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ORIGINAL CONTRIBUTION

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Grafting polyelectrolytes onto polyacrylamide for flocculation 2. Model suspension flocculation and sludge dewatering

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Abstract Low-molecular-weight high-charge-density cationic poly(diallyldimethylammonium chloride) (polyDADMAC) was grafted onto high-molecular-weight nonionic polyacrylamide (PAM) via a free radical mechanism using a gamma radiation technique. The graft copolymers having various charge densities were evaluated as flocculants for titanium dioxide (TiO_2) model suspensions, and as conditioners for a pulp and paper mill sludge. Their flocculation performance was optimized with respect to polymer composition, gamma irradiation time and polymer dosage. Measurements included turbidity, particle size distribution and drainage rates. The graft copolymers showed a significant improvement over the homopolymers and dual polymer systems in their flocculation and sludge dewatering performance.

Key words Flocculation – Dewatering – Titanium dioxide – Sludge – Particle size

Introduction

Water-soluble polyelectrolytes play an important role in papermaking, water and waste water treatment, and in mineral processing industries [1–7]. They have largely replaced the traditional inorganic agents such as alum, lime and ferric chloride. In particular, sludge dewatering has recently received considerable attention due to increasing public awareness and governmental pressures for environmental purposes. In order to achieve reasonable rates of water removal and solid contents, sludges are often conditioned prior to dewatering. Sludge conditioning has become an important process in determining the total expense of waste treatment.

Sludge conditioning, along with the above polyelectrolyte applications, is a colloidal process of flocculating small particles which are suspended in water. There are usually two mechanisms involved for charged particles: neutralization and bridging. Small molecular conditioners depend solely on charge neutralization. The electrolyte polymers have both functions: charged units attach to particle surfaces, while chain backbones link particles together.

Most commercial polymeric flocculants are cationic copolymers containing charge densities of up to 40%. Charges in such copolymers are randomly distributed along chain backbones. To be more effective, we believe that it is better to concentrate charge units on several sections of a polymer chain. These charge clusters provide stronger attaching points to anionic particle surfaces, and also save unnecessary charge centers on chain bridges between particles [8].

Flocculation is an important operation in solid-liquid separation. In flocculation processes using polymers, polymer characteristics such as molecular weight (MW) and charge density (CD) influence flocculating and destabilizing actions. Floc growth results from interparticle collisions promoted by agitation. Frequently, deaggregation occurs simultaneously with aggregation. The complex effects of flocculation variables, suspension and polymer properties, and mixing conditions make the literature on flocculation somewhat inconsistent.

The objective of this paper is to evaluate the graft copolymers synthesized in our previous work [8] as flocculants for a titanium dioxide (TiO_2) model suspension and as conditioners for a pulp and paper mill sludge. The tasks included: determination of the interrelationships among MW, CD and polymer dosage with particle size distribution (PSD); establishment of the optimum chemical conditions for floc formation; and elucidation of the flocculation mechanisms in the system.

Experimental

Materials

All materials obtained commercially were used without further purification. The graft copolymers were prepared by the procedure detailed in our previous work [8]. As polyacrylamide (PAM) tends to undergo degradation in a dilute solution [9], all solutions were used within 12 h of preparation. Deionized water was used throughout our experiments.

TiO_2 was purchased from Aldrich. The density of TiO_2 was 3.9 g/ml. Stock solutions of 50 mg/l TiO_2 with an ionic strength of 10^{-3} M NaCl were prepared. They were left for 24 h to ensure that particles were completely wet before use. Prior to flocculation tests, an ultrasonic bath was used to ensure that particles were completely dispersed.

Sludge samples were taken from a pulp and paper mill. The solids concentration was about 3 wt%. As sludge characteristics change with time, adequate sludge for all tests was collected and all of the tests were finished within 8 h.

Surface charge of TiO_2

A TiO_2 particle possesses a surface layer of metal hydroxide which is amphoteric. The zeta potential of colloidal particles at 25 ± 0.3 °C was determined in terms of mobility by electrophoresis measurements, using the Coutler Delsa 440 Doppler Electrophoretic Light Scattering Analyzer. Figure 1 shows the mobility of TiO_2 suspension versus pH value. It can be seen that the isoelectric point (IEP) is at a pH of 4.3. The TiO_2 particle surface charge changes from positive to negative with increasing pH value. Above a pH of 7, the mobility data level off. In this work, a pH value of 8 was chosen as the condition for the flocculation tests, to assure a negatively charged particle surface. The pH of TiO_2 suspensions was adjusted to 8 by adding a small amount of 0.01 M HCl or NaOH solution (Aldrich Chemical Inc.).

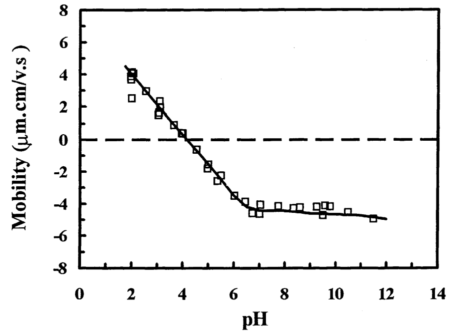

Fig. 1 Mobility of TiO_2 particles as a function of pH with 10^{-3} M NaCl

PSD measurement

A Brookhaven Instruments Disk Centrifuge Particle Sizer (DCP) was employed to analyze flocculation results. The disk spin speed was set at 3000 rpm. Polymer was quickly added to the suspension, the mixture was stirred for 30 seconds and the flocculated suspension was measured by a DCP. Each run was 15 min.

Typical particle size differential and cumulative mass distributions are shown in Fig. 2. This reveals that the PSD of our TiO_2 suspension is a bimodal distribution. The average volumetric diameter of the TiO_2 particle is 0.237 ± 0.15 μm. The quality of flocculation can be determined by analyzing the area under this curve. We have defined a parameter f, the fraction of large particles, as the ratio of the area under the second peak to the area under the entire curve. It is determined by the inflection point on the cumulative mass distribution curve. The relative fraction f_r is thus defined as follows:

$$f_r = \frac{f}{f_0}$$

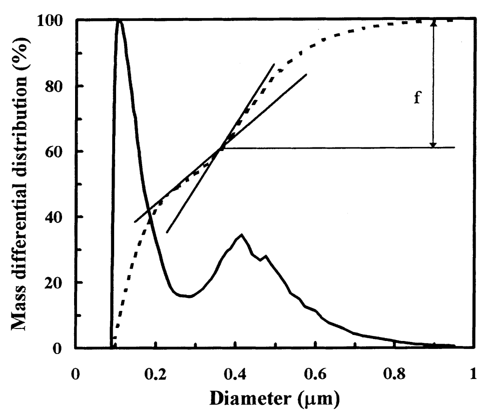

Fig. 2 Differential and cumulative mass distribution of TiO_2 particles: —— differential distribution, - - - - - - cumulative distribution

where f is the fraction of TiO_2 suspension flocculated by polymer, and f_0 is the fraction of un-flocculated TiO_2 suspension. The larger the f_r , the better the flocculation performance of the polymer.

Sludge dewaterability measurement

Graft copolymer was added to the sludge at 170 ppm, the recommended polymer dose for industrial practice. The conditioned sludge was inverted end-over-end seven times, using two beakers, to ensure complete polymer uptake. Each complete inversion took 2 s. The mixture was then poured onto a nylon mesh placed on a funnel and the drainage collected for the first 10 s. The dewaterability of the polymer was assessed by the volume of drainage. The drainage samples were also analyzed by turbidity measurement using a Hach 2100P turbidimeter. The sample without added polymer was used as the blank. Relative turbidity was calculated using:

$$T_r = \frac{T}{T_0}$$

where T is the turbidity of the treated sample, and T_0 is the turbidity of the blank.

Results and discussion

TiO_2 suspension flocculation

The PSDs of the TiO_2 suspension with various polymers are shown in Fig. 3a and b. It can be seen that after adding polymers the areas under the second peak become larger and the curves shift right, representing a larger particle diameter. This indicates the occurrence of flocculation.

Homo-PAM and homo-polyDADMAC show little effect on flocculation, but two of the graft copolymers show significant improvement. Graft copolymers of 3 h irradiation are shown in the figure as they gave the best flocculation performance. Among the three different charge density copolymers, the 30% polyDADMAC graft copolymer gives the best flocculation results; the 10% polyDADMAC graft copolymer has the worst. This can be explained as follows.

For a set period of irradiation, the sample with a higher polyDADMAC fraction results in a higher degree of grafting, e.g., in the sample with 30% polyDADMAC, there are about 10 polyDADMAC molecules grafted onto each PAM molecule and only 5 in the sample of 20% polyDADMAC [8]. The charged groups provide adsorption sites for electrostatic interaction with oppositely charged particle surfaces. They adsorb strongly onto the particle surface allowing for a flat configuration. The PAM backbone functions as a bridge to link all the attached particles. More cationic side branches give more adsorption sites for particles and therefore increase the chances for particles to aggregate.

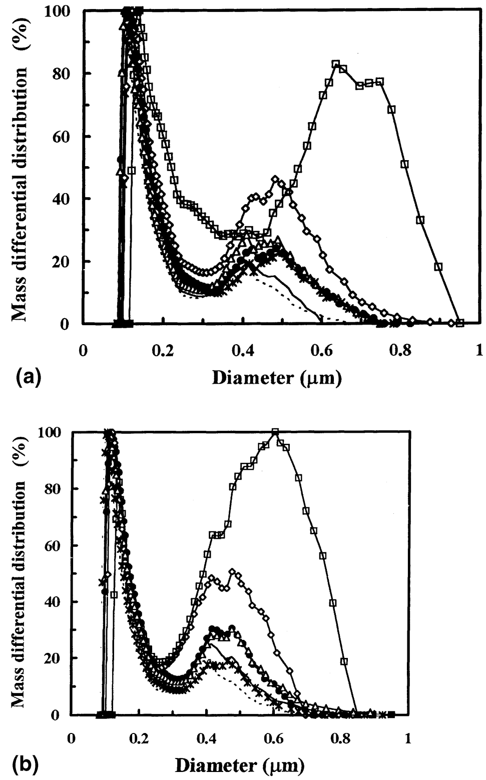

Fig. 3a Differential mass distribution curve of flocculated TiO_2 particles for 3 h irradiation and polymer dosage of 1 mg/g TiO_2: —— no polymer, - - - - - PAM, △ homo-polyDADMAC, ● 10% polyDADMAC graft copolymer, ◇ 20% polyDADMAC graft copolymer, □ 30% polyDADMAC graft copolymer. **b** Differential mass distribution curve of flocculated TiO_2 particles for 3 h irradiation and polymer dosage of 2 mg/g TiO_2: —— no polymer, - - - - - PAM, △ homo-polyDADMAC, ● 10% polyDADMAC graft copolymer, ◇ 20% polyDADMAC graft copolymer, □ 30% polyDADMAC graft copolymer

The relative fractions of graft copolymers after irradiation are shown in Fig. 4a and b. Homo-PAM and homo-polyDADMAC are used as the references for comparison. Homo-PAM does not show good flocculation performance and after irradiation it becomes even worse. This is because a water-insoluble gel is produced during irradiation and macro-gel is not usually a useful flocculant. Homo-polyDADMAC performs better than homo-PAM because its cationic groups can reduce the surface potential of particles, thus facilitating the floc formation. Homo-polyDADMAC shows a slight decrease in the relative fraction as a function of irradiation time. The MW of homo-polyDADMAC decreases after irradiation and this affects chain bridging on flocculating

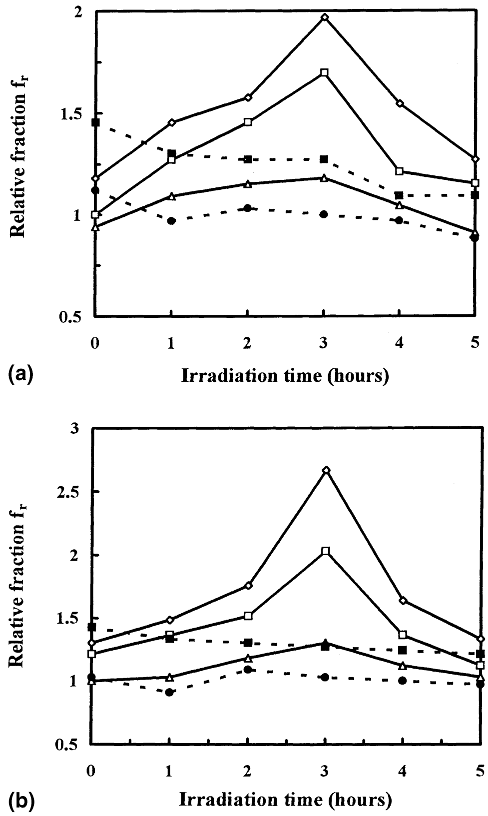

Fig. 4a Relative fraction versus radiation time at polymer dosage of 1 mg/g TiO_2: ● homo-PAM, ■ polyDADMAC, △ 10% polyDADMAC graft copolymers, □ 20% polyDADMAC graft copolymers, ◇ 30% polyDADMAC graft copolymers. **b** Relative fraction versus radiation time at polymer dosage of 2 mg/g TiO_2: ● Homo-PAM, ■ polyDADMAC, Δ 10% polyDADMAC graft copolymers, □ 20% polyDADMAC graft copolymers, ◇ 30% polyDADMAC graft copolymers

particles. Longer chain lengths have better flocculation performance where a chain bridging mechanism is predominant.

For homo-polyDADMAC, the irradiated samples have a similar charge to the nonirradiated sample but slightly lower MW; it is noticed that the irradiated homo-polyDADMAC resulted in a lower f_r. This implies that chain bridging may also be important in the homo-polyDADMAC flocculation of TiO_2 particles. Homo-PAM flocculates particles by bridging, since this is the only mechanism available to a nonionic polymer.

The sample with 10% polyDADMAC does not have good flocculation performance, although it is better than homo-PAM. The samples with 20 and 30 wt% polyDADMAC show a significant increase in f_r. With increasing irradiation time, f_r first increases and then decreases. Prior to irradiation, no grafting and low MW provide poor flocculation. After irradiation, both MW and grafting increase, and chain bridging plays a more important role in flocculation. However, further irradiation leads to macro-gel formation, and the flocculation performance degrades. Short irradiation times create graft copolymers with a lower degree of grafting and a lower MW. However, overexposure to irradiation can cause gel formation, which also results in poor flocculation.

It is worthwhile to point out that up to 3 h of irradiation, there are some gels in the polymer mixtures; these are soft gels. These samples perform much better than those with only 1 h irradiation, even though they contain some gel. This suggests that a certain amount of soft gel (micro-gel) facilitates flocculation, probably due to the sweeping action of a polymer network. Colloidal particles are captured if they are in the way of network sweeping. With a hard gel, a phase separation appears in the polymer solution and it cannot sweep off particle effectively. From the experimental results, 2, 3 or 4 h of irradiation and 30% polyDADMAC fraction are recommended.

Figure 5 shows particle electrophoretic mobility versus the polyDADMAC dosage. Initially the mobility appears negative. After the addition of polyDADMAC, the cationic charge on the polymer neutralizes some of negative charge on the particle surface. The mobility of the particles increases to zero. The IEP of the particles is found at a polyDADMAC dose of about 2.5 mg/g TiO_2. As more polyDADMAC is added, the mobility appears positive and finally levels off, indicating that the particles are completely coated. Overdosing with polyDADMAC results in particle charge reversal. Particles become positively charged due to the adsorption of excessive polyDADMAC molecules. When the polymer-particle adsorption reaches an equilibrium, the particles are completely coated by polymers and the particle mobility levels off. The point of zero charge determined by colloid titration appears to correlate well with the optimum dose required to flocculate turbid water [10].

Figure 6 shows f_r versus polymer dosage for the graft copolymers at an irradiation time of 3 h. It shows that when a lower polymer dose is applied, considerably less

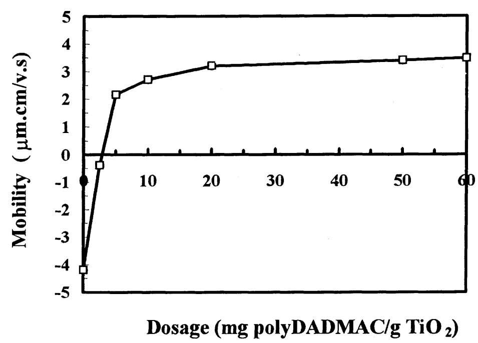

Fig. 5 Electrophoretic mobility of TiO_2 particles versus polyDADMAC dosage at pH = 8, T = 25 °C in 10^{-3} M NaCl solution

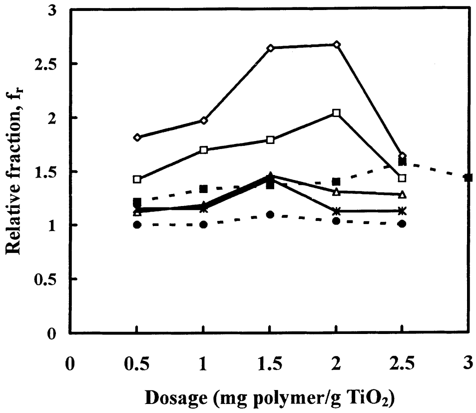

Fig. 6 Relative fraction as a function of polymer dosage. Graft copolymer irradiation time is 3 h: ● homo-PAM, ■ homo-polyDADMAC, △ 10% polyDADMAC graft copolymers, □ 20% polyDADMAC graft copolymers, ◇ 30% polyDADMAC graft copolymers

flocculation occurs, resulting in a lower f_r. In this case, the amount of polymer is insufficient, so that it gives only a limited number of bridging contacts. When the polymer is overdosed the particles are completely covered and the suspension becomes restabilized. There is an optimum dose range for a particular polymer/colloid system. Homo-polyDADMAC shows best flocculation at a dose of 2.5 mg/g TiO_2, which is around its IEP. This agrees very well with its electrophoretic mobility measurement. For 30% polyDADMAC graft copolymers, the optimum dose for TiO_2 suspension is between 1.5 and 2 mg/g TiO_2. For 20% polyDADMAC graft copolymers, the best dose is at 2 mg/g TiO_2. Homo-PAM and 10% polyDADMAC have poor flocculation performance for the entire range. The optimum dose range for 30% polyDADMAC graft copolymer is broader than that for 20% polyDADMAC graft copolymer.

The adsorption of polymer molecules on the particle surfaces often determines the stability of the particles. Polyelectrolytes of opposite charge to the suspension particles will adsorb strongly until the particle charge is neutralized. Polyelectrolytes assist flocculation by neutralizing the excessive particle surface charges, hence reducing the electrical repulsion of the electrical double layer. For a nonionic polymer, or a polymer with the same charge as that of particles, adsorption may occur due to hydrogen bonding. The oxide particles have a surface layer of hydroxyl groups; these groups are available for H-bonding with the amide group of PAM [11]. To obtain an effective flocculation, the number of PAM chains adsorbed onto the particles must provide enough bridges to form flocs of adequate strength.

No matter what the type of adsorption, the amount of polymer added should not be much in excess of the amount required for adsorption. If particles are completely coated by polymer, it becomes impossible for them to approach close enough to aggregate, thus introducing an eventual restabilization of particles. This effect is known as steric stabilization. An optimum polymer dose exists for flocculation and beyond this point the colloids may not be destabilized. The optimum flocculation usually occurs when half the adsorption sites on each particle are taken up by polymers [12].

La Mer and Healy [13] reported that the concentration of polymer needed for optimum flocculation is reversibly related to its MW. In another case of a cationic polyelectrolyte flocculating negatively charged particles, however, the dosage was found to be independent of MW [14, 15]. Gregory [16] reported that optimum flocculation was found to occur at the zero particle surface charge, and polymers with a higher CD performed better.

Our experimental results show that charge neutralization is important for polymer-particle interactions with homo-polyDADMAC. It needs a dose of 2.5 mg/g TiO_2 to neutralize the particle surface charge. The optimum dosage for graft copolymers is actually less than 2.5 mg/g TiO_2, although graft copolymers have many fewer cationic groups than homo-polyDADMAC. So, using graft copolymers, optimum flocculation occurs when the surface charge of the particle is not zero. Therefore, it is MW rather than charge neutralization that appears to be the predominant factor affecting the optimum dosage in our work.

Sludge dewatering

Figure 7 shows the paper mill sludge dewatering test results for homopolymers, polymer blends and graft

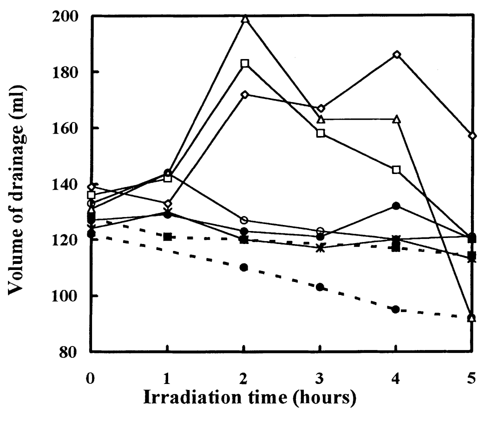

Fig. 7 Volume of drainage of a paper mill sludge as a function of polymer irradiation time for graft polyelectrolytes: - -●- - PAM, ■ polyDADMAC, △, □, and ◇ graft copolymers of 10%, 20% and 30% polyDADMAC, respectively; —○—, —●—, and —∗— polymer blends of 10%, 20% and 30% polyDADMAC, respectively

copolymers. Polymer blends are mixtures of two irradiated homopolymers. The volume of drainage without adding polymer is 95 ml. It can be seen that homo-PAM and homo-polyDADMAC do not have very high dewaterability, and neither do polymer blends. After irradiation homo-PAM shows worse dewaterability, because of gel formation, while homo-polyDADMAC shows a slight decrease with irradiation time. These results are consistent with the polymer viscosity results. Polymer blends perform better than homopolymers, since they can function in two ways. PolyDADMAC reduces the particle surface potential by charge neutralization, while PAM is able to bridge those potential reduced particles into bigger clumps. Senthilnathan and Sigler. [17] also reported improved dewaterability by different dual polymer systems.

It is clear that the graft copolymers show a significant improvement in performance over homo-PAM, homo-polyDADMAC and polymer blends. The discrepancy in dewatering results between polymer blends and copolymers also indicates that the products after irradiation are not just physical mixtures; changes have been made to their chemical structure. Two homopolymers have chemically reacted and polyDADMAC is grafted onto PAM.

All of the graft copolymers show increased drainage with irradiation time to a maximum, and then decreased drainage with further irradiation. For the samples of 10% and 20% polyDADMAC, 2 h of irradiation give the best results. For the sample of 30% polyDADMAC, 4 h is the optimum time. After 5 h of irradiation, the volume of drainage decreases, but it is still reasonably high for the samples of 20% and 30% polyDADMAC. This implies that the gel fraction is not as important as it is in the model TiO_2 suspension. After irradiation for 4 or 5 h there are sufficient gels to inhibit effective flocculation of the TiO_2 suspension. However, it is observed that sludge dewatering is not sensitive to polymer gel to the same extent as that of flocculating TiO_2 particles.

The results of turbidity measurements on the drainage fluid are shown in Fig. 8. The relative turbidity is plotted against the irradiation time. For homopolymers and their blends, good flocculation occurs at an irradiation time of 1 or 2 h. Compared to homopolymers, blends do not show improvement at longer irradiation times, but when irradiated for less than 3 h they do reduce the relative turbidity. As polyDADMAC changes little during irradiation, the only factor that affects dual polymer systems is PAM. At longer irradiation times, the gel fraction increases. Heavily gelled PAM is not helpful in bridging colloidal particles into larger flocs, although the particle surface potentials are reduced by polyDADMAC.

Graft copolymers exhibit a good performance in removing colloidal particles. The samples of 10% and 20% polyDADMAC are best at only 1 or 2 h of irradiation, but the sample of 30% polyDADMAC shows the lowest turbidity for any irradiation time investigated in this work.

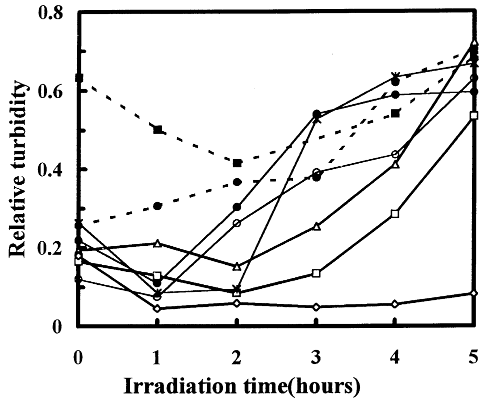

Fig. 8 Relative turbidity of drainage as a function of polymer irradiation time for homo-polymers, their blends, and graft copolymers: - -●- - PAM,- -■- - polyDADMAC, △, □, and ◇ graft copolymers of 10%, 20%, and 30% polyDADMAC, respectively;—○—,—●— , and —*— polymer blends of 10%, 20% and 30% polyDADMAC, respectively

It should be pointed out that there is no direct linear correlation between high sludge dewatering and low turbidity. If a polymer performs well in sludge dewaterability, it does not necessarily mean that it also has a good flocculation effect. Dewaterability depends on two major factors: flocculation effect and floc structure. Large floc formation is necessary for effective flocculation; flocs that have a more rigid structure and strong pore system are favorable in dewatering.

Conclusions

Compared with homopolymers and their blends, the graft copolymers give more effective flocculation for the model system, and pulp and paper mill sludge. In flocculation using graft copolymers, chain bridging is the predominant mechanism, and the cationic charges on polyDADMAC play a contributory role. Reaction time is a very important parameter affecting copolymer flocculation performance; either too little or too much irradiation will reduce the effectiveness of a flocculant. A small amount of microgel in the graft copolymer improves flocculation.

The adsorption behavior of polymers on particle surfaces is important in flocculation. The effect of polymer dosing is significant: there is an optimum dosage. The polyDADMAC fraction affects the charge density of the graft copolymers, thus affecting flocculation. The copolymers of 30% polyDADMAC have the best flocculation performance among the copolymers of three different polyDADMAC fractions. The copolymers of 10% polyDADMAC show little improvement in flocculation.

Graft copolymers not only increase the sludge dewaterability, but also reduce the turbidity of the drainage fluid. However, there is no direct correlation between the sludge dewaterability and the turbidity of drainage fluids. The dewaterability of the polymers depends largely on their flocculation effect and floc properties such as structure and strength.

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