The Synthesis of Water Soluble Cationic Microgels by Dispersion Polymerization: Their Performance in Kaolin Deposition Onto Fiber

Sedat Ondaral,[1] Mustafa Usta,[1] Menemse Gumusderelioglu,[2] Nergis Arsu,[3] Demet Karaca Balta[3]

[1]Department of Pulp and Paper Technology, Faculty of Forestry, Karadeniz Technical University, Trabzon 61080, Turkey
[2]Chemical Engineering Department, Hacettepe University, Ankara 06532, Turkey
[3]Chemistry Department, Yildiz Technical University, Istanbul 34210, Turkey

ABSTRACT: The water soluble cationic microgels (CMG), intramolecularly cross-linked cationic polymers of acrylamide (Am) and diallyldimethylammonium chloride (DADMAC), were synthesized with dispersion polymerization in the mixture of *tert*-butanol (TBA)/water in the presence N,N'-methylene-bisacrylamide (MBA) as the cross-linker, poly(N-vinylpyrrolidone (PVP) as the stabilizer and 2,2′-azobisisobutyronitrile (AIBN) as the initiator. The effects of monomer, cross-linker, initiator, and stabilizer concentration on both particle size and molecular weight of CMG were investigated. The well dispersed polymer particles were produced in the range of poly dispersity index 1.1–1.4 and the molecular weight distribution with bimodal. Additionally, the efficiencies of two CMGs in the clay deposition on the bleached kraft fibers were investigated and compared with commercially widely used cationic polyacrylamide (CPAM) and poly-diallyldimethylammonium chloride (poly-DADMAC). The experiments showed that the CMGs were found as the effective flocculation agents and their efficiencies depended on their molecular weight and charge density. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1157–1164, 2010

Key words: water soluble cationic microgels; dispersion polymerization; clay deposition; acrylamide; diallyldimethylammonium chloride

INTRODUCTION

The use of polyelectrolytes has continuously increased in the various industries: papermaking, water purification, waste water treatment, mineral processing, food, cosmetic industries, etc.[1–4] Among the polymers the cationic copolymers of acrylamide with higher molecular weight have been widely used in these applications because of lower cost and higher efficiency.[5–8] To produce cationic polyacrylamide, acrylamide, and cationic monomer have been polymerized via previously solution polymerization and recently inverse emulsion polymerization.[8–11] Additionally, they have been prepared with the dispersion polymerization having attractive advantages over these polymerization techniques: to produce micronsized polymer particles having homogeny size distribution in a single step process.[12–14] In this method, the polymerization of monomer is carried out in the presence of polymeric stabilizer in the convenient reaction mixture in which monomer and stabilizer can easily dissolved. But the reaction mixture is nonsolvent for the produced polymer.[15]

In the literature, there are very few studies about dispersion polymerization of acrylamide. The most of them have been related to homopolymerization of acrylamide carried out successively by using different initiator, stabilizer, reaction mixture, and synthesis conditions.[16–20] Additionally, recently the copolymer of acrylamide and cationic monomer (acryloyloxyethyl dimethylbenzyl ammonium chloride[12] and 2-methylacryloylxyethyl trimethyl ammonium chloride[21]) have been produced by this polymerization technique. Addition to polyelectrolyte, the water soluble intramolecularly cross-linked polymers, named as "microgel" in the literature, have been synthesized by dispersion polymerization. Compared with linear polymers, water soluble microgels can keep their molecular shape even if they can swell due to their compact structure.[22,23] It is also very likely that these polyelectrolytes will keep their 3D conformation once they are adsorbed to a solid surface. In our previous study in which the efficiency of water soluble cationic microgels (CMG) on the fixation of the dissolved and colloidal substances (DCS) to the both fiber and silicon oxide surfaces was investigated, it was found that CMG having higher charge density and molecular weight

gave better performance for DCS fixation to the fibers and also formed thicker polymeric layer on the SiO_2 surface and thus adsorb more DCS particles.[24] These results indicates that its 3D structure is important for interacting with more substances from the suspension, as due to the extension of the polymer outside the electrostatic double layer of the surface. In the recent work, the CMGs of AAm and DADMAC were synthesized by dispersion polymerization and the effects of the concentrations of ingredient chemicals on the polymerization were investigated. Moreover, the efficiencies of these polymers in the kaolin deposition onto cellulosic fibers were determined and compared with commercially available polymers, poly-DADMAC and cationic polyacrylamide (CPAM).

EXPERIMENTAL

Materials

Acrylamide (Am, Merck KGaA), diallyldimethylammonium chloride (DADMAC, Fluka) as the monomer, 2,2'-azobisisobutyronitrile (AIBN, Riedel-de-Haen) as the initiator, poly(N-vinylpyrrolidone) (PVP40, 4×10^4 g/mol K 28–32, Sigma) as the stabilizer and $tert$-butanol (TBA, Merck KGaA) as the solvent were used in the polymerization process as received without further purification.

Poly-DADMAC (Alcofix 111) and CPAM (Percol 230 HL), which is copolymer of acrylamide and acryloxyethyltrimethylammonium chloride, were supplied by Ciba Specialty Chemicals (Bradford, UK). Poly-DADMAC had a molecular weight of 624 kDa according to the supplier. Its charge density is 6.18 meq/g according to the theoretical chemical structure of the polymer. CPAM had a low charge density and high molecular weight according to technical data sheet from the supplier. Clay (Intrafill C, supplied by IMERYS) was used in the flocculation experiments. NaOH and NaCl used for pH adjustment were analytical grade. Deionized water was used throughout this work.

Totally chlorine-free (TCF) bleached chemical softwood fibers (SCA, Östrand Pulp Mill, Sundsvall, Sweden) were used in the experiments conducted for investigating the clay adsorption onto fiber. This pulp was in dry lap form and was thoroughly reslushed according to ISO 5263 : 195 standard. To convert the carboxyl groups on fiber to their sodium form and remove unwanted preadsorbed metal ions, fibers were treated in a washing procedure, first soaking with HCl at pH 2 for 30 min. Then the fibers were washed with deionized water several times. After treatment the fibers were treated with $10^{-3}M$ NaHCO$_3$ for 30 min and washed with deionized water until the conductivity of water was less than 2 μS/cm through a wire having 51 μm openings to remove small fibrous fines. The water was removed by simple filtration, and the so-prepared fiber pads were stored in a refrigerator before use.[25]

Preparation of CMG

CMGs were synthesized by dispersion polymerization in a solvent mixture of TBA/Water (1.3/1). All ingredients were easily dissolved in the solvent mixture. After dissolving chemicals, N_2 was bubbled through the solution at room temperature for 15 min to remove oxygen and the polymerization was initiated and conducted at 55°C for 6 h by mixing. Polymers were dialyzed with the aid of porous cellulose acetate membrane (Spectrum, MWCO: 1000) for three days against de-ionized water and then, freeze-dried.

Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047A), and three high resolution Waters columns (AQ3.0, AQ4.0, and AQ5.0). The effective molecular weight ranges were 1000–60,000; 10,000–400,000 and 50,000–4,000,000, respectively. Water was used as eluent at a flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear polyethylene oxide standards (Polymer Laboratories) was used to estimate the molecular weights. ^{1}H-NMR spectra of CMG was recorded on a Mercury 200 MHZ Varian NMR spectrometer with high concentration solutions of polymers in D_2O.

The size of CMGs was determined by scanning electron microscopy (SEC). Before taking SEM photos, the polymer solution was cleaned from unreacted chemicals by centrifugation at 7000 rpm for 30 min. This cleaning process was repeated three times by using TBA. The cleaned polymer was put on the SEM plate and excess polymer was removed with filter paper. $\overline{D}_n$ (the number average of particle diameter) and PDI (polydispersity index) values were determined by using the diameter of 50 particles selected randomly from SEM photos, according to following formulation:[18]

$$\overline{D}_n = \frac{\sum_{i=1}^{N} d_i}{N} \qquad (1)$$

$$\overline{D}_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3} \qquad (2)$$

$$PDI = \frac{\overline{D}_w}{\overline{D}_n} \qquad (3)$$

where $\overline{D}_w$ is the weight average of particle diameter, N is the total number of polymer particles and d_i is the diameter of the i_{th} particle.

Determination of charge densities

The particle charge detector (PCD III; MÜTEK GmbH, Herrsching) was used to determine the charge densities of polymers and filtrated suspensions by the polyelectrolyte titration. The volume of polyelectrolyte consumed for 0 mV of streaming potential of samples was recorded and the charge density (q) was calculated by following formulation:[26]

$$q = \frac{V.n}{m} \qquad (4)$$

where V is the volume of polyelectrolyte titrant (mL), n is titrant concentration (eq/mL), m is amount of polymer or aqueous sample (g or mL). Charge densities of polymer and suspension were calculated in meq/g and meq/mL units, respectively. P-DADMAC and polyethylenesulphonate sodium salt (PES-Na) purchased from MÜTEK GmbH were used as a cationic titrant and an anionic titrant, respectively.

Clay deposition onto fibers

The efficiency of polymers regarding clay deposition onto TCF bleached chemical softwood fibers was determined by monitoring adsorbed amount of clay and charge density of the sample taken from the suspension as a function of polymer concentration. The fibers (0.5 g) were disintegrated in 200 mL of deionized water by stirring with propeller at 750 rpm. One-hundred and fifty milligrams of clay (10 mL of main stock, 15 g/L) was added into fiber suspension and deionized water was added to make the total volume equal to 400 mL. The pH of suspension was adjusted to 6.0 ± 0.1 and thereafter; the polymer solution was added to the fiber-clay suspension. After mixing suspension for 10 min at 500 rpm, 10 mL sample was withdrawn by using syringe having 200 mesh screen tip to exclude fibers. The transmittance of this sample at 500 nm was determined by UV–VIS spectrophotometer (Specord 40, AnalyticJena). The amount of undeposited clay in the sample was calculated by means of the standard graphic. The amount of deposited clay onto fibers was calculated by subtracting the amount of undeposited clay from the amount of initially added clay.

RESULTS AND DISCUSSION

CMG synthesis and characterization

The water soluble CMGs were prepared by dispersion polymerization randomly and slightly cross-linked by adding MBA. The evidence of cross-linkage linkage in the polymer structure was found in
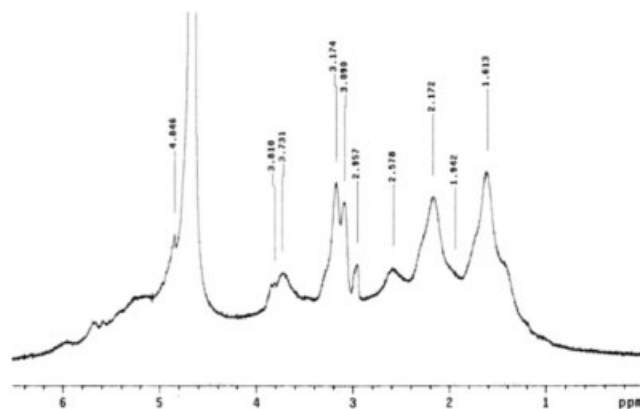

Figure 1 ^{1}H-NMR spectrum of CMG in D_2O (the signal of D_2O is about at δ = 4.75 ppm).

the ^{1}H-NMR spectrum at the signal of 4.846 ppm which indicates the protons of CH_2 groups linked NH in cross-linker MBA, as shown in Figure 1, in which the signal due to the D_2O observed about at δ = 4.75 ppm. The protons of cyclic groups of both DADMAC and PVP are observed at δ = 3.174, 3.090, 2.957 ppm.

The numbers of repeated monomer units in the polymer structure weren't investigated in this study. It is well known that repetition is related to the reactivity ratio of monomers to each other. Tanaka determined the reactivity ratios of AAm and DADMAC during copolymerization as r_{AAm} = 6.7 and r_{DADMAC} = 0.58, respectively.[9] That indicate that AAm reacts other AAm monomers readily and therefore, the repetition of AAm molecules will be higher. On the other hand, DADMAC monomers tend to react AAm instead of DADMAC monomers. The MBA, which was added at less concentration comparing with AAM and DADMAC to cross-link the polymer, is supposed to randomly bond between AAm and DADMAC monomers.

The CMGs produced dispersion polymerization were not soluble in the mixture of TBA/water and thus, could be separated out from unreacted chemicals by centrifugation. Figure 2 shows the SEM photographs of two CMGs (M2 and I1) prepared with different chemical concentrations. As can be seen from the SEM photographs, the polymer particles are polydisperse and there are some bigger and a fewer oval particles indicating the less coalescence and aggregation of the same sized particles during the polymerization.[18]

In the Figure 3, the molecular weight distributions of M2 and I1 which were selected for representing CMGs and used for the experiments, in which the efficiencies of polymers in clay deposition were investigated, are shown. It can be seen that CMGs have a large bimodal molecular weight distribution.
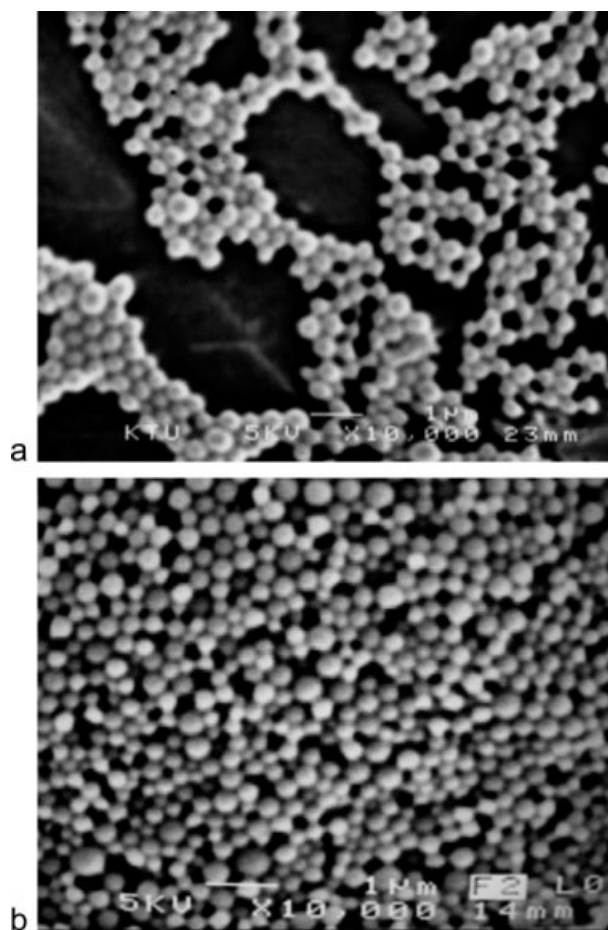
Figure 2 The SEM photograps of some CMGs: (a) M2 and (b) I1.

Probably, these fractions formed due to the some aggregation and coalescence in polymerization addition to intra cross-linking reaction of MBA.

Effect of monomer concentration

The results of copolymerization of AAm and DAD-MAC are presented in Table I. It has been observed that the particle size, monomer conversion, and molecular weight increased with increasing initial monomer concentration when 2.26 mmol/L MBA, 21.2 mmol/L AIBN, and %6.5 PVP were used. These results have been also detected earlier in the literature.[10–12] The critical degree of polymerization, i.e., critical chain length of polymer, for precipitation of the oligomeric molecules increases with increasing polymer solubility caused by increase in monomer concentration. An increase of the chain length indicates higher molecular weight.[13,15,27] Addition to this, it was reported that the stabilizer solubility increases and thus, adsorption of costabilizer was reduced.[11] Jayachadran and Chatterji[28] have found that the polymerization rate enhanced with increas-

ing monomer concentration and therefore, bigger polymer particles were formed before stabilization mechanism occurred completely. At higher monomer concentration (M3), stable dispersion couldn't be achieved because of the weak stabilization. Similarly, when the MBA concentration was kept 0.23% (M4* and M5*) depending on the total monomer concentration, the average size of polymer particles increased by increasing monomer concentration.

Effect of initiator concentration

In the experiments (I1-I3) in which the effect of initiator concentration was investigated, the AIBN were added at three concentrations (16.5, 21.2, and 26.5 mmol/l) when 17.5% monomer concentration, 1.13 mmol/l MBA and 6.5% PVP were constant. As shown in Table I, both the particle size and conversion increased with increasing initiator concentration while the molecular weight decreased. This increase in particle size of polymer has been attributed to different mechanisms. The higher initiator concentration can cause faster formation rate of oligomeric radicals comparing the stabilization rate and therefore, oligomers can aggregate before stabilization mechanism carried out fully.[29] Additionally, Ye et al.[19] have explained this size increase attributing the greater solubility of shorter oligomeric chains and their grafting on the particles formed in the reaction mixture. The grafting of oligomeric chain was claimed to impede the adsorption of stabilizer molecules to particles and therefore, unstable
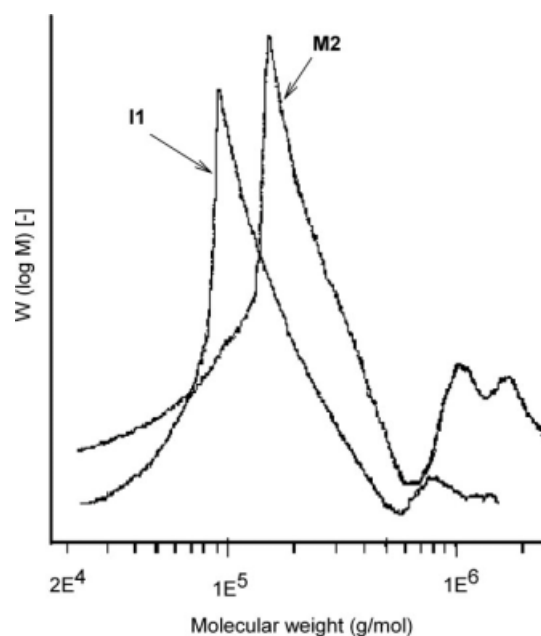

Figure 3 The molecular weight distributions of M2 and I1.

TABLE I
Results of Dispersion Polymerization of AAm and DADMAC in the Mixture of TBA/Water (1.3/1) Using AIBN as the Initiator at 55°C for 6 h

Polymer no	A + B (% w/v)	MBA (mmol/L)	AIBN (mmol/L)	PVP (% w/v)	$\overline{D}_n$ (nm)	PDI	Conversion (%)	M_w (kDa)	M_n (kDa)	MWD
M1	7.5	2.26	21.2	6.5	338	1.4	81	196	34	5.5
M2	10	2.26	21.2	6.5	526	1.2	87	425	95	4.5
M3	12.5	2.26	21.2	6.5			Aggregated			
M4[a]	10	1.50	21.2	6.5	236	1.1	82	237	132	1.8
M5[a]	12.5	1.76	21.2	6.5	350	1.1	88	233	118	2.0
I1	17.5	1.13	16.5	6.5	325	1.1	85	320	211	1.5
I2	17.5	1.13	21.2	6.5	337	1.1	88	293	186	1.5
I3	17.5	1.13	26.5	6.5	341	1.1	91	242	200	1.2
C1	12.5	0	21.2	6.5	426	1.1	95	185	54.3	3.4
C2	12.5	1.77	21.2	6.5	350	1.1	88	233	118	2.0
C3	12.5	2.26	21.2	6.5			Aggregated			
S1	10	2.26	16.5	1.1			Aggregated			
S2	10	2.26	16.5	6.5	320	1.2	78	240	40	6.2
S3	10	2.26	16.5	9.8	333	1.1	88	445	303	1.5
S4	15	1.13	16.5	1.1			Aggregated			
S5	15	1.13	16.5	3.3	451	1.1	75	287	146	1.9
S6	15	1.13	16.5	6.5	485	1.1	83	514	153	3.4

[a] The percentage of MBA based on the monomer amount was 0.23%.

polymer particles having greater size were formed. The faster formation of oligomeric radicals and decrease in the average numbers of monomer molecules reacting with each radical can be reasons for decrease in the molecular weight with increasing initiator concentration.[12,30]

Effect of cross-linker concentrations

When the MBA was added to polymerization (C1-C3), it was found that the particle size of polymers and conversion rate decreased by keeping concentrations of the other chemicals constant. The cross-linker made the polymer structure denser because of the internal cross-linkage. That prevented polymer particles from swelling when the oligomeric radicals entered into particles.[31] At the highest MBA concentrations (C3), the aggregated water insoluble particles was observed. That can be addressed by the inter cross-linkage between polymer particles addition to intra cross-linkage. The higher cross-linking caused to formation of bigger particle which were not to able to be stabilized by stabilizer and thus, aggregated polymer particle formed. The molecular weight of polymer increased when MBA increased. From these results, it can be speculated that the oligomeric radicals entered the formed particles during polymerization.

Effect of stabilizer concentration

As can be seen in Table I, the molecular weight of polymer, size of particles, and conversion rate of polymerization increased with increasing stabilizer

concentration (S1-S6). It was determined that polymer particles precipitated from the continuous phase and form aggregates due to the lack of stabilization of polymer particles when the PVP was added at lower concentration (1.1%) into polymerization systems (S1 and S4). At the higher stabilizer concentrations, the formation of stable polymer particles was observed. This result was also found by Liu and coworkers in their study.[14] The stabilization mechanisms in dispersion polymerization with PVP have been explained in two different types, referred as "adsorption stabilization" and "graft stabilization." Both mechanism of PVP have been detected in the dispersion polymerization of by Zhang et al.[32] In our polymerization system, both mechanism can be also suggested for stabilization of polymer particles. From this point, the PVP molecules were able to cause steric stabilization and graft into polymer chain from the continue phase, i.e., PVP-g-P(AAm-co-DADMAC), and they adsorbed on the surface of particles and prevent agglomeration. However, the further studies are needed to make clear the stabilization mechanism.

The bigger particle size at higher PVP concentrations is not similar with the expected trend as in literature. That may be attributed to the coagulation of polymer particles by stabilizer molecules before stabilization was achieved fully. The increase in molecular weight of polymer at higher PVP concentrations indicates that polymerization took place inside the particle phase capturing of oligomeric radicals from the continuous phase, yielding polymers with higher molecular weight due to the gel effect.[19]
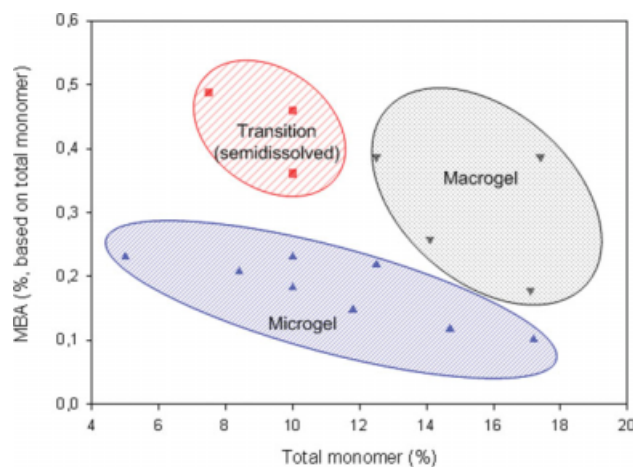
Figure 4 The effect of crosslinker and monomer concentrations on the polymer solubility. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

The polymerizations in which PVP and AIBN concentrations were kept constant 6.5% and 21.2×10^{-3} mol/L were evaluated and classified by means of their solubility. It was observed that the polymers had three different solubility properties which were dissoluble, semidissoluble and undissoluble polymers corresponding to microgel, transition region and macrogel region as shown in Figure 4. It is obviously clear that the monomer concentration should be decreased when the microgels with higher intra cross-linked structure are targeted at the constant stabilizer and initiator concentrations. The main reasons for that can be explained by considering the effects of monomer, cross-linker and stabilizer concentrations, as mentioned earlier. However, more future work should be done to make borders between the regions more distinct and clarify the effective mechanism behind this polymerization.

Clay adsorption onto fibers

The efficiencies of two CMGs (M2 and I1), prepared with the dispersion polymerization, in the adsorption of clay onto bleached kraft fibers was investigated and compared with two different commercial polymers (Poly-DADMAC and CPAM). The clay adsorption was monitored by means of the change in the absorbance and the charge density of the sample taken from the fiber-clay suspension.

As can be seen in Figure 5(a,b), the efficiencies of CMGs, CPAM, and poly-DADMAC are quite different. CMGs' mechanism can be well understood when the performance of commercial polymers are discussed. When poly-DADMAC was used, it can be clearly detected that the adsorbed amount of clay was the lowest comparing with other polymers. The

charge density of suspension changed to positive values at lower poly-DADMAC concentration due to its higher charge density and thus, clay adsorption increased. When the concentration increased, clay deposition decreased due to the restabilazation referring to this mechanism "patch type flocculation," in which the cationic polymeric patches formed on the particle surface interact with negatively charged sites without patches and thus, the flocculation takes place.[33] On the other hand, the efficiency of CPAM is the highest because of its high molecular weight. The responsible mechanism behind highest flocculation starting at lower CPAM concentrations in the negative charge region has been referred as "bridge type flocculation," in which the extended parts of polymer (loops and tails) adsorbed on the surface interact other particles.[33]

From these figures, it is clearly seen that the efficiency of M2 is different than that of I1. That can attributed to that M2 has the lower charge density and higher molecular weight compared with I1 (the
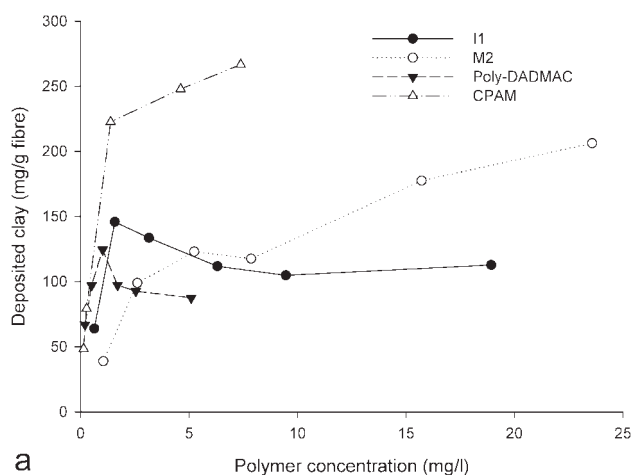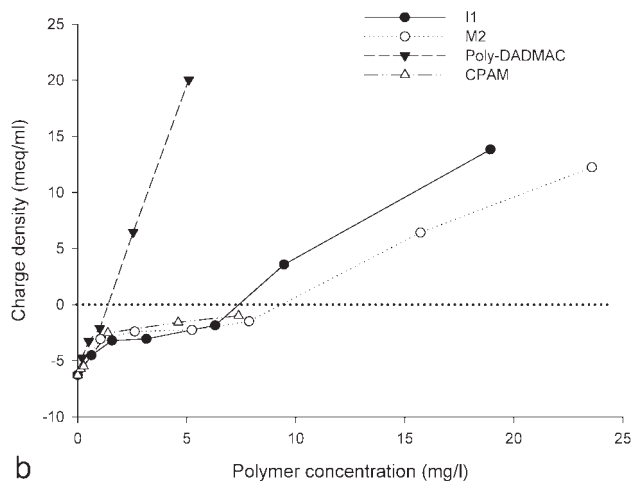
Figure 5 (a) Clay deposition to fibers and (b) change in charge density of suspension as a function of polymer types and concentrations.
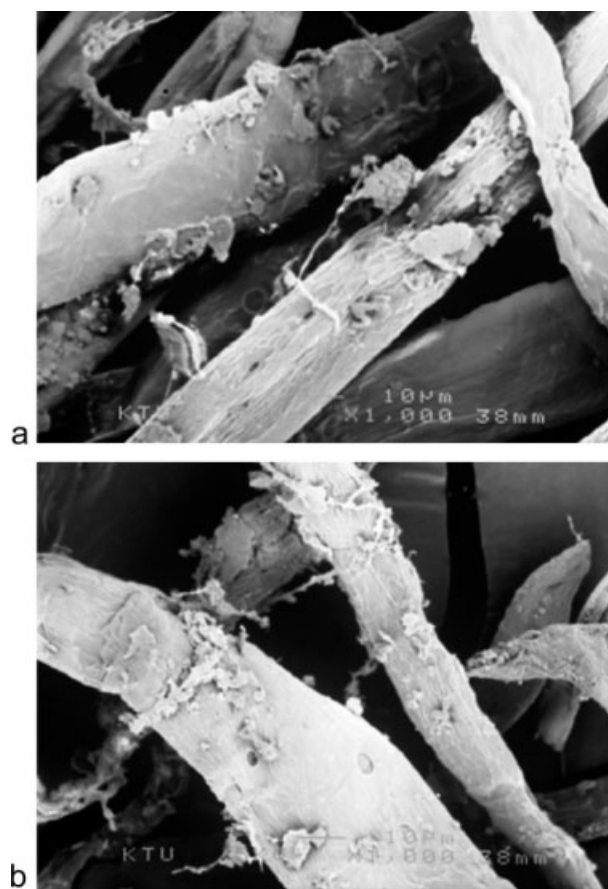
Figure 6 The SEM photos showing the clay deposition induced by addition of M-2 (a) and CPAM (b).

charge densities of M2 and I1 are, respectively, 0.9 meq/g and 1.2 meq/g). The adsorbed amount of clay continuously increased when the dosage of M2 increased even if the charge density reversed from anionic to cationic region. The fraction with higher molecular weight of cross-linked polymer can make more bridges between particles (fibers and clay particles). That indicates bigger size of polymer and thus, can lead to formation of thicker layer on the both fiber and clay surfaces. In the previous study, it was found that the thicker polymeric layer can extend to double layer providing more effective points for another surface to be adsorbed.[24] The increase of adsorbed clay after isoelectric point of fiber-free samples can be a sign of faster adsorption of M2 to clay particles than fibers. The surface coverage of fibers was still increasing in the cationic region (after 10 mg/L concentration of polymer). The clay adsorption continued increasing because the fibers couldn't be recharged actually. When the number of concentrations of fibers and clay particles are taken into consideration (at given conditions the number concentration of clay particles is $\sim 10^5$ times higher than the number concentration of fibers), it

can be clearly detected that the collision number between clay and polymer is higher than collision number between fiber and polymer. Therefore, polymer is firstly adsorbed on the clay particles and then, on the fibers. The cationic recharging of fiber-free sample indicated that the charge of clay-polymer matrix increased. The SEM photos (in Fig. 6) show clearly that M2 could deposit clay particles effectively onto fibers as CPAM.

On the other hand, the clay adsorption induced by addition of I1 firstly increased and then, near the isoelectric point of suspension started to decrease. The less efficiency of I1 can be explained by its smaller molecular weight. Its trend for clay adsorption is similar with poly-DADMAC. After reaching to maximum clay adsorption at lower I1 concentration, it can be speculated that the surface coverage exceeded 50%, which is proposed for patch model flocculation to be efficient, before IEP. These results show that the efficiencies of CMGs strongly depend on their molecular weight and charge density.

CONCLUSIONS

The water soluble cross-linked copolymers of AAm and DADMAC were prepared in the solvent mixture of TBA/water by dispersion polymerization in the presence of MBA as cross-linker and PVP as stabilizer. The polymers were cross-linked intramolecularly by adding small concentration of MBA into polymerization solution. The effect of monomer, cross-linker, initiator, and stabilizer concentration to size of polymer particles and molecular weight were investigated. According the results from the experiments, in which the well dispersed polymer particles were produced, the size of polymer particle in TBA increased with increasing monomer, initiator and stabilizer concentration while it decreased with cross-linker concentration. Additionally, the molecular weight of polymer measured in deionized water increased with increase in monomer, cross-linker, and stabilizer concentration while it decreased slightly with increasing initiator concentration. The aggregation of polymer particles after polymerization was observed depending on the monomer, cross-linker and stabilizer concentration, indicating macrogel formation and aggregation of polymer particles. The experiments conducted to determine clay deposition by means of polymer showed that CMGs were found as more effective than poly-DADMAC, attributing that three dimensional structure on the surface of both fiber and clay particle. On the other hand, it was determined that CPAM had the best efficiency in clay deposition onto fiber due to its considerably higher molecular weight and thus, formation of loop and tails on the surface. The results also

showed that the efficiency of CMGs depends on the molecular weight and charge density. The CMG with higher molecular weight and lower charge density had higher efficiency because more polymer adsorbed on the surface and possibly formed thicker layer which can let more possibility for interaction with other materials such as fibers and filler particles.

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