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## Synthesis of polymers containing isocyanate groups and use of polymers as paper dry and wet strength additives

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**Abstract** Results of the preparation and characterization of homopolymers of 2-methacryloyloxyethyl isocyanate (MOI) and co-polymers of MOI with styrene synthesized by radical polymerization are shown. The polymers were significantly effective as additives for paper dry and wet strength. Dry strength can be increased by 75% and wet strength retention of sheets can reach 30% based on the increased dry strength and about 50% based on the dry strength of untreated sheet. In terms of sheet wet strength improvement, based on isocyanate group consumption, co-polymers containing less isocyanate obtain a better effect than homopolymers. Furthermore, base paper containing a small amount of polyallylamine hydrochloride was used for polymer treatment and produced more wet strength improvement.

**Key words** 2-Methacryloyloxyethyl isocyanate · Styrene · Reactive polymer · Paper strength additives · Wet strength additives

### Introduction

Paper strength is mainly provided by hydrogen bonding between fibers, which takes place during the drying process. Conversely, when sheet is rewetted the bonding is weakened by water, and most of its strength disappears.<sup>1</sup> To build waterproof crosslinking, certain wet strength additives were selected to treat the sheets.

Two mechanisms can be used to explain wet strength development. One is as called homo-crosslinking, where the wet strength resins react with themselves and form networks of materials that physically entangle with the fibers.

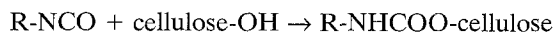
The other mechanism is called co-crosslinking, where the additives react with functional groups of fibers to form covalent bonds that are insensitive to water. Because a polymer has many functional groups, it can react with several fibers to connect fibers. This mechanism can lead to stronger, more permanent wet strength development.

Generally, urea-formaldehyde (UF), melamine formaldehyde (MF), and polyaminoamide-epichlorohydrin (PAE) resins have been widely used since the 1930s and act as a homo-crosslinking mechanism.<sup>2</sup> UF and MF resins require acid papermaking conditions that cause some problems in production. Furthermore, free formaldehyde has an environmental impact. From this point of view, PAE resin increases the absorbable organic halogen (AOX) level of mill effluent, which causes more pressure to make reformations. Polycarboxylic acid has been introduced to cause crosslinking of fibers by esterification and so improve the paper wet strength.<sup>3–5</sup> Because high temperature (>150°C) is required to achieve effective esterification of cellulose,<sup>4</sup> it has been difficult to put this procedure into production until now.

Polymers containing isocyanate groups (NCO) have been used as the crosslinking agent.<sup>6–8</sup> It is known that the polymers are effective as wood adhesive<sup>9</sup> and dental bioadhesive.<sup>10,11</sup> The isocyanate group can react easily with materials containing active hydrogen, such as amino or hydroxyl groups. When water exists, polymers with isocyanate groups can form self-linking at low temperatures.



The isocyanate group can also react with the hydroxyl group of cellulose to cause co-crosslinking.



In this study, homopolymerization of 2-methacryloyloxyethyl isocyanate (MOI) and copolymerizations of MOI with styrene (MOI-ST) at different molar ratios were performed using a radical initiator.<sup>12,13</sup> The polymers were characterized by Fourier transform-infrared spectroscopy (FT-IR), and the isocyanate content

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of polymer was determined. The effectiveness of these polymers as dry and wet paper strength additives was evaluated.

## Experimental

### Materials

The MOI (kindly provided by Showa Denko) was redistilled at reduced pressure prior to use. Styrene was washed several times with a 5% aqueous NaOH to remove the quinol used as an inhibitor. The resulting monomer was washed twice with distilled water and dried over Na<sub>2</sub>SO<sub>4</sub>. Pure monomer was then obtained by distillation under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Tetrahydrofuran (THF) was dried with LiAlH<sub>4</sub> and redistilled. Hexane was redistilled prior to use.

Bleached hardwood pulp was beaten to 400ml Canadian Standard Freeness (CSF). Handsheets were made according to TAPPI standard T205 om-88. Sheets with polyallylamine hydrochloride (PAAm) were similarly made after PAAm had been added at the level of 0.2% to pulp with stirring for 3 min.

### Polymerizations

Homopolymerization of MOI was carried out at room temperature (20°–25°C). The experiment was carried out in such a way as to avoid exposure to air and moisture. THF 100ml and MOI 10g was added to a 125-ml flask. The mixture was purged for 10min with nitrogen gas. Then AIBN (4wt% on MOI) was added to the solution with stirring, and the mixture was allowed to react for 24h.

Co-polymerizations of MOI with styrene were carried out at 50°C under a nitrogen atmosphere. THF 100ml and a total of 10g of monomers were added to the flask. The amount of each monomer varied according to the molar ratios of MOI and styrene as shown in Table 1. AIBN (4wt% on total monomers) was added, and the mixture was kept at 50°C for 18h with stirring.

The intrinsic viscosities of co-polymers (MOI-ST1 and MOI-ST3) measured in THF at 34°C are given in Table 1. When the constants<sup>14</sup>  $k$  ( $15 \times 10^{-3}$ ) and  $\alpha$  (0.694) for polystyrene were tentatively applied for MOI-ST1, the molecular weight was about  $1.2 \times 10^4$ .

Polymers were precipitated by dropping the polymer solutions into a large amount of hexane with stirring. After

sedimentation, the clear mother liquor was decanted off. The polymers were washed by hexane, centrifuged, and dried at room temperature in vacuo.

### Sheet treatment

Handsheets were made at pH 7.5–8.0 and conditioned at 20°C and 65% relative humidity (RH) for more than 24h. Sheet strips cut to 15mm width from hand sheets were dipped for 0.5min in THF solutions that contained homopolymer or co-polymers adjusted to certain concentrations. The soaked strips were taken out and dried in the air for 10min. The strips were cured by heat in an oven at certain temperatures.

### Characterizations

Infrared spectroscopic measurements. Paper samples were ground to a powder to hold uniformity prior to assay. FT-IR spectra in a KBr disk were recorded on Perkin Elmer System 2000 FT-IR spectrometer in transmission intensity mode. Scannings were repeated 50 times for each sample at a resolution of  $4\text{ cm}^{-1}$ .

Assay of isocyanate content. A standard titration procedure was operated on the basis of the reaction of isocyanate with di-*n*-butylamine in THF solution. HCl was used as a titrant to determine extra di-*n*-butylamine. Bromocresol green was an indicator. Isocyanate content was calculated based on the following formulation:  $\text{wt\% NCO} = 4.2N(B - S)/WC$ , where  $N$  is the normality of the HCl titrant;  $B$  is the volume of HCl required for titration of the reagent blank;  $S$  is the volume of HCl required for titration of the sample;  $W$  is the mass of sample assayed; and  $C$  is the polymer concentration of the sample.

Nitrogen content of sheets. The elemental analysis was carried out at the analytical center in Kyushu University.

### Paper wet strength testing

Sheet strips were soaked in deionized water for 1 h and then surface water was removed with filter paper. The tensile strength was tested according to TAPPI standard T494 om-88.

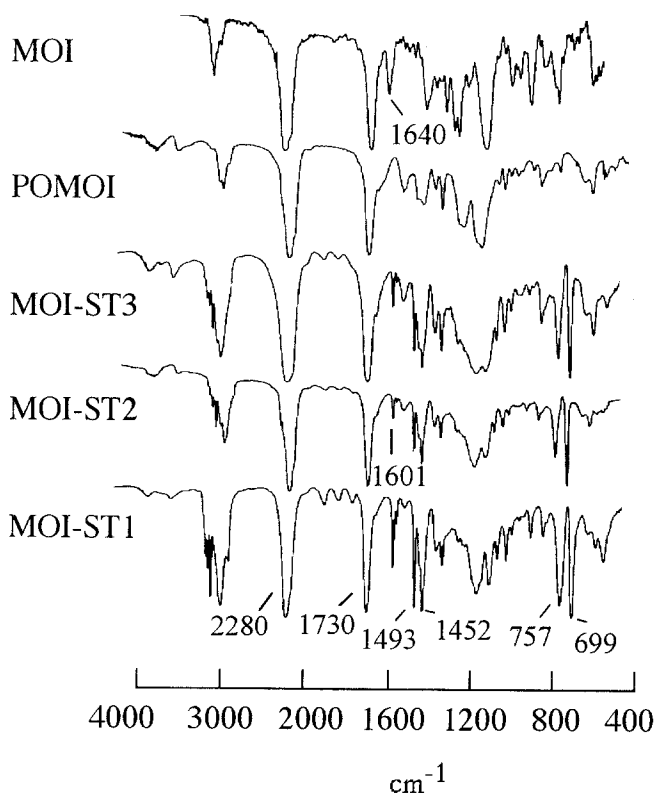
**Table 1.** Polymerization conditions

Code	Name	Molar ratio (MOI/styrene)	Temp. (°C)	Time (h)	Catalyst (AIBN %)	NCO content (wt%)	$[\eta]$ (ml/g)
1	MOI-ST1	1:9	50	18	4	2.5	10.5
2	MOI-ST2	3:7	50	18	4	9.9	–
3	MOI-ST3	5:5	50	18	4	16.1	8.1
4	POMOI	10:0	20–25	24	4	26.8	–

MOI-ST, co-polymer of 2-methacryloxyethyl isocyanate with styrene; POMDI, homopolymer of MOI; NCO, isocyanate groups

## Results and discussion

Parts of polymerization mixtures were dispersed in hexane and gave fine white powders after the centrifuged residue was dried. The infrared spectra of MOI, the homopolymer of MOI, and co-polymers of MOI with styrene are shown in Fig. 1. The vibration of the isocyanate bond and the stretching mode of ester carbonyl appear at  $2280$  and  $1730\text{ cm}^{-1}$ , respectively. The monomer and all the polymers show strong absorbance at these bands. The band at  $1640\text{ cm}^{-1}$  is due to carbon-carbon double bond vibration, which disappears after polymerization. Because isocyanate groups remained intact in the polymers, it can be confirmed that they

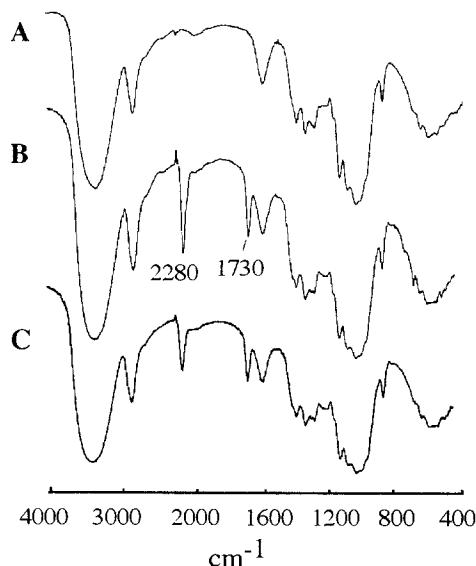


**Fig. 1.** Infrared spectra of 2-methacryloyloxyethyl isocyanate (MOI) and polymers with isocyanate groups

were formed by vinyl polymerizations through a free radical mechanism (Fig. 2). The bands at  $1493$ ,  $1452$ ,  $757$ , and  $699\text{ cm}^{-1}$  are indications of aromatic groups that became stronger when styrene was used as the reactant in large amounts.

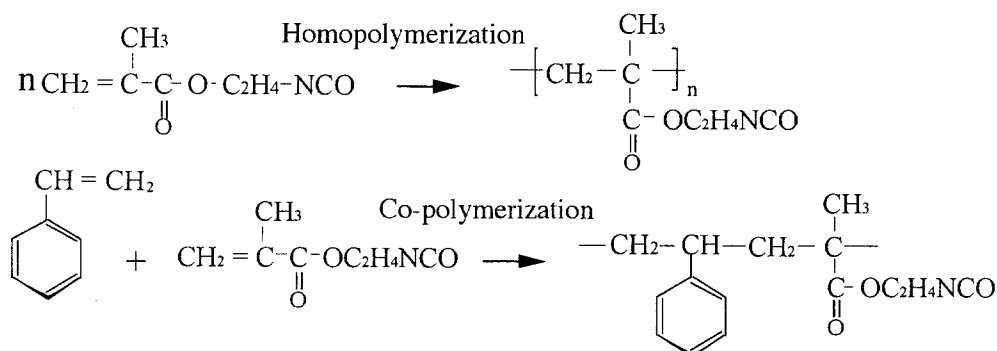
There was an obvious NCO band at  $2280\text{ cm}^{-1}$  in the sheet when MOI-ST3 was added to the handsheet (B in Fig. 3). The absorbance was reduced after heat curing because of the reaction of the NCO groups. The absorbance of isocyanate, however, can be still found in the spectrum of the cured sheet. It indicates that a certain amount of the isocyanate groups remained unreacted even after curing at  $100^\circ\text{C}$  for 10 min. This finding suggests that some isocyanate groups surrounded by adjacent phenyl groups are not highly reactive and continue to enhance the sheet strength on storage.

Nitrogen analyses of sheets were performed for quantitative measurement of the polymer contents. Figure 4 shows the improvement in dry strength and wet strength of the



**Fig. 3.** Infrared spectra of the sheets with or without polymer treating. A, without treatment; B, MOI-ST3 addition before curing; C, after curing of B at  $100^\circ\text{C}$  for 10 min

**Fig. 2.** Vinyl polymerizations of a homopolymer of MOI and co-polymers of MOI with styrene by a radical mechanism



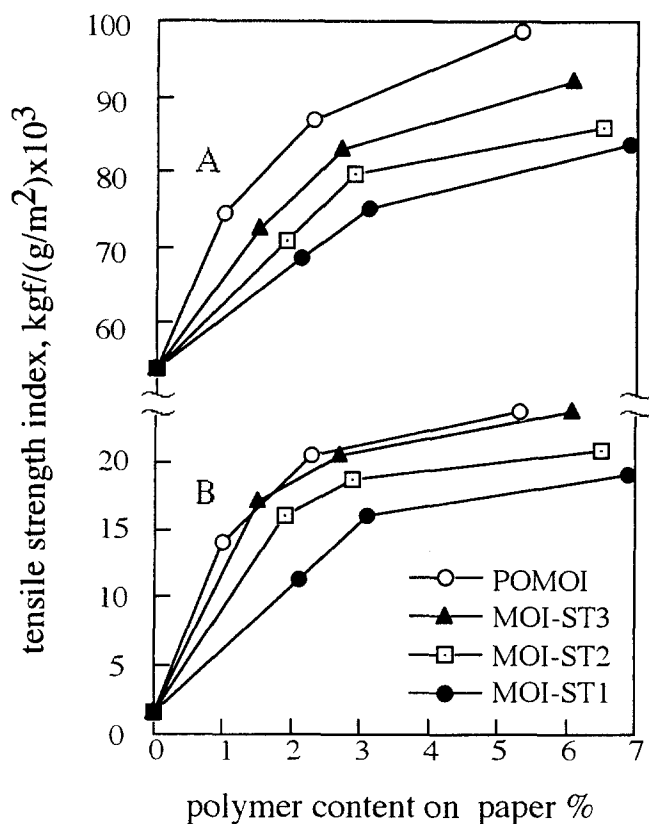


Fig. 4. Effect of polymers containing isocyanate groups on the tensile strength of sheets (cured at 120°C for 10 min). A Dry strength. B Wet strength

hardwood pulp sheets treated by the polymers. The paper strength increased with increasing NCO group in polymers, but the wet strength increases leveled off when the polymer content was higher than 2%. The sheet wet strength was supposed to be developed by self-linking of polymers and ester bonds forming between polymer and cellulose according to the reactions stated above. The wet strength increased with increasing content of MOI in the co-polymer at the same addition level. The homopolymer did not show the high effectiveness expected. It can be presumed that the NCO group is too reactive in the case of the homopolymer. When this group is surrounded by phenyl groups, its stability may be protected from water attack, and it may remain unreactive until curing.<sup>15,16</sup> This can cause more crosslinkings with cellulose and improve the wet strength of the sheet. To prove this hypothesis, 5 ml of the THF solution of POMOI or MOI-ST3 was reacted with 20 ml of water under stirring. After 5 min the amount of NCO groups remaining in the polymer was determined using the usual amine-HCl method noted above. Only about 35% of the isocyanate groups of POMOI remained, whereas about 60% of the isocyanate groups of MOI-ST3 survived. This finding confirms that the co-polymer is more stable in water than the homopolymer. It also suggests that co-polymers containing a small amount of isocyanate (MOI < 10 mol%) can be used to make an emulsion and can be added to the pulp suspension before sheet-making to im-

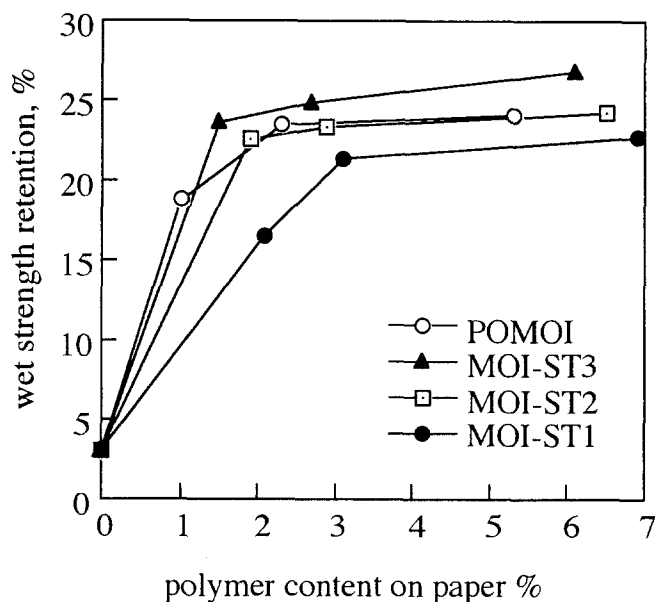


Fig. 5. Effect of polymers containing isocyanate groups on wet strength retention (wet strength/dry strength) (cured at 120°C for 10 min)

prove the sheet strength. Further details of this work are in progress.

The wet strength retention, defined as wet strength/dry strength, was calculated based on Fig. 4 and is shown in Fig. 5. The wet strength retention increased up to about 25% at the addition level of 2% but leveled off thereafter probably because of a significant improvement in dry strength of treated paper.

Considering the possibility of emulsion preparation and chemical cost, polymers with fewer isocyanate groups are preferred in research. The four polymers we have synthesized contain different NCO groups, as shown in Table 1. Because the paper strength increased slowly after the polymer content reached 2% in paper, as described above, the dry and wet strengths of treated sheets with 2% of polymer added were compared to the strength improvement effects of different polymers that contain different amounts of isocyanate (Fig. 6). It was shown that the dry strengths increased quickly with an increase in the MOI component in reactants. In the case of wet strength, there was a steep increase at the initial stage after which, it soon leveled off. This is because of the different stabilities of the polymers and because of the leveling off of the wet strength with an increased amount of isocyanate. Thus the possibility of using polymers that contain fewer NCO groups to achieve effective wet strength improvement is promising.

To increase crosslinking between cellulosic fibers, polyallylamine (PAAm) was applied to sheet-making. The PAAm-added sheets at a level of 0.2% were treated by NCO-containing polymers using the same procedure as for the sheets without PAAm. The dry and wet strengths are shown in Fig. 7. Compared with the results in Fig. 4, the dry strength was minimally increased but the wet strength

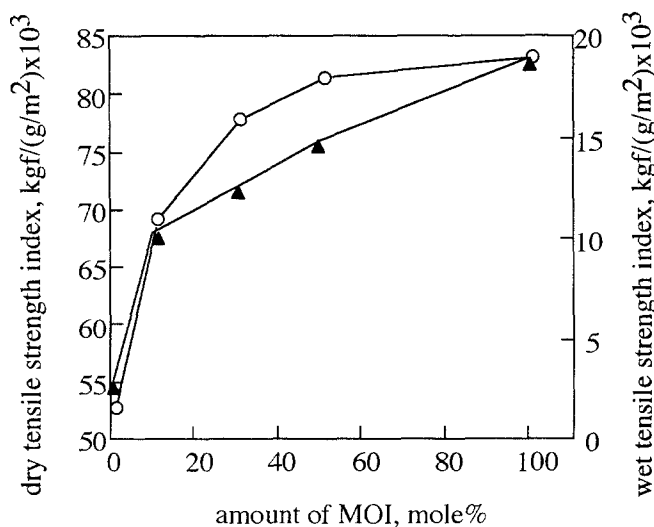


Fig. 6. Relation between MOI percentage in reactants of polymerization and paper strength improvement

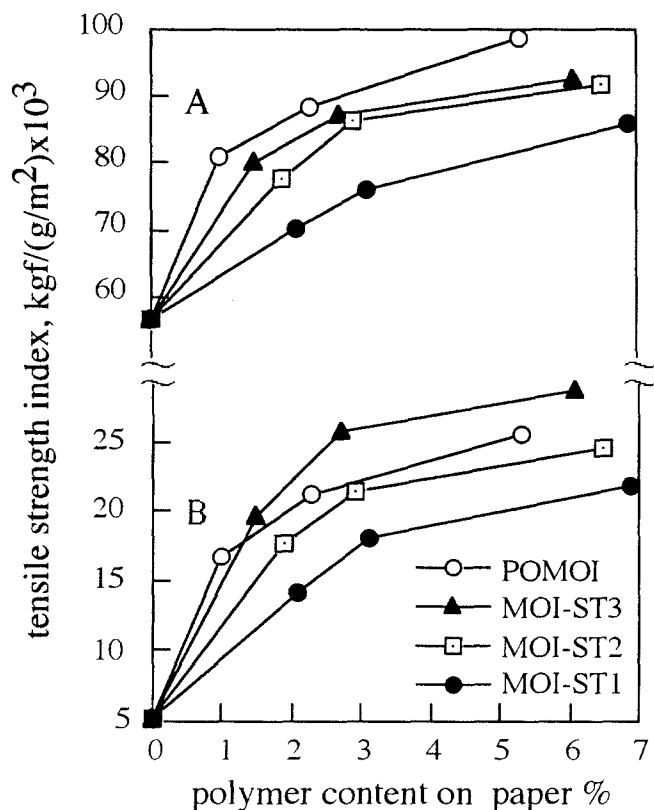


Fig. 7. Effect of polymers containing isocyanate groups on the tensile strength of sheets with 0.2% PAAm (cured at 120°C for 10 min). **A** Dry strength. **B** Wet strength

showed a moderate improvement after PAAm addition (except the homopolymer). As shown in Fig. 8, the wet strength retention of the sheet with MOI-ST3 reached 30%, which corresponds to 50% of the dry strength of the sheet without additives. Because NCO groups reacted easily with  $-NH_2$  groups to increase crosslinkings between cellulosic

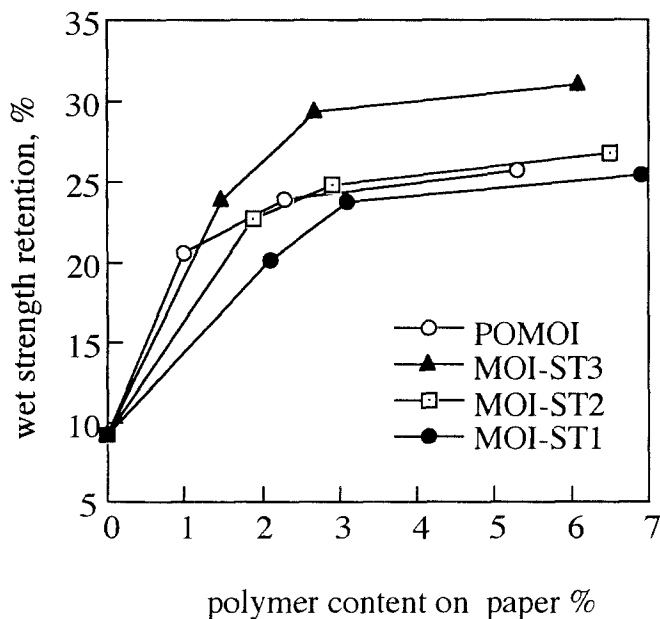


Fig. 8. Effect of polymers containing isocyanate groups on the wet strength retention of sheets with 0.2% PAAm

fibers, the paper was strengthened by forming covalent bonds that were insensitive to water.

## Conclusion

To obtain polymers containing different amounts of isocyanate groups, a homopolymer and co-polymers of MOI with styrene in different molar ratios were prepared and characterized. Polymers containing isocyanate groups significantly improved the paper's dry and wet strengths. The high reactivity of the isocyanate group led to crosslinking between cellulosic fibers that were insensitive to water. Though the homopolymer had more isocyanate groups than the co-polymers, it did not function as well as expected. The experimental results showed that the isocyanate group becomes stable to water attack when it is placed between adjacent phenyl groups, which implies that co-polymers with more styrene components can be used to make an emulsion without significant loss of the isocyanate in the co-polymer backbone. It also shows that the co-polymers that contain fewer isocyanate groups can perform well in improving paper wet strength.

Finally, PAAm was used as a reinforcing agent for isocyanate to make more crosslinking between cellulose fibers. It was highly effective in terms of improving paper strength.

## References

1. Britt KW (1981) Wet strength. In: Caysey JP (ed) Pulp and paper chemical technology, 3rd edn, vol 3. Wiley Interscience, New York, pp 1609-1626

2. Crisp MT (1997) Chemistry of wet strengthening paper: trends, recent developments and applications. In: Proceedings of wet end chemistry conference, May 28–29, pp 87–105
3. Zhou YJ, Luner P, Caluwe P (1995) Mechanism of crosslinking of papers with polyfunctional carboxylic acids. *J Appl Polym Sci* 58:1523–1534
4. Yang CQ, Xu Y, Wang D (1996) FT-IR spectroscopy study of the polycarboxylic acids used for paper wet strength improvement. *Ind Eng Chem Res* 35:4037–4042
5. Yang CQ, Xu Y (1998) Paper wet performance and ester crosslinking of wood pulp cellulose by poly(carboxylic acid)s. *J Appl Polym Sci* 67:649–658
6. Xiao HX, Frisch KC, Kordomenos PI, Ryntz RA (1987) Polyurethane-acrylic coatings: interpenetrating polymer networks. *Polym Mater Sci Eng* 56:546–550
7. Zhong B, Chen D, Zhou Z (1998) Curing behavior of self-crosslinkable polyacrylate coating: TBA and in situ FT-IR studies. *J Appl Polym Sci* 69:1599–1606
8. Xu J, Dimonie VL, Sudol ED, El-Aasser MS (1998) Crosslinking of isocyanate functional acrylic latex with telechelic polybutadiene. II. Film formation/crosslinking. *J Appl Polym Sci* 69:965–993
9. Umemura K, Takahashi A, Kawai S (1998) Durability of isocyanate resin adhesives for wood. I. Thermal properties of isocyanate resin cured with water. *J Wood Sci* 44:204–210
10. Kao FJ, Manivannan G, Sawan SP (1997) UV curable bioadhesives-copolymers of N-vinyl pyrrolidone. *J Biomed Mater Res* 38:192–196
11. Chappelow CC, Byerley TJ, Pinzino CS, Millich F, Eick JD (1996) Design and development of isocyanatoacrylates as dental adhesives. *J Dent Res* 75:761–767
12. Chappelow CC, Pinzino CS, Byerley TJ, Eick JD (1995) Tri-n-butylborane oxide-initiated homopolymerization of vinyl monomers containing cyano or isocyanato groups. *J Appl Polym Sci* 58:1147–1150
13. Brown RG, Glass JE (1986) Ultraviolet spectroscopic determination of copolymer composition in IEM-containing copolymers. *Polym Mater Sci Eng* 54:690–694
14. Kurata M, Tsunashima Y, Iwama M, Kamada K (1974) Viscosity-molecular weight relationships and unperturbed dimensions of linear chain molecules. In: Brandrup J, Immergut EH (eds) *Polymer handbook*, 2nd edn, Wiley-Interscience, New York, p. IV-17
15. Xu J, Dimonie VL, Sudol ED, El-aasser MS (1998) Crosslinking of isocyanate functional acrylic latex with telechelic polybutadiene. I. Synthesis and characterization. *J Appl Polym Sci* 69:965–993
16. Mohammed S, Daniels ES, Klein A, El-aasser MS (1996) Emulsion terpolymerization of dimethyl meta-isopropenyl benzyl isocyanate (TMI<sup>®</sup>) with acrylic monomers: process development and kinetics. *J Appl Polym Sci* 61:911–921