

Flocculation Studies of Fine coal Using Acrylamide and Acrylic Acid Graft Copolymer By Gamma Irradiation

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Abstract: Most coal preparation processes were carried out in water medium. The water content of coal product has a negative impact on handling and specific energy value. The moisture content may be attributed to the proportion of fine coal, which presents the greatest dewatering problem. A novel polymeric flocculant has been developed by graft copolymerization of acrylamide (AAM) with acrylic acid (AAc) using gamma irradiation technique. The grafted copolymer P(AAM/AAc) was characterized using Fourier-transform infrared spectroscopy (FTIR), and thermo-gravimetric analysis (TGA). The effects of reaction parameters, such as total absorbed dose, and monomer concentration on grafting yield were investigated. The flocculation performance of the graft copolymer P(AAM/AAc) was investigated in coal suspension. It was observed that the grafting ratio was one of the key factors for the flocculating effects. The copolymers with various grafting ratios showed different flocculating properties. It was found that as the grafting ratio increased, the flocculating effect also increased. The flocculation performance of the grafted copolymer was better than that of the commercial flocculant, poly-acrylamide (Magnafloc 1011).

Key words: Acrylamide (AAM); acrylic acid (AAc); Flocculation; Grafting; Irradiation; Coal

INTRODUCTION

In a coal cleaning operation (coal preparation), raw coal is crushed and screened into coarse and fine sizes. The coarse and intermediate size fractions are then cleaned by the specific gravity difference between the coal and other associated minerals in either dense medium or jigs. Grinding coal to fine particles (<100 µm) may be necessary to achieve liberation between coal and other associated minerals which are cleaned by a froth flotation process. Dewatering of the coarser sizes is usually effective by means of screens. The dewatering of fine flotation product is centrifuged or filtered (vacuum) to a moisture content of 15–30 wt% before it is rebled with the coarse fraction (Dzinomwa *et al.*, 1997).

Most of the water content of the fine coal is held between and on the surface of the coal particles, and it is not absorbed by the coal. Excessive moisture in the final product may lead to high transportation costs; reduced energy value; freezing in cold climates and poor coking properties (for coking coal). Thermal drying is associated by high operational cost and the safety hazards (Sastri 1991). Studies have been conducted to investigate the feasibility of microwave drying (Chatterjee and Misra 1991), vacuum filtration (Daykin *et al.* 1987; Keleghan, 1986) electro-osmotic dewatering (Bendit *et al.*, 1992; Lockhart and Stickland 1984). Many studies on absorbent polymers have been investigated (Parekh 2009).

On the other hand, the separation of coal particles in coal-washery effluent slurries “blackwater” is usually accomplished through sedimentation, filtration and flotation or some combination of them. Coal particles are colloidal in nature and for this reason, coagulants and/or flocculants are usually added to destabilize the suspension and to promote the aggregation of particles before separation is carried out. Coagulants and flocculants are effective in promoting aggregation of colloidal coal particles (Orumwense 2001), but some controversy exists about their adverse effect on filtration and flotation processes.

Flocculation is a process of bringing together smaller particles to form large particles, often highly porous in nature. Flocculation of suspensions is brought about by addition of minute quantities of chemicals known as flocculants of various characteristics (Nayak, and Singh 2001).

The flocculants are classified into two types, inorganic and organic. Among inorganic flocculants, the salt of multivalent metals like aluminum and iron are mostly used. The organic flocculants are essentially polymeric in nature which are more effective as they are required only in minute quantities, they produce less sludge, and do not require any pH adjustments (Krishnamoorthi and Singh 2006). Both synthetic and natural water soluble polymers are used as organic flocculants. Starch, alginic acid, and guar gum are among the natural polymers

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used in flocculation. They have the advantage of being of low cost, nontoxic, and biodegradable. But the biodegradability of the natural polymers acts as a drawback, as it reduces storage life as well as performance (Tripathy *et al.*, 2001).

The synthetic flocculants are divided into three categories: cationic, anionic, and nonionic. They are mostly linear water soluble polymers such as polyacrylamide, polyacrylic acid, polydiallyl dimethyl ammonium chloride (DADMAC) and poly-styrene sulphonic acid etc. Synthetic polymers are highly efficient and can be tailored to the needs of a particular application, but often suffer from their shear degradability (Singh *et al.*, 2000; Sen and Pal, 2009; Biswal and Singh, 2006; Laue and Hunkeler, 2006). Synthetic polyacrylamides and polyacrylic acid are effective flocculants and can be easily tailored by controlling the molecular weight and weight distribution, the chemical structure of the polymers, and the nature and ratio of functional groups on the polymeric backbone. However, the synthetic polymer flocculants are not shear resistant or biodegradable (Brostow *et al.*, 2008; Gui *et al.*, 2010; Scott *et al.*, 1996). Superabsorbent polymers are highly hydrophilic, three-dimensional polymeric networks have attracted much attention as functional polymers that possess properties of water absorption (Zohuriaan-Mehr *et al.*, 2010).

The major mechanisms of flocculation by polymers are charge neutralization and bridging. For neutral flocculants, flocculation is caused mainly by polymer bridging. Surface-charge neutralization occurs if the charge of flocculant is opposite in sign to that of the suspended particles. When very long-chain polymer molecules are absorbed on the surface of particles, they tend to form loops that extend some distance from the surface into the aqueous phase, and their ends may also dangle. These loops and ends may come into contact with, and attach to, another particle, forming a bridge between the two particles. This is the bridging mode of flocculation (Bratby, 1980).

Later studies on the flocculation behavior, the graft copolymerization is most attractive because it is a useful technique for modifying the chemical and physical properties of polymers (Subramanian *et al.*, 2002, Akgün *et al.*, 2007; Subramanian *et al.*, 1999). The chief method of synthesis of grafted copolymers involves use of chemical free radical initiator (conventional method) and high energy radiations. The conventional method of synthesis uses a chemical free radical initiator (e.g. ceric ammonium nitrate or CAN) to generate free radical sites on the backbone polymer, where the monomer of the graft gets added up to form the graft chain (Joshi and Sinha 2006). This method of synthesis has low reproducibility and is not very suitable for commercial scale synthesis. A better method of graft copolymer synthesis is by using high energy radiation (gamma rays or electron beam) as the free radical generator (Wang *et al.*, 2009; Francis *et al.*, 2009; Abd El-Mohdy and Abd El-Rehim 2009; Abou Taleb *et al.*, 2008). Radiation-induced grafting is of high efficiency and does not cause any further contamination associated with chemical initiators.

Based upon the above considerations the present study has been conducted to synthesis a graft copolymerization of acrylamide (AAm) and acrylic acid (AAc) by means of gamma irradiation. The effects of the reaction parameters, such as the total radiation dose, and monomer concentration on the grafting yield were systematically investigated. The flocculation characteristics of grafted copolymers (AAm/AAc) with different composition were investigated in fine coal suspensions. Their performance was compared with commercially available flocculants namely; Magnafloc 1011.

MATERIALS AND METHODS

Materials:

Acrylic acid (AA) and acrylamide (AAm) of purity 99% (Merck, Germany) were used as received. Other chemicals were of reagent grade and used without further purification.

Magnafloc1011, is a commercial anionic flocculant was supplied by Allied Chemicals, UK. It is polyacrylamide based and their structures are totally classified by their manufacturers.

A coal concentrate of Maghara coal (Sinai, Egypt) was obtained by column flotation process which has 1.01% total sulphur and particle size = -200 mesh (-74 μm) was employed in this study (Abdel Khalek 2002).

The Synthesis of the Graft Copolymer:

Acrylamide was used as the backbone for all graft copolymerization. A desired amount of solid acrylamide (AAm) was dissolved in 150 ml distilled water. The amount of AAm was kept constant, but the amount of acrylic acid (AAc) was changed for each synthesizing experiment to prepare a series of P(AAm/AAc) samples with various grafting percentage. The mass ratio of AAm and AAc was 1:1, 1:3 and 1:5, respectively. The mixtures were then poured into test tubes and the solutions were made free from oxygen by purging nitrogen gas for 10 min. The irradiation was carried out in ^{60}Co gamma cell with irradiation dose 10 kGy at a dose rate of 1.2 kGy/h. After irradiation, the sample solutions were precipitated in acetone and separated by filtration. The homopolymer formed during the reaction was removed through Soxhlet extraction using ethanol for 24 h. The grafted copolymer was then dried in a vacuum oven at 50 $^{\circ}\text{C}$ until a constant weight was obtained. The grafting percentage was calculated using the following equation:

$$\text{The grafting percent (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

Where W_0 and W_g represent the weight of acrylamide and grafted copolymer, respectively.

FTIR Measurements:

Analysis by infrared spectroscopy was carried out using a Mattson 1000, Unicam spectrometer, England in the range from 400 to 4000 cm^{-1} .

Thermal Gravimetric Analysis (TGA):

Shimadzu TGA system of type TGA-50 was used for measurement of TGA. The nitrogen gas flow at constant rate was about 50 ml/min to prevent thermal oxidation processes of polymer samples. The heating rate was 10°C/min from ambient up to 600°C.

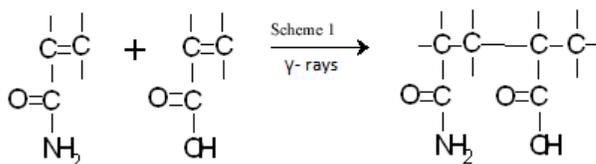
Flocculation Studies:

Flocculation capacity of the grafting copolymer was evaluated using 0.25 wt% of coal suspension. The flocculants in solution form were added into the coal suspensions of 500 ml jars. The suspension was immediately stirred at a constant speed of 100 rpm for 2 min, followed by a slow stirring at 30 rpm for 5 min. Thereafter, the sample was left to settle for 10 min. The clean supernatant liquid was drawn and its turbidity was measured by a digital Nephelo turbidimeter. The turbidity was expressed in Nephelo turbidity units (NTU).

Settling test employs a 100 ml stoppered graduated cylinder and stopwatch. The polymer solution was added to a 5 wt % suspension sample taken in the cylinder. The cylinder was turned upside down 10 times for thorough mixing. After that the cylinder was set upright, and the height of interface between water and settling solid bed is measured over time (Bratby1980).

RESULTS AND DISCUSSION

Graft copolymers based on AAm have been synthesized by grafting AAc onto AAm by a free radical polymerization technique using gamma irradiation. A series of the P(AAm/AAc) samples with various grafting ratios were successfully prepared. The polymerization mechanism of AAc grafted AAm was shown in Scheme 1.



Scheme 1 : Schematic illustration of the graft copolymer P(AAm/AAc) synthesis.

1. Factors Affecting the Grafting Yield:

1.1. Total Absorbed Dose:

Fig. 1 shows the effect of total irradiation dose on the grafting yield. Generally, the grafting percentage increased with increasing irradiation dose. This was mainly attributed to the increase in the number of free radicals with an increase in total absorbed dose. It can be noted that, with an increase in absorbed dose up to 10 kGy, the rate of grafting decreases due to the system viscosity increase which accompanies the graft copolymerization and the homo-polymerization of AAc.

1.2. Monomer Concentration:

As shown in Table. 1, the grafting percentage significantly increased with increasing AAc content in the P(AAm/AAc). The presence of a high content of AAc in the polymerization medium provided a greater availability of AAc molecules to react with the AAm radicals, leading to a higher grafting percentage.

2. Characterization of the Grafting Copolymer:

2.1. FTIR Spectrum:

FTIR is a powerful technique for elucidating the molecular structure for both natural as well as synthetic polymers (Ibrahim and Koglin 2005; Ibrahim *et al.*, 2009; Ibrahim *et al.*, 2010).

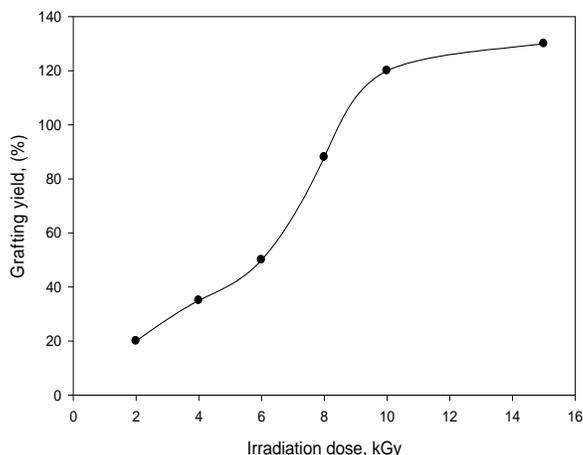


Fig. 1: Effect of irradiation dose on the grafting yield (AAm : AAc, 1:1 wt%).

Table 1: Effect AAc concentration on the grafting yield at irradiation dose 10 kGy.

AAm : AAc	Grafting yield,%
1 : 1	120
1 : 2	154
1 : 3	188
1 : 4	209
1 : 5	225

The infrared spectra of P(AAm), P(AAc), and P(AAm/AAc) are illustrated in Fig. 2. In the FTIR spectra of P(AAm/AAc), characteristic broad band appearing in the spectral range of 3100–3500 cm^{-1} are assigned to O–H and N–H vibration bands. The reason for this wide band broadening may be explained by the existing hydrogen bonding between the studied molecules. The absorbance at 1100–1200 cm^{-1} could be attributed to C–N band and were observed in the PAAm and also in P(AAm/AAc). The weak band around 2900 cm^{-1} has been assigned to the C–H stretching vibrations. While $-\text{CH}_2-$ groups on the chain appear at 1460 cm^{-1} . The bands at 1661 and 1641 cm^{-1} have been assigned to $-\text{CONH}_2$ group band in PAAm and the bands at 1570, 1400, and 1714 cm^{-1} could be attributed to the carboxyl band of PAAc. The C=O band of the carbonyl group was observed at 1658 cm^{-1} in P(AAm/AAc). These data indicated that the synthetic copolymer was P(AAm/AAc).

2.2. Thermal Analysis:

The thermograms of P(AAm), P(AAc), and P(AAc/AAm) were investigated and given in Fig.3. The temperature for the maximum weight loss (T_{max}) and the temperature for the half-life ($T_{1/2}$) were found directly from their dynamic thermograms. It was found that, P(AAm) gives a 20% residue at 500°C. The temperature for the maximum weight loss of P(AAm) is $T_{\text{max}} = 394^\circ\text{C}$ and $T_{1/2} = 407^\circ\text{C}$. For PAAc the temperature for maximum weight loss is $T_{\text{max}} = 410^\circ\text{C}$ and the temperature for half-life is $T_{1/2} = 385^\circ\text{C}$ and gives a 10% residue at 500°C. There are three decomposition peaks on its thermogram and they are 245, 300, and 410°C, respectively. P(AAc), degrades by forming an anhydride structure, the anhydride decomposes by heating P(AAc), at about 400°C, resulting in rapid decomposition to carbon dioxide and volatile hydrocarbons. On the other hand by investigating the thermogram of the P(AAm/AAc), it was observed that, this graft copolymer gained new thermal characteristics, namely T_{max} for P(AAc/AAm) is 417°C and $T_{1/2}$ is 382°C.

3. Flocculation Characteristics:

An attempt has been made to compare the flocculation characteristics of the grafted copolymer P(AAm/AAc) with a commercially flocculant in coal suspension.

The flocculation performance of the grafted copolymer and the commercial flocculant, Magnafloc 1011, in 0.25 wt% coal suspension was investigated and shown in Fig. 4. In this case, the turbidity of the supernatant liquid after flocculation was plotted against the polymer concentration. It is obvious from these results that grafted copolymer P(AAm/AAc) by having branches structure is better flocculant in coal suspension than that of the commercial one which is a linear polymer.

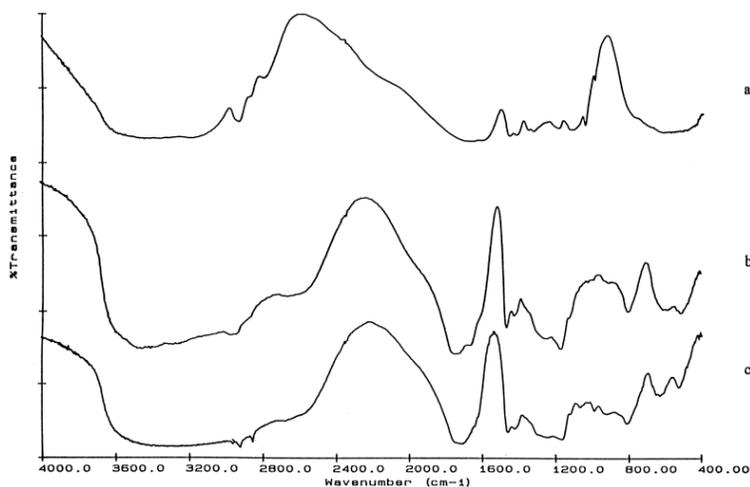


Fig. 2: FTIR spectra of P(AAm) (a), P(AAm/AAc) (b), and P(AAc)(c).

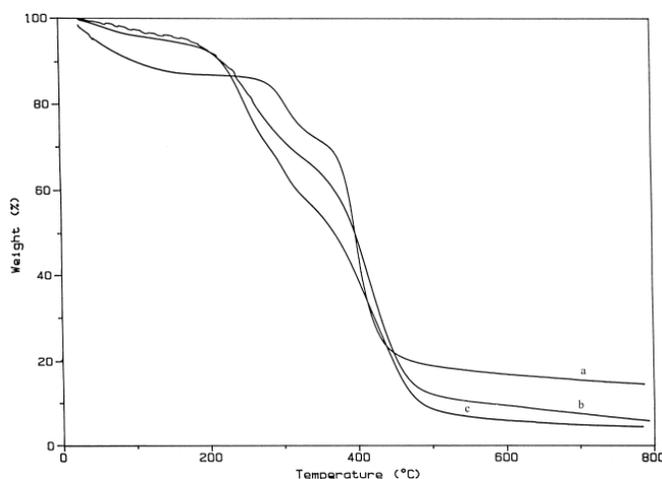


Fig. 3: Thermogram of P(AAm)(a), P(AAm/AAc) (b), and P(AAc)(c).

The flocculation performance of different composition of the grafted copolymer is shown in Fig. 5. It is obvious from this figure that the higher the grafting yield the higher the flocculation performance, i.e. more AAc content in the graft copolymer leads to high flocculation performance. This may be due to increasing of the carboxylic (COOH) groups which results in electrostatic repulsion, and chain straightening, thus increasing the flocculation efficiency.

The flocculation performance of a particular polymer can be correlated with settling velocity. The settling tests were carried out in 10 wt% coal suspension at the flocculant dosage (10 ppm). In this case, the settling time was plotted against the height of interface. Figure 6 shows the settling characteristics in coal suspension for the grafted copolymer P(AAm/AAc), and the commercial flocculant. It is clear that the settling time of the commercial flocculant is 6 times higher than that of grafted copolymer to reach 80% settling.

Generally, the commercial flocculant, Magnafloc 1011, is polyacrylamide-based linear polymer, hence their performance is inferior to the graft copolymer. The graft copolymer, due to the better approachability of the dangling grafted chains onto the rigid backbone, can easily bind the colloidal particles through bridging to form flocs. This type of intense bridging is not possible in the case of linear polymers. Hence, for graft copolymers, bridging will be better and easier than that of linear polymers (Rey and Varsanik, 1986).

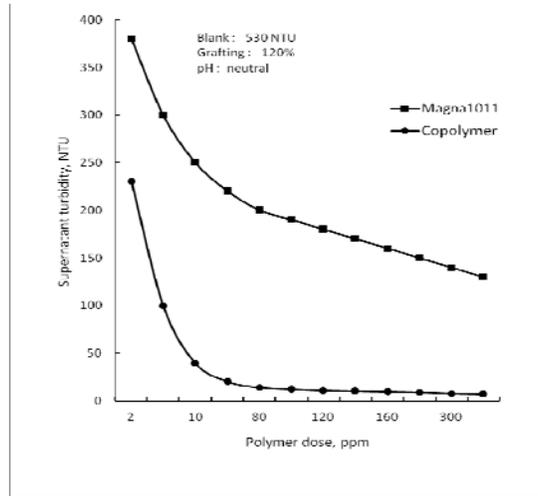


Fig. 4: Comparison of flocculation characteristics of grafted copolymer with commercial flocculant in the Maghara coal fine suspension.

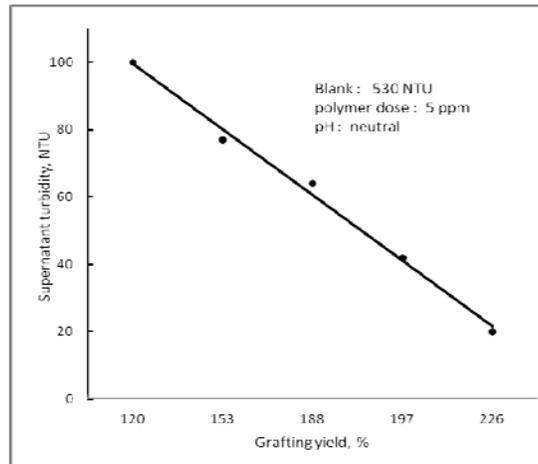


Fig. 5: Flocculation characteristics of different grafted copolymer compositions in the Maghara coal fine suspension.

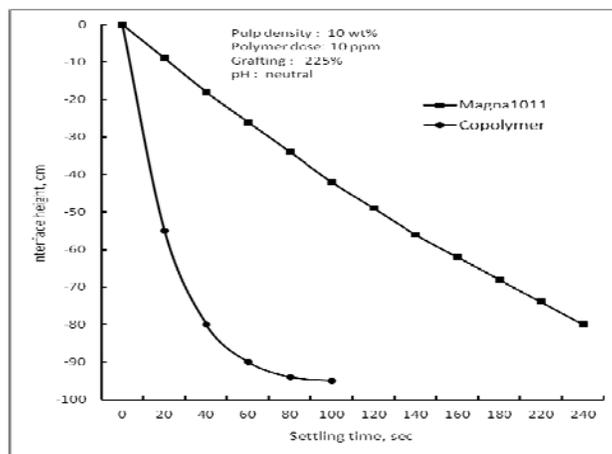


Fig. 6: Settling curves for Maghara coal suspension with addition of grafted copolymer and commercial flocculants.

Conclusion:

The grafting of AAc onto AAm was achieved through γ -ray irradiation for the production of a new flocculant. The grafted copolymer was characterized using FTIR, and TGA measurements. The effects of various reaction parameters, such as total absorbed dose, and concentration of monomer on the grafting percentage were systematically investigated. Results show that the grafting percentage increased with the increasing total absorbed irradiation dose up to 10 Gy. The grafting percentage increased with increasing monomer concentration which increases the availability of AAc molecules to react with AAm, leading to an increase in grafting yield. The flocculation characteristics of the grafted copolymers P(AAm/AAc) with different composition were investigated in fine coal suspensions. From the flocculation study, it can be concluded that the grafted copolymer showed better performance in coal suspension than that of Magnafloc 1011, as a commercial flocculant. The higher performance of grafted copolymer may be due to the branches structure as compared to linear structure of commercial flocculant. Finally we recommend the present grafted polymer as an efficient flocculent based upon the investigated measurements as well as comparison with well known flocculent.

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