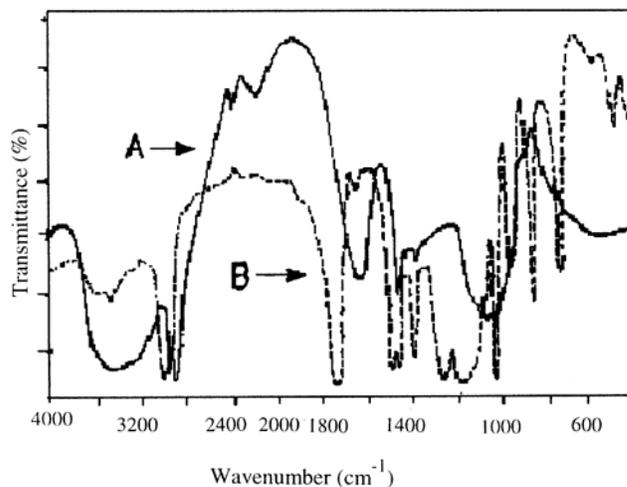The physical properties of the AG and the grafted polymer (PEMA-g-AG with GR=14.1) are shown in

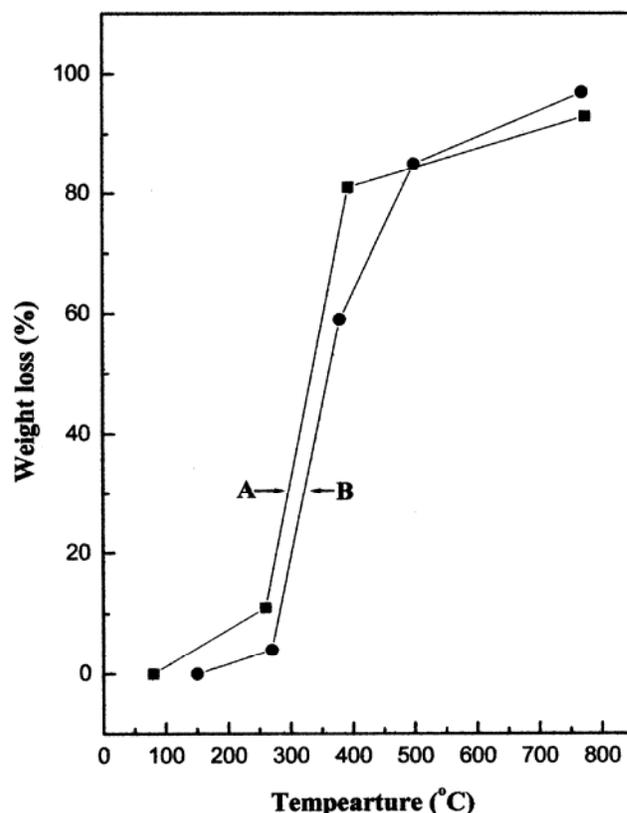Fig. 1 — FTIR spectra of acacia gum (A) and PEMA grafted acacia gum (B)

Fig. 2 — Weight loss versus temperature plots of acacia gum (A) and PEMA grafted acacia gum (B)

Table 1. Hardness, tensile strength and elongation at break of the grafted polymer are improved compared to virgin polymer. Swelling coefficient values show that grafted polymer is not soluble in acetone but highly swelled. The swelling behavior in aqueous

medium indicates that the resulted polymer is hydrophobic in nature.

Bio-degradation studies

The data given in Table 2 have clearly demonstrated that grafting of PEMA on AG has reduced its biodegradability. The extent of biodegradation was reduced with the increase of grafting level. The biodegradability of AG has been reduced considerably at the grafting ratio of 14.1. The increase in hydrophobic character reduces the biodegradability of the grafted polymer.

Effect of chain length

A comparative experimental data of the grafted polymers (AG-g-PMMA and AG-g-PEMA) are given in Tables 1 and 2. Table 1 shows that both the polymers have similar hardness and tensile strength. However, elongation at break of the polymer AG-g-PEMA is more than that of AG-g-PMMA, indicating its higher chain flexibility due to bulkier ethyl group. Swelling coefficient data reflects that PEMA grafted polymer possesses higher hydrophobic character owing to ethyl group. The enhanced hydrophobic nature of AG-g-PEMA causes its lower biodegradability compared to AG-g-PMMA (Table 2).

Variation of monomer concentration

Table 3 and Fig. 3 show the effect of EMA concentration on the extent of grafting. The table (S_1-S_4) indicates that the GE increases with the increasing concentration of EMA up to 0.066 mol/dL and then it decreases with further the increase of EMA. The initial increase in GE is due to greater availability of monomer molecules in the proximity of
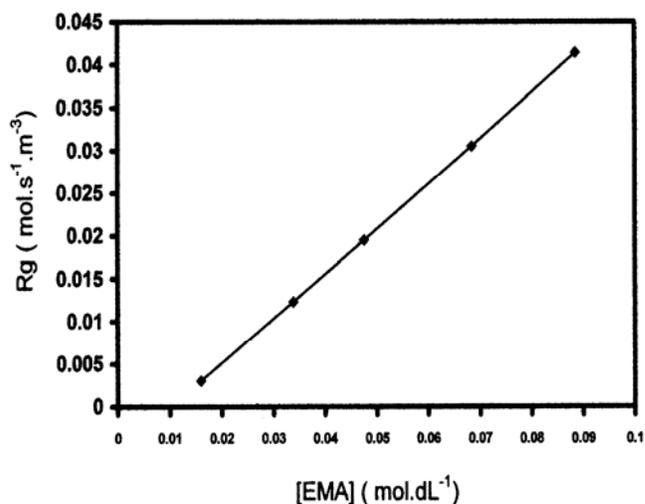

Fig. 3 — Variation of rate of grafting with monomer concentration

Table 1 — Physical properties AG, PEMA-g-AG and PMMA-g-AG

Parameters	AG (GR=0.0)	PEMA-g-AG (GR=14.1)	PMMA-g-AG (GR=14.0)
Hardness (Shore A)	22.0	61.00	63.00
Tensile strength (N/nm^2)	00.7	01.68	01.71
Elongation at break (%)	02.0	15.00	11.00
Swelling coefficient (water)	Insoluble	02.60	01.50
Swelling coefficient (acetone)	Soluble	01.60	02.50

Table 2 — Data for biodegradation of virgin AG, PEMA-g-AG and PMMA-g-AG

Sample	Grafting ratio	Biodegradation (%)				
		30 days	60 days	90 days	120 days	150 days
AG	nil	1.1	2.1	5.1	12.3	37.5
PEMA-g-AG	06.79	0.7	1.6	3.6	08.7	26.7
PEMA-g-AG	09.35	0.5	1.2	2.7	05.5	20.8
PEMA-g-AG	14.10	0.2	0.8	1.1	02.9	05.4
PMMA-g-AG	14.00	0.6	0.1	1.5	03.5	06.1

Table 3 — Effect of reaction parameters on the grafting of acacia gum

Sample	[EMA] (mol/dL)	[CAS] (mol/dL)	[AG] (g/dL)	[H$_2$SO$_4$] (mol/dL)	Time (h)	Temp. (^{o}C)	GE (%)	GR	H (%)	pH
S$_1$	0.016	0.0009	0.4	0.037	3.5	50	33.56	01.53	05.10	---
S$_2$	0.033	0.0009	0.4	0.037	3.5	50	40.16	03.77	09.20	---
S$_3$	0.066	0.0009	0.4	0.037	3.5	50	75.00	14.10	18.21	2.2
S$_4$	0.082	0.0009	0.4	0.037	3.5	50	62.02	14.49	30.10	---
S$_5$	0.066	0.0002	0.4	0.037	3.5	50	14.77	02.78	25.16	---
S$_6$	0.066	0.0005	0.4	0.037	3.5	50	34.84	06.55	20.30	---
S$_7$	0.066	0.0016	0.4	0.037	3.5	50	82.76	15.42	10.10	---
S$_8$	0.066	0.0022	0.4	0.037	3.5	50	86.64	16.29	04.50	---
S$_9$	0.066	0.0009	0.1	0.037	3.5	50	18.08	13.54	76.10	---
S$_{10}$	0.066	0.0009	0.2	0.037	3.5	50	36.24	13.63	57.70	---
S$_{11}$	0.066	0.0009	0.6	0.037	3.5	50	74.60	09.35	18.40	---
S$_{12}$	0.066	0.0009	0.8	0.037	3.5	50	74.50	07.01	08.30	---
S$_{13}$	0.066	0.0009	0.4	0.000	3.5	50	---	---	---	---
S$_{14}$	0.066	0.0009	0.4	0.018	3.5	50	35.10	06.58	07.20	---
S$_{15}$	0.066	0.0009	0.4	0.074	3.5	50	45.20	08.50	10.30	---
S$_{16}$	0.066	0.0009	0.4	0.037	0.0	50	---	---	---	2.6
S$_{17}$	0.066	0.0009	0.4	0.037	1.0	50	30.20	05.68	05.20	2.5
S$_{18}$	0.066	0.0009	0.4	0.037	2.0	50	50.60	09.52	07.30	2.4
S$_{19}$	0.066	0.0009	0.4	0.037	3.0	50	65.10	12.25	10.60	2.3
S$_{20}$	0.066	0.0009	0.4	0.037	4.0	50	77.20	14.52	14.80	2.2
S$_{21}$	0.066	0.0009	0.4	0.037	5.0	50	79.10	14.88	16.10	2.1
S$_{22}$	0.066	0.0009	0.4	0.037	3.5	30	12.00	02.26	01.42	---
S$_{23}$	0.066	0.0009	0.4	0.037	3.5	40	42.00	07.90	08.30	---
S$_{24}$	0.066	0.0009	0.4	0.037	3.5	60	69.40	13.05	19.32	---
S$_{25}$	0.066	0.0009	0.4	0.037	3.5	70	49.50	09.31	33.13	---

gum macro radicals. The decrease in GE after a certain level of EMA is due to higher extent of homopolymerization. Percentage of grafting (GR × 100) increases up to 0.066 mol/dL of EMA and then it remains almost constant. The loss of monomer due to homo-polymerization is increased with the increase of its concentration. About 18.21 % monomer is lost at 0.066 mol/dL EMA. However, in the same reaction condition[19], the loss of MMA was found to be 35%. Figure 3 reveals that the order of reaction is one with respect to monomer.

Variation of initiator concentration

The results obtained by changing the initiator concentration on the graft polymerization are presented in Table 3 and Fig. 4. It was observed from the table (S$_3$ and S$_5$-S$_8$) that the GE increases steadily with the increase of initiator (CAS) up to 0.0009 mol/dL and then it rises gradually. This increase is due to the production of greater number of gum macro-radicals in presence of metal ions. Higher concentration of ceric ion reduces the production of homopolymer. Figure4 shows that the order of grafting reaction is half order with respect to initiator.
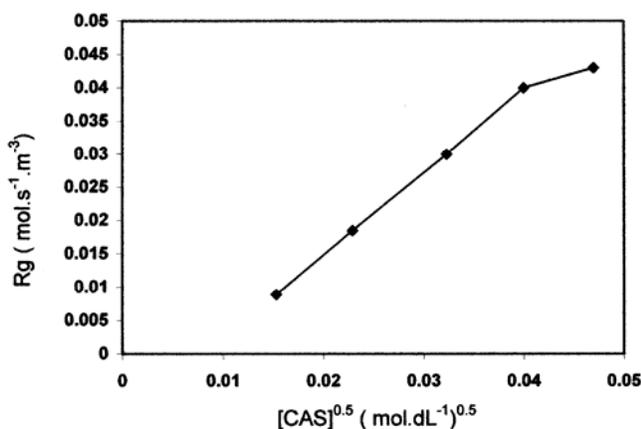
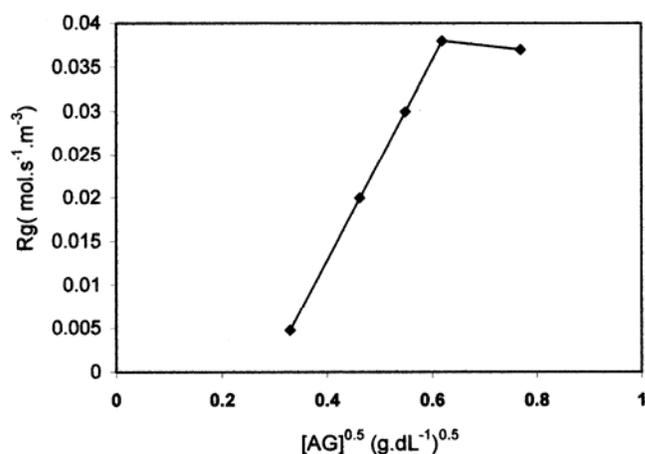Fig. 4 — Variation of rate of grafting with initiator concentration

Fig. 5 — Variation of rate of grafting with gum concentration

Variation of gum concentration

The effect of gum concentration on grafting is shown in Table 3 and Fig. 5. From the table (S_3 and S_9-S_{12}), it is evident that GE increases steadily with the increase of gum level up to 0.4 g/dL and thereafter it remains almost constant. Thus, the minimum concentration of AG required for the fruitful grafting is 0.4 g/dL, which is in line with the previous studies with MMA[19]. Percentage of grafting (GR × 100) depends largely on the amount of AG used. GR decreases steadily with the increase of AG level. The table shows that the high yield of homopolymer is obtained by using AG up to 0.1 g/dL. On the other hand to minimize the homopolymer, one should use AG beyond 0.4 g/dL. Figure 5 reveals that the grafting reaction is half order with respect to gum concentration.

Effect of acid concentration

Experimental results (S_3 and S_{13}-S_{15} of Table 3) reveal that the presence of 0.037 mol/dL sulphuric acid gives rise to the optimum condition for grafting. The acid concentration both below and above the optimum level has an adverse effect on grafting. Since the system produces H^+ ions through Eq. (2) (reaction scheme), much sulphuric acid is undesirable. Similarly, very low acid concentration could not prevent the hydrolysis of the ceric salt.

Variation of reaction time

The effect of time on GE is shown in Table 3 (S_3 and S_{16}-S_{21}). GE increases rapidly with time up to 3 h and then increases marginally with further increase of reaction interval. It is obvious that the higher the contact time of monomer with gum, the higher will be extent of grafting. The leveling of GE, after a certain time interval (3.5 h) may be attributed to the depletion of initiator and monomer concentration with the progress of the reaction. The gradual decrease of *p*H of the system is due to production of H^+ through Eq. (2).

Effect of temperature

The study of temperature effect on the polymerization shows that as the temperature is increased from 30 to 50°C, grafting efficiency of the system and percentage of grafting increase and become maximal at 50°C (S_3 and S_{22}-S_{25} of Table 3). At higher temperature, it is likely that the complex formed by the reaction between ceric ion and AG may decompose giving rise to AG-COO• free radicals (Eq. 2). These free radicals are responsible for increasing grafting yield. But at much higher temperature (>50°C) the formation of homo-polymer dominates over the graft co-polymerization, which results in decreasing grafting efficiency and ratio.
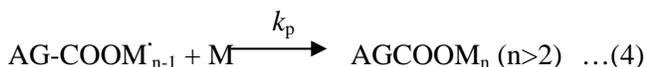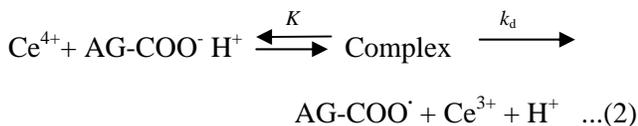
Reaction kinetics and mechanism

The rate of graft polymerization is largely dependent on the concentration of gum, monomer and initiator at a fixed level of acid concentration. The relationship between (a) *Rg* and [MMA], (b) *Rg* and $[CAS]^{1/2}$, and (c) *Rg* and $[AG]^{1/2}$ (Figs 3-5) are linear, indicating graft polymerization is first order with respect to monomer, half order to initiator and half order to gum concentration. Therefore, the following rate equation is established.
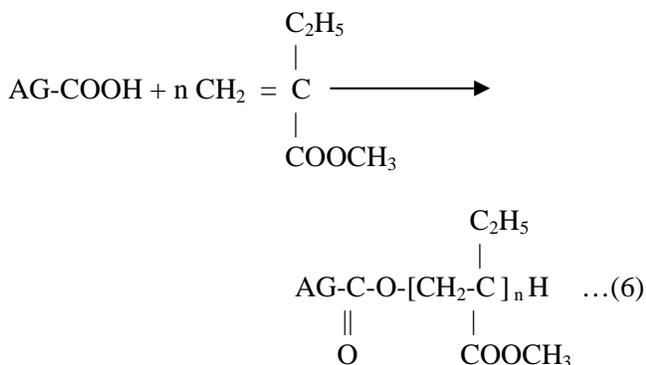
$$Rg = k. [EMA]. [CAS]^{1/2}. [AG]^{1/2} \qquad …(1)$$

where *k* is the rate constant for the polymerization.

The mechanism of grafting is suggested as follows:

$$Ce^{4+} + AG\text{-}COO^- H^+ \underset{K}{\overset{K}{\rightleftharpoons}} Complex \xrightarrow{k_d}$$

$$AG\text{-}COO^{\cdot} + Ce^{3+} + H^+ \quad ...(2)$$

$$AG\text{-}COO^{\cdot} + M \xrightarrow{k_i} AGCOOM \qquad ...(3)$$

$$AG\text{-}COOM^{\cdot}_{n-1} + M \xrightarrow{k_p} AGCOOM_n \ (n>2) \ ...(4)$$

$$2AGCOOM^{\cdot}_n \xrightarrow{k_t} Graft\ polymer \qquad ...(5)$$

Net reaction:

$$AG\text{-}COOH + n\ CH_2 = \overset{\displaystyle C_2H_5}{\underset{\displaystyle COOCH_3}{\overset{|}{\underset{|}{C}}}} \longrightarrow$$

$$AG\text{-}C\text{-}O\text{-}[CH_2\text{-}\overset{\displaystyle C_2H_5}{\underset{\displaystyle COOCH_3}{\overset{|}{\underset{|}{C}}}}]_n H \quad ...(6)$$

Ce^{4+}, AGCOOH and M represent ceric ion, acacia gum and monomer, respectively. The following rate expressions are derived on the basis of the reactions shown in Eqs (2-5) and assumption of steady state for the free radical (AGCOO$^{\cdot}$ and AGCOOM$^{\cdot}_n$).

$$d[AGCOO]/dt = K.k_d.\ [Ce^{4+}].[AGCOOH].$$

$$[AGCOO^{\cdot}]\ [M]\ ...(7)$$

$$[AGCOO^{\cdot}] = K\ k_d.[Ce^{4+}].[AGCOOH]/k_i.[M] \qquad ...(8)$$

$$d[AGCOOM^{\cdot}_n]/dt = k_i.[AGCOO^{\cdot}].$$

$$[M] - k_t.[AGCOOM^{\cdot}_n]^2 \ ...(9)$$

$$[AGCOOM^{\cdot}_n] = \{K.k_d/k_t\}^{1/2}.[Ce^{4+}]^{1/2} \qquad ...(10)$$

$$Rg = k_p.\ [AGCOOM^{\cdot}_n]\ [M]$$

$$= k_p.\{K.k_d/k_t\}^{1/2}\ [Ce^{4+}]^{1/2}.[AGCOOH]^{1/2}.[M]\ ...(11)$$

Eq. (11) is identical with Eq. (1), established from the experiment. The formations of grafted polymer through ester linkage have been confirmed by FTIR spectroscopy. The conversion of Ce^{4+} to Ce^{3+} has been confirmed by spectroscopic measurement at 380 nm, following the procedure as described earlier[19]. The decrease in pH of the system during polymerization indicates the formation of H^+ ion through Eq. (2).

Conclusion

Ethyl methacrylate (EMA) can be successfully graft co-polymerized onto acacia gum using ceric ammonium sulphate as an initiator in aqueous acidified medium. The EMA is found to be more suitable than MMA for grafting AG from economical point of view. The carboxylic acid group (COOH) is regarded as the grafting site of AG. The reaction variable, such as monomer, initiator, gum, time, pH and temperature affect the grafting efficiency considerably. Physical properties of the grafted polymer depend on the percentage of grafting. Percentage of grafting may be controlled by the ratio of acacia gum to monomer. The AG-g-PEMA has better thermal stability and physical properties than that of virgin polymer. The grafted polymer (at GR=14.1) possesses well-balanced hydrophilic and hydrophobic character. The biodegradability of AG has been reduced considerably at grafting ratio of 14.1. The grafting of AG makes it smart material with respect to biodegradation, thermal stability, mechanical strength and solubility, and could be used as an effective drag reducer. The bulkier ethyl group of AG-g-PEMA plays significant role to make the material suitable for end use.

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