

# On the mechanism behind wet strength development in papers containing wet strength resins

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**SUMMARY:** The improvement in strength when a polyamide-amine epichlorohydrine (PAE) polymer is added to a number of carboxymethylated pulps has been investigated in order to see whether or not there is a reaction between the PAE polymer and the carboxyl groups on the fibres. Study of a series of carboxymethylated pulps showed that the carboxyl group content increases the fibres' adsorption capacity of wet strength resins. This is important to reach high levels of wet strength. The resin is however able to improve the dry strength only for weak sheets which are bond limited. An increase in the carboxyl group content also increases the swelling and hence the totally bonded area in the sheet. The carboxyl groups may also react with the wet strength resins.

Sheets were prepared with different densities from a carboxymethylated pulp and a reference pulp, with and without 4 kg/t PAE. To enable the effects of increased bond strength and increased bonded area on the sheet strength to be separated. The shear bond strength between the fibres was then calculated by the approach suggested by Page (1969). The increase in shear bond strength is much higher for the carboxymethylated pulp than for the non-carboxymethylated pulp, which indicates that there is a reaction between the carboxyl groups on the fibres and the added wet strength resin.

The last part of the work involved a FTIR investigation of sheets from a carboxymethylated pulp (D.S.= 0.06) with and without the addition of PAE. The difference spectrum between these different sheets clearly show the existence of a saturated ester in the cured sheets containing the wet strength resin. An investigation of the PAE polymer itself showed no such saturated ester.

In summary it can hence be stated that a higher concentration of carboxyl groups on the fibre surface will increase the adsorption of PAE molecules and hence the wet strength. Furthermore, the results show that an increase in the number of carboxyl groups will increase the shear bond strength between the fibres at a constant addition of PAE. The FTIR investigation also showed that an ester linkage is formed between the wet strength resin and, most probably, the carboxyl groups on the fibre surface.

No attempt has been made to rank the importance of these different factors, but this should be possible in future investigations with the techniques used in the present work.

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The chemistry of the different wet strength additives has been thoroughly reviewed (Westfelt 1979; TAPPI Monograph 1965; Neal 1988; Dunlop-Jones 1991). Since the introduction of these different chemicals, the real mechanism behind the wet strength improvement has been discussed and it is difficult to find any unified view on the mechanism for the different chemicals. Today it is generally believed (Neal 1988; Dunlop-Jones 1991) that urea formaldehyde (UF) and melamin formaldehyde (MF) resins mainly impart wet strength through an internal

crosslinking in the resin itself. There are, however, some indirect evidence that the MF-resins can react with cellulosic model compounds (Bates 1966). For the polyamideamine epichlorohydrine (PAE) polymer resins it was first shown (Bates 1962) that there was no chemical reaction between the resin and films of methyl-β-D-glucoside, used as a model substance for cellulose. It was therefore concluded that this kind of resin did not react with cellulosic fibres. Later work (Espy 1988) has however shown that the azetidinium ring of the PAE resins may form an ester linkage with carboxyl groups on the fibres. This result has also been used to explain (Stratton 1989, Neal 1988) the common use of carboxymethylcellulose (CMC) together with PAE types of resins to increase the wet strength of different papers.

The formation of the ester linkage was however only indirectly shown (Espy 1988) and the importance of the concentration of the carboxyl groups on the fibres was not investigated. This naturally leads to doubt regarding the existence of the ester linkage. The purpose of the present investigation was therefore to seek direct evidence for the suggested existence of an ester linkage between PAE resins and cellulosic fibres and to investigate the influence of the concentration of carboxyl groups on the fibres.

## Determination of bond strength

A series of carboxymethylated pulps were prepared and treated with a wet strength resin, and the reaction between the two components was investigated both by spectroscopic methods, described in the experimental section, and by estimating the increase in bond strength between the differently substituted fibres as a result of the introduction of the wet strength resins.

The bond strength was evaluated by the method introduced by Page (1969) and later used by several workers (Howard 1989; Gaspar 1983; Stratton 1991). The relatively bonded area (RBA) of the sheets is altered by the use of different pressures during the wet pressing of the sheets. The shear bond strength between the fibres,  $b$ , can be evaluated from the slope of the line obtained when  $1/T$  is plotted as a function of  $1/RBA$  according to the following equation (Page 1969):

$$1/T = 9/(8Z) + 12C/(P \cdot L \cdot b \cdot RBA) \quad [1]$$

where  $T$  = Tensile strength of the sheet (kNm/kg)  
 $Z$  = Zero span strength (kNm/kg)  
 $C$  = Fibre coarseness (kg/m)  
 $P$  = Fibre perimeter (m)  
 $L$  = Fibre length (m)  
 $b$  = Shear bond strength (kNm<sup>2</sup>)  
RBA = Relatively Bonded Area

## Experimental

### Methods

**Pulp treatment and carboxymethylation.** The pulp was delivered in dry lap form and was reslashed according to

