

# Anionic Acrylamide Co-Polymer as Dry Strength Additive for Paper

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## ABSTRACT

Paper strength increased considerably when polymers are adhered on fibers in large amounts. Substantial gain in breaking length and bursting strength were achieved through the sequential addition of cationic and anionic polymers. Many different synthetic and natural chemical additives are used in the manufacture of paper for a variety of different reasons during the wet formation process. Need for an effective internal dry strength additive for papers that is readily soluble with water and easily compatible with the papermaking fibre is increasing and opens new opportunities of research in this field. Copolymers consisting acrylamide and unsaturated acids like acrylic acid along with acrylate monomers such as methyl methacrylate were synthesized and applied to chemical pulp and their strength improvement potential was evaluated in comparison to commercially available dry strength resin.

Increasing the acrylic group in acrylamide backbone gives a dry strength resin imparting better strength to paper. Addition of acrylate group like methacrylate still further enhances the efficiency. As Indian paper mills utilizing mostly short fibered pulps of diversified raw materials, the need for developing a suitable Dry strength resin to cope with increasing machine speeds is warranted.

## Introduction

Paper makers can face considerable challenges in meeting dry strength requirements, depending on the furnish composition and the paper grade. Paper strength depends on fiber length, fiber width, coarseness and fines content of the pulp. The hemicellulose component of fibers shares many of these same attributes, so it is not surprising that addition of hemicellulose products to papermaking furnish tends to increase the strength. The need to meet tensile strength requirements can be especially challenging when the furnish includes short fibers like hardwood, bagasse, straw and secondary fibers, which has inferior ability to form inter-fiber bonds.

In papermaking process, different chemical additives are utilized to enhance specific sheet properties of paper. The main categories are wet-end additives, surface treatment additives, and paper-coating additives. These additives are generally classified as functional additives and control additives. Functional additives such as dyes, internal sizing agents, wet and dry strength agents and fillers are used to improve the quality of paper. Control additives such as biocide, drainage

aides, retention aids, defoamers etc., are added to ensure trouble free papermaking process.

The strength of paper is a property classified under three categories viz dry strength, wet strength, and wet web strength. Dry strength is tensile strength exhibited by the dry paper sheet, typically conditioned under uniform humidity and room temperature conditions prior to testing. Wet strength is the tensile strength exhibited by a paper sheet that has been fully dried and then rewetted with water prior to testing. Wet web strength is the strength of a cellulose fiber mat prior to drying to paper, which mat has water content of about 40-80 weight percent.

Dry strength is an inherent structural property of paper, which is due to the development of fibre to fibre bonds during consolidation and drying of the paper network. Paper strength is dependent on the strength of individual fibres, strength of inter-fibre bonds, the number of bonds and the distribution of fibres and bonds. Hydrogen bonds and van der waals interactions are believed to be responsible for the dry strength.

## Dry strength additives

Dry strength additives are hydrophilic polymers, which enhance the effective bonding area, surface energy or hydrogen bonding ability. A resin, which is used to improve dry strength of paper, is called dry strength additive and

must fulfill following requirements.

- ❖ It should improve dry strength by at least 15% over the normal dry strength of paper.
- ❖ It should confer low degree of wet strength
- ❖ It should not adversely affect the drainage rate of the cellulose web on the paper machine.

Dry strength additives generally work by supplementing the number of inter-fibre hydrogen bonds. Hydrogen bonding between cellulose molecules results in the high strength of cellulose fibres. These hydrogen bonds result from the dipole interaction of the proton on hydroxyl group with the oxygen of another hydroxyl group. The large number of hydrogen bonds formed in paper gives higher in the dry strength of paper.

Commonly used dry-strength additives include derivatives of biopolymers such as starch, guar gum and carboxymethylcellulose. Among these, due to chemical stability and good adhesive properties starch is used in paper conservation for surface coating most widely used. Chemically starches are polymers with repeating units D-glucose joined through hemiacetal glycosidic bonds. The ability of starch to aid in inter-fiber bonding is a function of the tendency of starch to form hydrogen bonds and its high molecular weight.

Different types of synthetic additives are used as wet end additives in paper making process to increase the dry

strength of paper. The key mechanisms governing, the bond development between cellulosic fibers include capillary action, three-dimensional mixing of macromolecules on facing surfaces, conformability of the materials, and hydrogen bonding. Dry-strength additives need to adsorb efficiently onto fibers, have a hydrophilic character, and have a sufficiently high molecular mass. Acrylamide based synthetic resins can form hydrogen bond through the amide group. Hence, these synthetic dry strength resin are often more efficient than natural polymers.

### Acrylamide Copolymers

This class of papermaking additives includes a wide range of molecular mass, degree of branching (often linear copolymers), and relative proportion of charged nonnumeric groups. By definition one of the monomers is plain acrylamide i.e.,  $-\text{CH}=\text{C}(\text{CONH}_2)$  in which the group in brackets is attached to the second carbon. For production of an anionic copolymer, the co-monomer is often acrylic acid,  $-\text{CH}=\text{C}(\text{COOH})$ . Cationic co-monomers typically have quaternary ammonium groups, and they are attached to the nitrogen of the amide,  $-\text{CH}=\text{C}(\text{CONH-RN}^+(\text{CH}_3)_3)$ , where R can take a variety of forms. Polymerization is achieved by "Zipping" the double bonds together-so the polymer backbone consists of single bonds (unsaturated). Polyacrylamide copolymers used as dry-strength resins are usually solution copolymers (no oil present) with molecular masses upto 1 million g/mole.

### Scope of the Present Work

Need for an effective internal dry strength additive for papers that is readily soluble with water and easily compatible with the papermaking fibre is increasing as more and more mills are increasing the ash content in paper and this opens new opportunities of research in this field. Keeping this in view with all the requirements, in the present investigation, the following copolymers consisting of acrylamide, methyl methacrylate along with DADMAC were synthesized and applied on paper hand sheets and their strength properties improvements were evaluated.

### Experimental Methods

#### Typical synthesis procedure:

Copolymers of acrylamide with other said monomers were prepared in

solution polymerization through free radical polymerization using re-dox initiation. Polymerization reaction was carried out in an inert atmosphere created by passing nitrogen gas through out the reaction. Synthesis was carried out by using a three-way neck reactor vessel, fitted with rotating stirrer and heater arrangements and kept in a water bath. Calculated quantity of monomers were combined and made up to 300 ml with distilled water. Prior to the charging, the reactor was purged with nitrogen gas. Then the combined monomer solution was charged into the reaction vessel. This reaction mixture was heated to required temperature. After reaching the required temperature, 30 ml of initiator solution was added to the reactor over a period of 60 min. The polymerization reaction was continued for 120 minutes. The reaction mixture (copolymer) was removed from the reactor and analyzed.

### Viscosity and Total solids measurement

The total solid content was obtained by keeping the copolymer at 70°C in vacuum oven for four hrs and on finding the difference in weight total solid content was calculated. Viscosity of the thick product was measured using Brook-field Programmable DV-II + viscometer with LV spindle -2 at room temperature.

### Purification of copolymer

Known quantity of copolymer from the reactor was poured in a beaker containing acetone for re-

crystallization. The crystallized polymer was removed and dried in vacuum oven at 70°C overnight and dissolved in water for further characterization and applications.

### Evaluation of copolymer on Paper strength improvement

The copolymers prepared with the above said manner were used in making hand sheets for testing the effectiveness of the polymers as strength additives. Hand sheet were prepared with calculated amount of polymer solution and other related additives like sizing chemical and fixing agent. The 60 gsm hand sheets were prepared by ISO method (5269). Then, these sheets were dried at 26°C with 65% relative humidity for 24 hrs. These dried sheets were kept in an oven for 20 minutes at 105°C for curing and then these sheets were again conditioned with 65% RH and at 26°C for four hrs before testing. The tensile strength, Bursting strength, Tensile Energy absorption (TEA) and elongation were determined by ISO method (1924,2758).

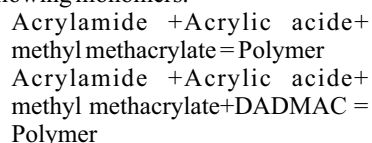
### Results And Discussion

By changing the monomer composition five copolymers with different monomer compositions were prepared. The polymerization was carried out through free radical solution polymerization using PDA-TGA redox initiator at 60°C temperature and 120 min reaction time. During polymerization the temperature of the solution got increased to 55°C from 30°C, due to exothermic reaction. The

**Table -1**  
Synthesis of copolymer of acrylamide, Acrylic acid, methyl methacrylate and DADMAC

| Acrylamide Mole % | Acrylic acid Mole % | MMA Mole % | DADMAC Moles % | Total Solids % | Viscosity at 30°C - cps | [PDS ] = 2 % : [TGA ] = 0.3 ml : Time = 120 min; Temp = 60°C |
|-------------------|---------------------|------------|----------------|----------------|-------------------------|--|
| 85                | 15                  | 0          | 0              | 14.0           | 31000                   |  |
| 85                | 10                  | 5          | 0              | 17.4           | 12500                   |  |
| 85                | 5                   | 10         | 0              | 20.3           | 6400                    |  |
| 85                | 5                   | 5          | 5              | 20.0           | 3200                    |  |
| 80                | 5                   | 5          | 10             | 21.0           | 2200                    |  |

co-polymer backbone contains the following monomers.



The two-component initiator system consists of an oxidizing and reducing component that forms free radicals on reaction with each other. The initiator can be added at the same rate throughout the reaction to control the molecular weight of copolymer.

The conditions of synthesis of copolymer with total solids and viscosity is given in Table-1. The paper properties with polymer at various addition levels and strength improvement over the blank values are presented in Table2-4.

Table : 2

**Paper strength properties with copolymer of Acrylamide, Acrylic acid, Methyl methacrylate and DADMAC**  
**Influence of copolymer on strength properties of paper**

| Copolymer composition moles % | Copolymer Addition % (w/w) | Tensile Index Nm/g | Burst Index KPa m2/g | TEA J/g | Stretch % |
|-------------------------------|----------------------------|--------------------|----------------------|---------|-----------|
|                               |                            |                    |                      |         |           |
| 85 / 15 / 0 / 0               | 0.2                        | 52.5               | 3.66                 | 63.0    | 2.5       |
|                               | 0.3                        | 54.6               | 3.78                 | 68.5    | 2.8       |
|                               | 0.5                        | 56.0               | 3.90                 | 73.0    | 2.8       |
|                               | 1.0                        | 58.6               | 4.10                 | 83.0    | 2.9       |
| 85 / 10 / 5 / 0               | Blank                      | 48.2               | 3.30                 | 54.0    | 2.4       |
|                               | 0.2                        | 53.0               | 3.70                 | 64.5    | 2.7       |
|                               | 0.3                        | 55.4               | 3.80                 | 69.0    | 2.8       |
|                               | 0.5                        | 58.0               | 4.00                 | 74.0    | 2.9       |
|                               | 1.0                        | 60.2               | 4.16                 | 84.0    | 3.0       |
| 85 / 5 / 10 / 0               | Blank                      | 48.2               | 3.30                 | 54.0    | 2.4       |
|                               | 0.2                        | 54.0               | 3.80                 | 66.0    | 2.8       |
|                               | 0.3                        | 56.0               | 4.08                 | 70.0    | 2.9       |
|                               | 0.5                        | 59.1               | 4.29                 | 76.5    | 3.0       |
|                               | 1.0                        | 61.1               | 4.43                 | 86.0    | 3.2       |
| 85/5/ 5 / 5                   | Blank                      | 48.2               | 3.30                 | 54.0    | 2.4       |
|                               | 0.2                        | 53.4               | 3.72                 | 64.3    | 2.6       |
|                               | 0.3                        | 55.2               | 3.88                 | 68.5    | 2.8       |
|                               | 0.5                        | 57.5               | 4.05                 | 73.0    | 2.9       |
|                               | 1.0                        | 59.5               | 4.14                 | 82.0    | 3.0       |
| 80/5/ 5 / 10                  | Blank                      | 48.2               | 3.30                 | 54.0    | 2.4       |
|                               | 0.2                        | 53.6               | 3.78                 | 65.3    | 2.7       |
|                               | 0.3                        | 56.0               | 3.98                 | 69.5    | 2.8       |
|                               | 0.5                        | 58.5               | 4.10                 | 74.5    | 2.9       |
|                               | 1.0                        | 60.5               | 4.24                 | 84.5    | 3.0       |

Table : 3

**Effect of acrylamide, Acrylic acid and Methyl methacrylate and DADMAC copolymer on tensile strength and bursting strength of paper**  
**Influence of copolymer addition on tensile and bursting strength**

| Copolymer composition moles %           | Copolymer Addition % (w/w) | Tensile Index |                | Burst Index    |                |
|---|----------------------------|---------------|----------------|----------------|----------------|
|   |                            | Value Nm/g    | Improve ment % | Value Kpam2/ g | Improv ement % |
| AA / AAc / MMA / DADMAC 85 / 15 / 0 / 0 | Blank                      | 48.2          |                | 3.30           |                |
|   | 0.2                        | 52.5          | 8.9            | 3.66           | 10.9           |
|   | 0.3                        | 54.6          | 13.2           | 3.78           | 12.7           |
|   | 0.5                        | 56.0          | 16.2           | 3.90           | 15.4           |
|   | 1.0                        | 58.6          | 21.6           | 4.10           | 24.2           |
| 85 / 10 / 5 / 0                         | Blank                      | 48.2          |                | 3.30           |                |
|   | 0.2                        | 53.0          | 10.0           | 3.70           | 12.1           |
|   | 0.3                        | 55.4          | 14.9           | 3.80           | 15.2           |
|   | 0.5                        | 58.0          | 20.3           | 4.00           | 21.2           |
|   | 1.0                        | 60.2          | 25.0           | 4.16           | 26.1           |
| 85 / 5 / 10 / 0                         | Blank                      | 48.2          |                | 3.30           |                |
|   | 0.2                        | 54.0          | 12.0           | 3.80           | 15.2           |
|   | 0.3                        | 56.0          | 16.2           | 4.08           | 23.6           |
|   | 0.5                        | 59.1          | 22.6           | 4.29           | 30.0           |
|   | 1.0                        | 61.1          | 26.8           | 4.43           | 34.2           |
| 85/5/ 5 / 5                             | Blank                      | 48.2          |                | 3.30           |                |
|   | 0.2                        | 53.4          | 10.8           | 3.72           | 12.7           |
|   | 0.3                        | 55.2          | 14.5           | 3.88           | 17.6           |
|   | 0.5                        | 57.5          | 19.3           | 4.05           | 22.7           |
|   | 1.0                        | 59.5          | 23.4           | 4.14           | 25.5           |
| 80/5/ 5 / 10                            | Blank                      | 48.2          |                | 3.30           |                |
|   | 0.2                        | 53.6          | 11.2           | 3.78           | 14.5           |
|   | 0.3                        | 56.0          | 16.2           | 3.98           | 20.6           |
|   | 0.5                        | 58.5          | 21.4           | 4.10           | 24.2           |
|   | 1.0                        | 60.5          | 25.5           | 4.24           | 28.5           |

Table : 4

**Effect of 0.5 % addition of different composition of acrylamide, Methyl methacrylate and acrylic acid copolymer on paper strength**  
**Improvement of strength properties with copolymer over the blank.**

| Copolymer composition moles %           | Copolymer Addition % (w/w) | Tensile Index % | Burst Index % | TEA % | Stretch % |
|---|----------------------------|-----------------|---------------|-------|-----------|
| AA / AAc / MMA / DADMAC 85 / 15 / 0 / 0 | 0.5                        | 16.2            | 15.4          | 35.2  | 16.7      |
| 85 / 10 / 5 / 0                         | 0.5                        | 20.3            | 21.2          | 37.0  | 20.8      |
| 85 / 5 / 10 / 0                         | 0.5                        | 22.6            | 28.7          | 41.7  | 25.0      |
| 85/5/ 5 / 5                             | 0.5                        | 19.3            | 22.7          | 35.2  | 20.8      |
| 80/5/ 5 / 10                            | 0.5                        | 21.4            | 24.2          | 38.0  | 20.8      |
| Commercial Dry strength resin – A       | 0.5                        | 12.5            | 13.3          | 28.3  | 8.6       |
| Commercial Dry strength resin – B       | 0.5                        | 15.8            | 15.6          | 31.0  | 12.3      |
| Commercial Dry strength resin – C       | 0.5                        | 14.6            | 14.4          | 32.0  | 15.5      |

**Copolymer of Acrylamide, Acrylic acid and Methyl methacrylate**

This is the anionic polymer consisting of amide and acrylic group. Polyacrylamide is non-ionic, which contains water soluble fraction of primary amide groups and a few carboxyl groups. It is believed to be located at the end of short branches originating at secondary amide linkages in the main chain. The amide group, which has a carbonyl double bond, is one of two reactive centers of acrylamide. In acrylamide, the amide functionality provides cross-linking sites, and even the binders are self-crossing linkable which gives the capacity to increase inter-fibre bonding.

**Copolymer of Acrylamide, acrylic acid, methyl methacrylate and DADMAC.**

This is the amphoteric copolymer consisting of amide, acrylic group and cationic monomer of DADMAC. In this copolymer, the percentage of

acrylamide monomer was fixed as 85-mole %, while the remaining 15% was adjusted with one anionic monomer Acrylic acid, methyl methacrylate and a cationic monomer namely DADMAC. In water-soluble polymers, polymeric quaternary ammonium compounds have been the most important and extensively used as cationic polyelectrolyte. Poly (DADMAC) possesses a backbone of cyclic units resulting from cyclopolymerization. Additionally, the highly hydrophilic permanently charged quaternary ammonium groups provide the polymer with high water solubility and solution property. Hence in this system DADMAC was introduced along with acrylic acid in acrylamide backbone by varying, more ratios of acrylic group and DADMAC.

### **Viscosity and Concentration**

Viscosity is a measure of resistance to flow of a liquid and it is directly related to the concentration, charge density and molecular weight of copolymers. The structure of the polymer chain too has an effect on the viscosity of polymers. The preparative conditions and properties like viscosity and total solids of acrylamide-co-acrylic acid and acrylamide, MMA and DADMAC copolymer at different ratios of monomers are given in Table. The above results suggest that the viscosity is increased with increase in percentage of Acrylic acid and with decrease in acrylamide, in the copolymer. Perusal of results reveals that the higher viscosity observed with higher percentage of acrylic acid, which clearly demonstrates the higher hydrogen bonding capacity of carboxylic acid groups of acrylic acid. Introducing DADMAC into the copolymer reduces the viscosity.

### **Tensile and Bursting strength**

The improvement of tensile index and burst index at 0.5% addition of different composition of acrylamide with MMA copolymers were compared (Table-2). From the perusal of this data, it is clear that the increase of MMA content in the polymer results in better strength development. This strength increase is to be attributed to the better absorption of acrylate group on cellulose and the better ability of acrylate to form hydrogen bonding leading to higher inter-fibre bonding.

The improvement of tensile index and burst index at 0.5% addition of different composition of acrylamide and MMA copolymers were compared (Table-3).

Here, the tensile and burst improvement was slightly on the higher side over the earlier system at same level addition. The strength development with these co-polymers are better when compared to that of commercial dry strength resin.

### **Tensile energy absorption and Stretch**

Tensile energy absorption (TEA) represents the amount of energy absorbed per unit mass of paper during stretching until the onset of rupture in a tensile test. The TEA depends on the tensile index, the stretch at break. Paper with high extensibility and high TEA can absorb and withstand heavy impact without breaking. The results indicate that TEA and stretch improvement was similar to tensile and burst improvement with polymer treated papers. In each composition, the TEA improvement is proportional to polymer addition like tensile and bursting strength improvement. The results indicate that there is no improvement in stretch with less polymer addition and the slight improvement was observed with increasing the polymer when compared to TEA improvement. The same trend has observed with acrylamide, MMA and DADMAC system.

### **Polymeric Enhancement Of Inter-Fiber Bonding**

Two concepts continue to be important when water-soluble polymer additives are used to enhance Inter-fiber bonding, beyond what can be achieved by forming paper from the untreated fibers. The first concept, as already noted, is that there is reason to believe that inter-fiber contact is likely to be inefficient, especially if papermakers are under constraints that limit the degree of refining of the fibers. The second notion is that events taking place on a scale of nanometers during drying are likely to play a huge role in the development of paper strength, with or without polymer additives.

For improving dry strength, the polymer promotes better inter-fibre bonding by acting as an effective bridging compound. The results show that the improvement of tensile properties of paper indicating the absorption of polymer contributes to the inter-fibre bonding. The tensile and burst continued to increase when polymer concentration was increased. The deposition of polymer on the fiber takes place through the absorption of the polymer with an oppositely charge

in the system. It is also favorable to deposit the dry strength agent on the outer surfaces of the fiber wall because the low molecular fraction will be re-distributed during the adsorption and penetrate into pores of the fiber where its use from a fiber bonding). The reinforcement of bonds between the fibers implies those bonds of a physico-chemical nature, ie primary hydrogen bonds or covalent bonds. Bonds of covalent nature are usually not broken in contact with water, but contribute to the strength of the paper after wetting. If the reinforcing bonds are of the hydrogen bond type, the acetal type or hydrolysable type is obtained, which decreases as a function of wetting. Hence the cross-links of a covalent nature mainly inhibit swelling and water sorption and there by preserve the original hydrogen bonds.

The hydrogen bonds, which give the paper its strength in the dry state, are broken down during wetting. If polar groups are introduced in to the paper, the inter-fiber attraction can be introduced. These forces of attraction can be either ionic or of the hydrogen bond in nature. This investigation has demonstrated that the attachment of copolymer onto cellulose fibers can yield substantial strength increases in paper. The principal action of a dry strength resin is to enhance fiber bonding. This may do either by consolidating the sheet or enhancing the specific bond strength. The result presented indicates that this copolymer is enhancing the bonded area and inter-fiber bonding.

### **Effect of amide group on strength**

The better inter-fibre bonding due to the polyacrylamide is because the carbonyl oxygen is involved in intermolecular hydrogen bonding. In this case as compared to hydrogen bonds between the two-hydroxyl groups of the adjacent cellulose chains. This is because the carbonyl is known dipole and it is polarized with a higher negative charge on the carbonyl carbon.

### **Effect of carboxylic group on strength**

During pulping process the end-CH<sub>2</sub> OH group in the carbohydrate moieties is oxidized to COOH group and gets ionized to carboxylate ion (COO<sup>-</sup>), and the extent of dissociation depends on pH. The carboxyl groups present as functional groups in chemical pulp fibres play significant roles in paper

making. Some of the carboxyl groups originate from sacharannic acids forming part of hemicellulose present in native wood, and others are introduced into bleached kraft pulps by oxidative reactions during chemical pulping and bleaching processes especially hypochlorite bleaching. These carboxyl groups in pulp are the principal reaction sites of various wet end additives in pulp suspensions. Furthermore, carboxyl groups in pulps have an affect on their flexibility and swelling ability in water, the extent of inter-fibre bonding during pressing and drying processes, and consequently the mechanical properties of dried sheets. Previous studies have shown that multifunctional carboxylic acids have potential to become environmental friendly strength additive.

### Effect of DADMAC on strength

The mechanism of fiber retention by DADMAC is based on inherent negative charge present in the fibers, which keeps them away in the slurry. When DADMAC, which has a cationic charge, is added, the inherent negative charge on the fibers is neutralized and an agglomeration of fines results which gets retention on the fibers. Since these fines also have carbohydrate molecules possessing primary and secondary hydroxyl groups, they can also promote hydrogen bonding between adjacent fibers. The very fact that it promotes dry strength development rather than wet strength development it clearly shows that the steric requirements of hydrogen

bonds are met only when the water and other media are taken out during drying. Hence the combined effect of DADMAC with acrylic copolymers develops better inter-fiber bonding resulting improvement on strength properties.

### Conclusions

In anionic / amphoteric acrylamide copolymers the amide functionality provides cross linking sites and even the binders is self-crosslinkable which gives the capacity to increase inter-fibre bonding. Permanently charged quarternary ammonium groups in acrylamide backbone alongwith and acrylate group which are hydrophilic with higher solubility and solution properties. The tensile and bursting strength improvement of paper is proportional to polymer addition in each composition of copolymer and the increase of MMA content in polymer results better strength development. Increasing DADMAC proportions in acrylamide-acrylate copolymer lowers the viscosity.

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