

# New Acrylamide Copolymer as Dry Strength Additive for Papermaking

P. Marimuthu, \* A. Gopalan and G. Venkoba Rao.,

Tamilnadu Newsprint and Papers Ltd, Kagithapuram, Tamilnadu

\* Dept. of Industrial Chemistry, Alagappa University, Karaikudi, Tamilnadu

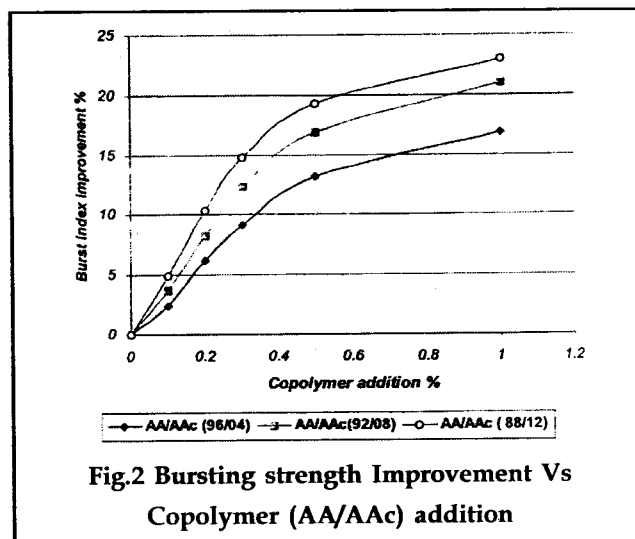
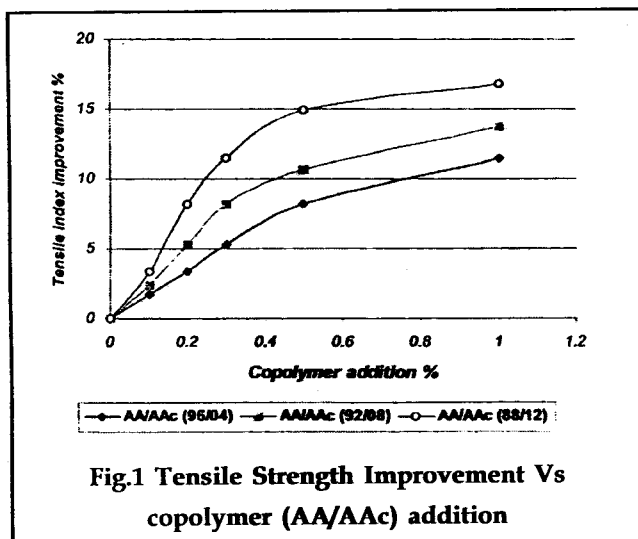
Need for an effective internal dry strength additive for papers that is readily soluble with water and easily compatible with the papermaking fibre is growing fast and open new opportunities of research in this field. Copolymers consisting of (a) acrylamide and acrylic acid, (b) Acrylamide, acrylic acid and diallyl dimethyl ammonium chloride monomers were synthesized and applied to wood and bagasse pulp and their strength improvement potential was evaluated in comparison to commercially available dry strength resin. Increasing the acrylic acid in acrylamide backbone gives a dry strength resin imparting better strength to paper. Addition of DADMAC still further enhances the efficiency along with acrylamide and acrylic acid, in addition to reducing the viscosity of the resin. 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

In papermaking process, different chemical additives are utilized to enhance specific sheet properties of paper or to aid in the process of papermaking. The main categories are wet-end additives, surface-treatment additives, and paper-coating additive. 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 additive such as biocides, drainage aides, retention aids,

defoamers etc are added to improve the 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 a 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 cellulosic fibre mat prior to drying to paper,



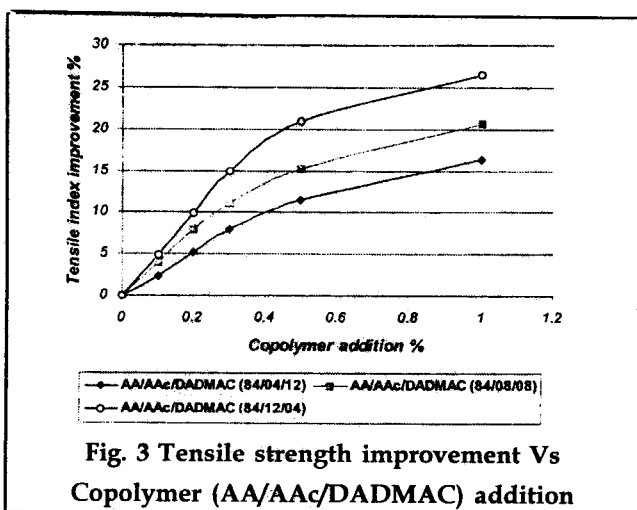


Fig. 3 Tensile strength improvement Vs Copolymer (AA/AAc/DADMAC) addition

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 fibres 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 [2]. 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 [3].

- It should improve dry strength by at least 10 % over the normal dry strength of paper

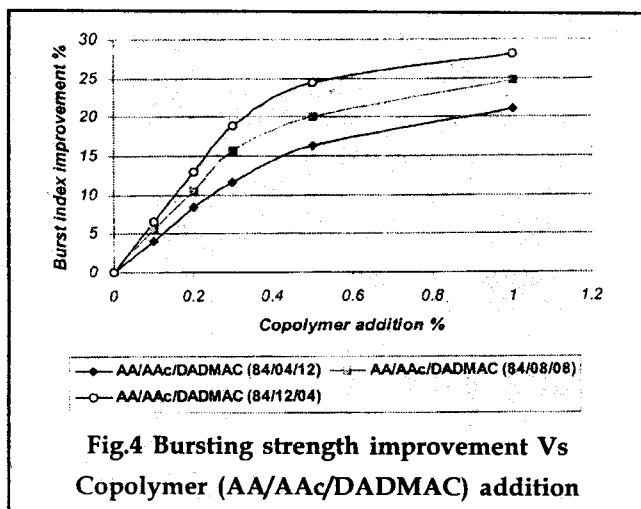


Fig.4 Bursting strength improvement Vs Copolymer (AA/AAc/DADMAC) addition

- 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 [4]. 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 is the dry strength of paper.

The predominant group of dry strength agent is starch derivatives. Starch is a high molecular weight polymer of  $\alpha$ -D glucose units, which shows both similarities and differences from cellulose in its structure [5,6]. Different types of synthetic additives are used as wet end additives in papermaking process to increase the dry strength of paper. 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 [7].

#### Scope of This 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 growing fast and open 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 (AA), acrylic acid (AAc), along with diallyl dimethyl ammonium chloride (DADMAC) monomers were synthesized and applied on paper hand sheets and their strength properties improvements were evaluated.

#### EXPERIMENTAL METHODS

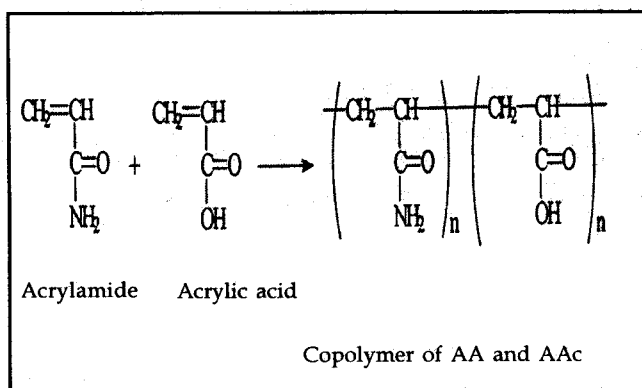
##### Typical synthesis procedure

Copolymers of acrylamide with other said monomers were prepared in solution polymerization through free radical polymerization using redox 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 90 minutes. The reaction mixture (copolymer) was removed from the reactor and analyzed.

### Synthesis of Acrylamide and Acrylic acid copolymer

By changing the monomer composition different copolymers were prepared. The polymerization was carried out through free radical solution polymerization using PDA- TGA redox initiator at 60°C temperature and 90 min reaction time. During polymerization the temperature of the solution got increased to 55 °C from 30 °C, due to exothermic reaction [8]. The scheme of polymerization reaction is outlined below.

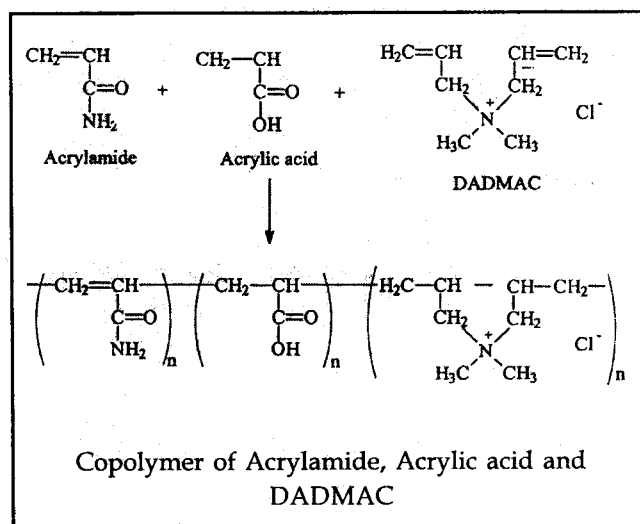


The two-component initiator system consists of an oxidizing and reducing component that forms free radicals on reaction with each other. The initiator can

be added at the same rate throughout the reaction to control the molecular weight of copolymer.

### Synthesis of Acrylamide, Acrylic acid and DAD MAC copolymer

In this copolymer, the percentage of acrylamide monomer was fixed as 88-mole %, with the remaining 12% was adjusted with one anionic monomer acrylic acid and a cationic monomer namely DADMAC. The polymerization was carried out through free radical solution polymerization using PDA- TGA redox initiator at 80°C temperature and 150 min reaction time. The scheme of polymerization reaction is outlined below.



### Viscosity and Total solids measurement

The total solid content was obtained by keeping the copolymer at 70°C in vacuum oven for 4 hrs and on finding the difference in weight total solid content was calculated. Viscosity of the thick product was measured using Brookfield Programmable DV - II + viscometer with LV spindle-2 at room temperature.

**Table- 2 Preparative conditions for the synthesis of copolymer of acrylamide, acrylic acid and DADMAC Percentage solids obtained and viscosity of copolymers**

[PDS/TGA] = 2.0 %: Time = 120 min : Temp = 60°C

Acrylamide Mole %	Acrylic acid Mole %	DAD MAC Mole %	Total solids %	Viscosity at 30 °C-cps
84	4	12	20.8	3400
84	8	8	20.3	6900
84	12	4	20.1	12700

**Table- 3 Molecular weights of copolymer of acrylamide, Acrylic acid and DADMAC**

Polymer	Molecularweight - Daltons	
	Weight average Mw	Number average Mn
Acrylamide / Acrylic acid (96 / 04)	$7.8 \times 10^4$	$3.1 \times 10^4$
Acrylamide / Acrylic acid (92/08)	$8.8 \times 10^4$	$3.7 \times 10^4$
Acrylamide / Acrylic acid (88 / 12)	$1.03 \times 10^5$	$4.1 \times 10^4$
Acrylamide / Acrylic acid / DADMAC (84/04/12)	$1.34 \times 10^5$	$4.0 \times 10^4$
Acrylamide / Acrylic acid / DADMAC (84 / 08 / 08)	$1.31 \times 10^5$	$4.1 \times 10^4$
Acrylamide / Acrylic acid / DADMAC (84/12/04)	$1.32 \times 10^5$	$4.1 \times 10^4$

**Table - 4 Effect of acrylamide and acrylic acid copolymer on tensile strength and bursting strength of paper**

Copolymer Concentration mole ratio AA / AAc	Copolymer Addition % (w/w)	Tensile index		Burst index	
		Value Nm/g	Improvement %	Value Kpa m <sup>2</sup> /g	Improvement %
96 / 04	Blank	41.6		2.43	
	0.1	42.3	1.7	2.49	2.5
	0.2	43.0	3.4	2.58	6.2
	0.3	43.8	5.3	2.65	9.1
	0.5	45.0	8.2	2.75	13.2
	1.0	46.4	11.5	2.84	16.9
92 / 08	0.1	42.6	2.4	2.52	3.7
	0.2	43.8	5.3	2.63	8.2
	0.3	45.0	8.2	2.73	12.3
	0.5	46.0	10.6	2.84	16.9
	1.0	47.3	13.7	2.94	21.0
88 / 12	0.1	43.0	3.4	2.55	4.9
	0.2	45.0	8.2	2.68	10.3
	0.3	46.4	11.5	2.79	14.8
	0.5	47.8	14.9	2.90	19.3
	1.0	48.6	16.8	2.99	23.0

**Table - 5 Effect of acrylamide, acrylic acid and DADMAC copolymer on tensile strength and bursting strength of paper**

Copolymer Concentration Mole ratio AA/AAc/DADMAC	Copolymer Addition % (w/w)	Tensile Index		Burst index	
		Value Nm/g	Improve ment %	Value KPa m <sup>2</sup> /g	Improve ment %
	Blank	44.6		2.75	
84 / 04 / 12	0.1	45.7	2.4	2.86	4.0
	0.2	46.9	5.1	2.98	8.4
	0.3	48.2	8.0	3.07	11.6
	0.5	49.7	11.4	3.20	16.4
	1.0	51.9	16.3	3.33	21.1
84 / 08 / 08	0.1	46.4	4.0	2.90	5.5
	0.2	48.2	8.0	3.04	10.5
	0.3	49.5	11.0	3.18	15.6
	0.5	51.4	15.2	3.30	20.0
	1.0	53.8	20.6	3.43	24.7
84 / 12 / 04	0.1	46.8	4.9	2.91	5.8
	0.2	49.0	9.9	3.11	13.0
	0.3	51.3	15.0	3.29	19.6
	0.5	54.0	21.0	3.47	26.2
	1.0	56.4	26.5	3.58	30.2

#### Purification of copolymer

Known quantity of copolymer from the reactor was poured in a beaker containing acetone for recrystallization. The crystallized polymer was removed and dried in vacuum oven at 70°C overnight and dissolved in water for further characterization and applications.

#### Molecular weight determination

The molecular weights, Number average (Mn) and Weight average (Mw) of the purified copolymers were determined using Shimadzu R-7 A (data module: LC-10 AD pump) gel permeation chromatograph. Two linear columns in series were used for separation. The flow rate for DMA was 2 µl min<sup>-1</sup> at 40°C using polystyrene as standard.

#### 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. To make the hand sheet bleached Kraft hard wood pulp

and bleached Kraft chemical bagasse pulp were mixed in the ratio 50 : 50 on weight basis. From this mixture 30 gm pulp was taken and diluted to 1.5% (w/v) consistency. This pulp slurry was disintegrated in a standard disintegrator for thorough mixing first with 1 % rosin. Then calculated amount of polymer solution was added based on pulp weight, and it was mixed with the pulp by disintegration. Finally 3% alum was added and mixed thoroughly. This pulp slurry was diluted and 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

##### Copolymer of Acrylamide and Acrylic acid

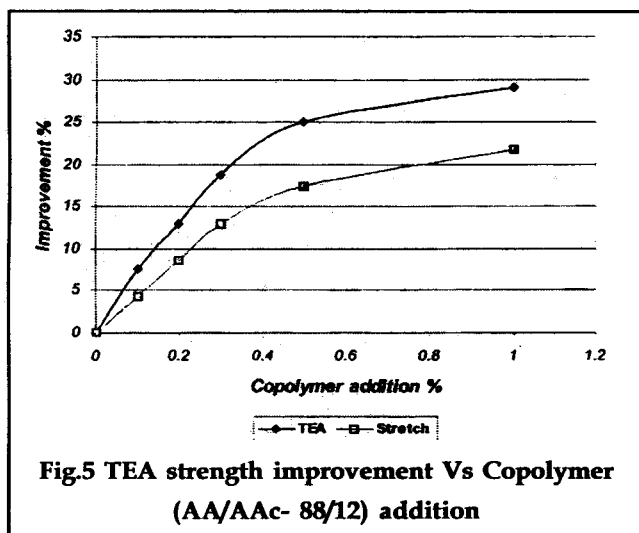
Polyacrylamide is non-ionic, which contains water-soluble fraction of primary amide groups and a few

**Table - 6 Effect of acrylamide and acrylic acid copolymer on tensile energy absorption and stretch of paper**

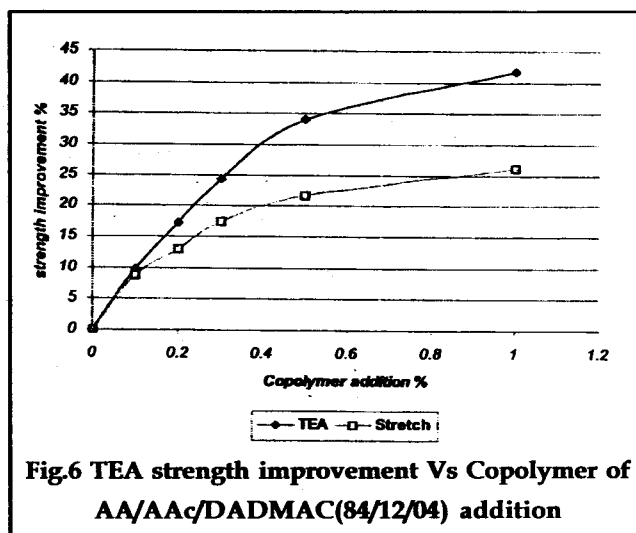
Copolymer Concentration mole ratio AA/AAc	Copolymer Addition % (w/w)	Tensile energy adsorption		Stretch	
		Value J/gm	Improvement %	Value %	Improvement %
96 / 04	Blank	46.0		2.3	
	0.1	48.0	4.3	2.4	4.3
	0.2	50.0	8.7	2.5	8.7
	0.3	52.0	13.0	2.6	13.0
	0.5	56.0	21.7	2.7	17.4
	1.0	60.0	30.4	2.8	21.7
92 / 08	0.1	49.0	6.5	2.4	4.3
	0.2	51.0	10.9	2.5	8.7
	0.3	54.0	17.4	2.6	13.0
	0.5	58.0	26.1	2.8	21.7
	1.0	61.0	32.6	2.9	26.1
88 / 12	0.1	49.5	7.6	2.4	4.3
	0.2	52.0	13.0	2.5	8.7
	0.3	54.6	18.7	2.6	13.0
	0.5	57.5	25.0	2.8	21.7
	1.0	59.4	29.1	3.0	30.4

**Table - 7 Effect of acrylamide, acrylic acid and DADMAC copolymer on tensile energy absorption and stretch of paper**

Copolymer Concentration Mole ratio AA / AAc / DADMAC	Copolymer Addition % (w/w)	Tensile energy adsorption		Stretch	
		Value J/gm	Improvement %	Value %	Improvement %
84/ 04 / 12	Blank	51.5		2.3	
	0.1	54.0	4.9	2.4	4.3
	0.2	56.5	9.7	2.5	8.7
	0.3	60.0	16.5	2.7	17.4
	0.5	64.0	24.3	2.8	21.7
	1.0	69.0	34.0	2.9	26.1
84 / 08 / 08	0.1	55.0	6.8	2.4	4.3
	0.2	58.0	12.6	2.5	8.7
	0.3	62.0	20.4	2.7	17.4
	0.5	68.0	32.0	2.8	21.7
	1.0	71.0	37.9	2.9	26.1
84 / 12 / 04	0.1	56.5	9.7	2.5	8.7
	0.2	60.4	17.3	2.6	13.0
	0.3	64.0	24.3	2.7	17.4
	0.5	69.0	34.0	2.8	21.7
	1.0	73.0	41.7	2.9	26.1



**Fig.5 TEA strength improvement Vs Copolymer (AA/AAc- 88/12) addition**



**Fig.6 TEA strength improvement Vs Copolymer of AA/AAc/DADMAC(84/12/04) addition**

carboxyl groups. It is believed to be located at the end of short branches originating at secondary amide linkages in the main chain [8]. 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-crosslinkable which gives the capacity to increase inter-fibre bonding [9]. The anionic copolymer of acrylamide with acrylic acid were prepared and used as additive and its impact on paper strength was evaluated.

**Copolymer of Acrylamide, Acrylic acid and DADMAC.**

In this copolymer, the percentage of acrylamide monomer was fixed as 88-mole %, with the remaining 12% was adjusted with one anionic monomer acrylic acid 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 [10]. Additionally, the highly hydrophilic permanently charged quaternary ammonium groups provide the polymer with high water solubility and solution property [11]. Hence in this system DADMAC was introduced along with acrylic acid in acrylamide backbone by varying mole ratio of

**Table - 8 Improvement of tensile strength and bursting strength of paper by the commercial dry strength resin**

Dry strength resin	Resin Addition % (w/w)	Tensile index		Burst index	
		Value Nm/g	Improvement	Value Kpa m <sup>2</sup> /g	Improvement %
<b>Commercial dry strength resin</b>					
	Blank	47.3		3.06	
	0.1	49.0	3.6	3.20	4.6
	0.2	51.3	8.5	3.38	10.5
	0.3	53.3	12.7	3.57	16.7
	0.5	55.8	18.0	3.74	22.2
	1.0	58.0	23.0	3.90	27.5

**Table - 9 Improvement of tensile energy absorption and stretch of paper by the commercial dry strength resin**

Dry strength resin	Resin Addition % (w/w)	Tensile energy adsorption		Stretch	
		Value J/gm	Improvement %	Value %	Improvement %
Commercial dry strength resin					
	Blank	61.0		2.4	
	0.1	66.0	8.2	2.4	0.0
	0.2	70.2	15.0	2.5	4.2
	0.3	73.4	20.3	2.6	8.3
	0.5	77.4	26.9	2.7	12.5
	1.0	80.8	32.5	2.8	16.7

acrylic acid 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, acrylic acid & DADMAC copolymer at different ratios of monomers are given in Table 1&2. 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.

### Molecular weight

Molecular weight is a primary indication of polymerization. In the case of linear homopolymers, molecular weight is proportional to the chain length. The mechanical properties of most of the polymers are dependent on their molecular weight. The polymer molecules need to be long enough to provide good adsorption and have enough sites for hydrogen bonding. The molecular weight of 7 improvement of paper is proportional to the copolymer addition in each composition of polymer. This proves that when polymer proportion increases in the pulp slurry, the strength of

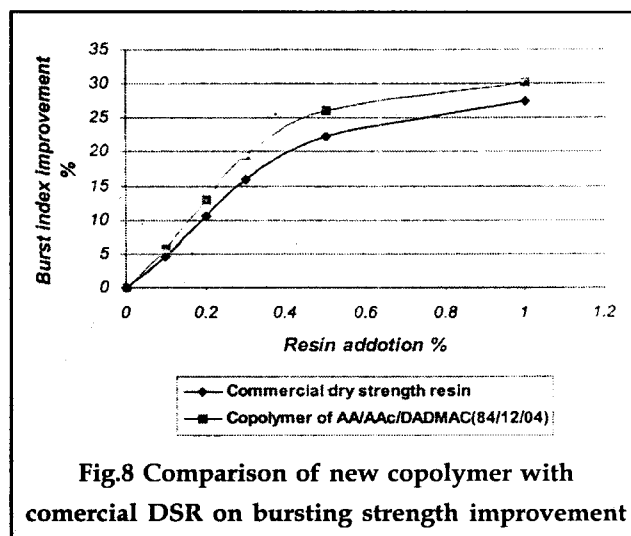
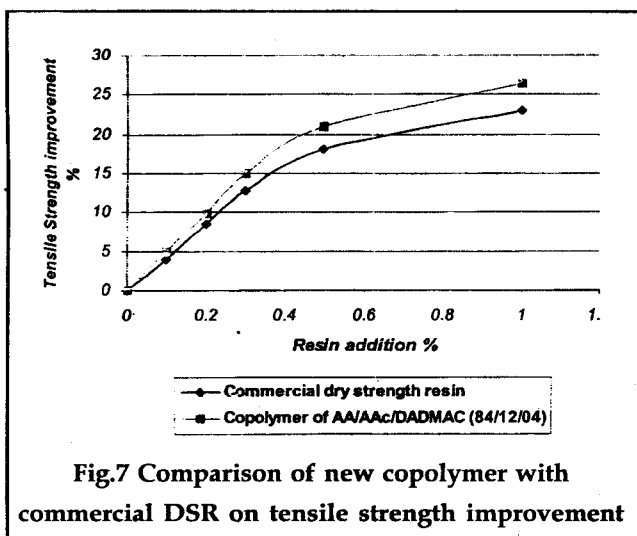
paper increases as the polymer increases to have the maximum possible inter-fibre bonding.

The improvement of tensile index and burst index at 0.5% addition of different composition of acrylamide and acrylic acid copolymers AA/AAC (96/4), AA/AAC (92/8) and AA/AAC(88/12) were compared. From the perusal of this data, it is clear that the increase of acrylic acid content in the polymer results in better strength development. This strength increase is to be attributed to the better absorption of acrylic acid copolymer on cellulose and the better ability of acrylic acid to form hydrogen bonding leading to higher inter-fibre bonding. In case of acrylamide, acrylic acid and DADMAC copolymers, the tensile and burst improvement was slightly on the higher side over the earlier system at same level addition. This higher strength improvement is due to presence of DADMAC in the system

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. In earlier studies, Tatsumi [13] reported that the polyacrylamide concentration is found more at quite high level on fibre surface. This points out that the possibility of polyacrylamide polymers forms some sort of adhesion on the surface of fibre, which promotes better inter-fibre bonding between adjacent fibres.

### 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, stiffness and 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, acrylic acid and DADMAC system.

#### 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 papermaking [14]. Some of the carboxyl groups originate from saccharinic 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 [15-17]. 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 [18, 19]. Previous studies have shown that multifunctional carboxylic acids have potential to become environmental friendly strength additive [20].

#### Effect of DADMAC on strength

In papermaking process, the hydrophilic nature of cellulose plays an important part. In cellulose, the individual polymer chains can bring together by extensive hydrogen bonding with adjacent polymer chains. From this system we can conclude that, introduction of DADMAC monomers has not shown appreciable strength-improvement. The slight improvement may be due to the effect of retention of fines due to DADMAC addition. The mechanism of fibre retention by DADMAC is based to inherent negative charge present in the fibres, which keeps them away in the slurry. When DADMAC, which has a

cationic charge, is added, the inherent negative charge on the fibres is neutralized and an agglomeration of fines results which gets retention on the fibres. Since these fines also have carbohydrate molecules pressing primary and secondary hydroxyl groups, they can also promote hydrogen bonding between adjacent.

## CONCLUSIONS

1. In anionic 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.
2. Higher viscosity is observed with higher percentage of acrylic acid in copolymer due to higher hydrogen bonding capacity of carboxylic acid groups of acrylic acid.
3. Permanently charged quarternary ammonium groups in acrylamide backbone alongwith and acrylic acid which are hydrophilic with higher solubility and solution properties.
4. The molecular weight of copolymers increases as the percentage of acrylic acid increases in the feed monomer.
5. The tensile and bursting strength improvement of paper is proportional to polymer addition in each composition of copolymer and the increase of acrylic acid content in polymer results better strength development. Increasing DADMAC proportions in acrylamide-acrylic copolymer lowers the viscosity.
6. The presence of DADMAC alongwith acrylamide and acrylic acid, gives better strength improvement over the acrylamide and acrylic acid copolymer.
7. This new copolymer developed shows better improvement in strength over the commercial Dry strength resin.

## ACKNOWLEDGEMENT

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