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Approaches to Crosslinking Unique, Water Soluble Polymers Used in Ink Jet Receptive Coatings

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Ink receptive, water soluble polymers are commonly used in ink jet coatings and applications. To render these coatings more resistant to water, crosslinking of these materials is often desirable. Several recent developments in the approach to improved water resistance for some unique, water soluble polymers will be described. Namely, techniques for crosslinking of poly(vinyl pyrrolidone-co-N-[3-(dimethylamino)propyl]methacrylamide) neutralized with sulfuric acid, poly(vinyl caprolactam-co-N-[3-(dimethylamino)propyl] methacrylamide-co-hydroxyethylmethacrylate) neutralized with hydrochloric acid, and poly(2-ethyl-2-oxazoline-co-ethyleneimine) (Aquazol®/PEI). Crosslinking chemistries to be explored will include commercial aziridine, epoxy, and melamine/formaldehyde crosslinking agents. Judicial selection of a crosslinkable polymer can enable insight into polymer architecture via a blended ink jet receptive surface coating. This technique will be explored with hydroxyethyl methacrylate-co-N-[3-(dimethylamino)propyl]methacrylamide neutralized with hydrochloric acid and polyvinyl pyrrolidone (PVP) chemistries.

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Introduction

Of the wide variety of materials employed in ink jet receptive materials, water soluble polymers contribute some of the most important properties to final product performance. Product properties that can benefit from the use of water soluble polymers include film formation, gloss, and fluid management of print ink. Water soluble polymers typically employed include cellulose, gelatin, polyvinyl alcohol (PVOH), polyethylene oxide (PEO), polyethyleneimine (PEI), poly(2-ethyl-2-oxazoline) (Aquazol®), and polyvinyl pyrrolidone (PVP). Many of these materials are excellent glossy, film formers capable of absorbing or displacing the print ink. However, the ability to bind dyes and pigments, resulting in enhanced image resolution and high optical density, is not universal for water soluble polymeric materials.

Currently, an important industry trend for ink jet receptive materials is to deploy these materials into more extreme environments, where exposure to water, UV radiation, and ozone can be severe. As a result, the initially positive print attributes of water soluble polymers need to be properly balanced by the physical requirements of the finished product.

This article will focus on one environmental exposure issue: water resistance. One possible approach to forming water resistive ink jet materials from water soluble polymers is via crosslinking during the process of film formation.[1–3] Such an approach can result in a single composition of crosslinked polymer, a semi-interpenetrating network structure, an interpenetrating network structure, or a myriad of other variations. A single composition of crosslinked material is comprised of only one polymer where the polymer chains are connected in some intermolecular fashion (XL). A semi-interpenetrating network (SPN) is comprised of an entanglement of a linear (or branched) polymer and a crosslinked polymer material. In this case, neither polymeric species is inter-molecularly bonded. An interpenetrating network (IPN) is comprised of two types of entangled crosslinked polymers that are entangled but not chemically bonded together. This article will narrowly focus on crosslink architectures XL and SPN.

Experimental

PVP based materials are available from International Specialty Products (ISP) under the respective trade names ViviPrint™ 530 (PVP K90) and ViviPrint™ 540 (MCPVP). Poly(vinyl pyrrolidone-co-N-[3-(dimethylamino)-propyl]methacrylamide) neutralized with sulfuric acid (PVP/DMAPMA/H_2SO_4), poly(vinyl caprolactam-co-N-[3-(dimethylamino)propyl] methacrylamide-co-hydroxy ethylmethacrylate) neutralized with hydrochloric acid (VCL/DMAPMA/HEMA/HCL), hydroxyethyl methacrylate-co-N-[3-dimethylamino)

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Figure 1. Comparative water submersion test results for uncrosslinked and crosslinked VCL/DMAPMA/HEMA/HCL.

TABLE I. Sample Composition for VCL/DMAPMA/HEMA/HCL Terpolymer and CX-100

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	CX-100 (g)	% Crosslinker
VCL/DMAPMA/HEMA/HCL	20.0	10.0	2.0	0.053	2.6

Note: Crosslinker level for VCL/DMAPMA/HEMA/HCL was not optimized. Percent Crosslinker = CX-100/(CX-100 + VCL/DMAPMA/HEMA/HCL polymer solids)

TABLE II. Gloss for Composition of VCL/DMAPMA/HEMA/HCL Terpolymer and CX-100

Product	Gloss (60°) Uncrosslinked	Gloss (60°) Crosslinked
VCL/DMAPMA/HEMA/HCL	95.7	92.2

propyl]methacrylamide neutralized with hydrochloric acid (HEMA/DMAPMA), materials are available from International Specialty Products (ISP) under their respective trade names, ViviPrint™ 121, ViviPrint™ 200, and ViviPrint™ 300. Aquazol®/PEI was prepared as described elsewhere.[4] Aquazol® is manufactured by Polymer Chemistry Innovations (PCI) and commercially available from ISP. Polyfunctional aziridine CX-100 is available from NeoResins Corporation, Wilmingon, MA. Polyfunctional aziridine XAMA-7 is available from Bayer Corporation, Pittsburgh, PA. Polyfunctional epoxy Heloxy 67 is available from Resolution Performance Products, Houston, TX. The melamine/formaldehyde Berset 2506 is available from Bercen, Cranston, RI. Concentrated, technical grades of phosphoric acid and ammonium hydroxide were obtained from Aldrich, Milwaukee, WI. Distilled water was used when necessary.

To determine the effect of crosslinking, solutions of water soluble polymer were prepared using pseudo-optimal crosslinking levels that were previously determined. These aqueous solutions were cast onto DuPont-Teijin Melanex polyester film. For ~5% solutions, a #48 Meyer rod was employed. For ~10% solutions, a #38 Meyer rod was employed. The film was placed in an ~135°C air oven until dry and allowed to cool for at least 24 hours. The resulting coating weight is approximately 10 gm/m^2. An ink jet test pattern was printed onto the film using the Hewlett-Packard HP 880C, in Premium Photo Paper Glossy Mode (Palo Alto, CA). Gloss was measured at 60° using a BYK micro-TRI-gloss meter (Model 4430; Geretsried, Germany). The printed film was allowed to stand for 24 hours. Portions of the printed film were also subjected to a distilled water submersion test (with agitation). Swatches of crosslinked and uncrosslinked prints are placed side-by-side for visual, comparative purposes. Proposed chemical reaction mechanisms presented in this article are determined spectroscopically from solutions of samples prepared in similar fashion, but with much higher levels of crosslinker. In some cases, model compounds were employed. These particular experimental details are beyond the scope of this article.

Results and Discussion

Polymeric solutions of the polyfunctional aziridine CX-100 and VCL/DMAPMA/HEMA/HCL were prepared as indicated in Table I. These solutions were adjusted to pH~9 using concentrated ammonium hydroxide in order to stabilize the polymer crosslinker solution.

To determine the suitability of this particular crosslinker with the polymer, gloss measurements were performed, reported in Table II.

Results of 15 minute, agitated, water submersion tests are presented in Fig. 1. The neat polymer is a good film former and is very printable. Results demonstrate that this film is very sensitive to water. Upon crosslinking, a dramatic improvement to the film's water resistance is observed. Note that the film is still quite printable.

A representation of a possible crosslinking reaction between the monomeric constituent DMAPMA and aziridine is presented in Fig. 2. The partially free proton, present via neutralization of the polymer with hy-

TABLE III. Sample Composition for Aquazol®-PEI Copolymer and Heloxy 67

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	Heloxy 67 (g)	% Crosslinker
Aquazol®-PEI	20.0	10.0	2.0	0.11	5.2

Note: Crosslinker level for Aquazol®-PEI was not optimized. Percent Crosslinker = Heloxy 67/(Heloxy 67 + Aquazol®-PEI polymer solids)

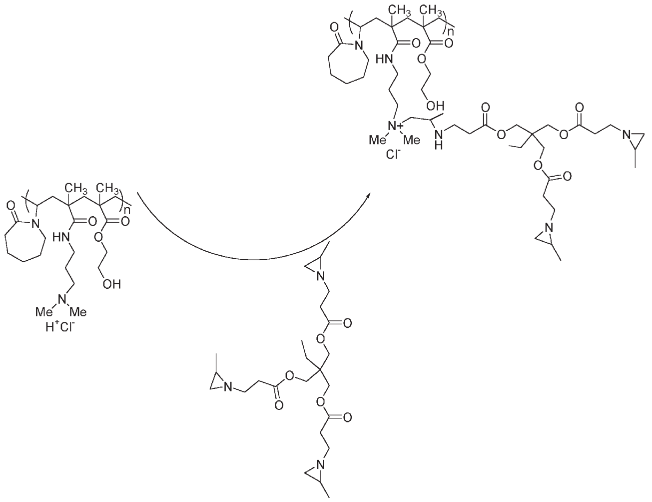

Figure 2. Proposed crosslinking mechanism for CX-100 and VCL/DMAPMA/HEMA/HCL.

drochloric acid, enables the activation of the 3-membered aziridine ring via protonation. Upon ring opening, the resulting carbocation rapidly attacks the amine nitrogen of DMAPMA, resulting in formation of a crosslinked network structure. Interestingly, such a reaction is desirable for ink jet printing because the cationic nature of the film is further enhanced by the quaternization, resulting from the carbocation's new covalent bond to the DMAPMA nitrogen. The resulting network structure in this system is primarily crosslinked.

Polymeric solutions of the polyfunctional epoxy Heloxy 67 and Aquazol®-PEI were prepared as indicated in Table III.

TABLE IV. Gloss Properties for Composition for Aquazol®-PEI Copolymers and Heloxy 67

Product	Gloss (60°) Uncrosslinked	Gloss (60°) Crosslinked
Aquazol®-PEI	92.6	93.7

To determine the suitability of this particular crosslinker with the polymer, gloss measurements were performed, reported in Table IV.

Results of 5 minute, agitated, water submersion tests are presented in Fig. 3. The neat film is a moderate film former and quite tacky. Upon crosslinking, the film forming properties are enhanced and the tackiness is somewhat reduced. Crosslinking produces a noticeable improvement to the water soluble polymer's ability to resist water.

The crosslinking reaction between the ethyleneimine moiety of Aquazol®-PEI and epoxy is presented in Fig. 4. In this system, Aquazol®-PEI behaves essentially as a coreactive amine curing agent for the epoxy resin. The nucleophilic attack of the Aquazol®-PEI secondary amine towards the epoxy's terminal methylene group results in the formation of a new polymer comprised of a tertiary amine and a secondary alcohol.[5,6] The final network structure in this system is primarily crosslinked.

Polymeric solutions of the melamine/formaldehyde Berset 2506 and VP/DMAPMA/H_2SO_4 were prepared as indicated in Table V. Note that in this experiment, the polymer pH was reduced by further addition of phosphoric acid.

To determine the suitability of this particular crosslinker with the polymer, gloss measurements were performed, as reported in Table VI.

Results of 30 minute, agitated, water submersion tests are presented in Fig. 5. The neat film is an excellent film

Figure 3. Comparative water submersion test results for uncrosslinked and crosslinked Aquazol®-PEI.

TABLE V. Sample Composition for VP/DMAPMA/H_2SO_4/H_3PO_4 Copolymers and Berset 2506

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	Heloxy 67 (g)	% Crosslinker
VP/DMAPMA/H_2SO_4/H_3PO_4	18.2	5.5	1.0	0.11	9.9

***Note**: crosslinker level for VP/DMAPMA/H_2SO_4/H_3PO_4 was not optimized. Also, the pH was adjusted to ~3 with conc. H_3PO_4. Percent Crosslinker = Berset 2506/(Berset 2506 + VP/DMAPMA/H_2SO_4/H_3PO_4 polymer solids)*

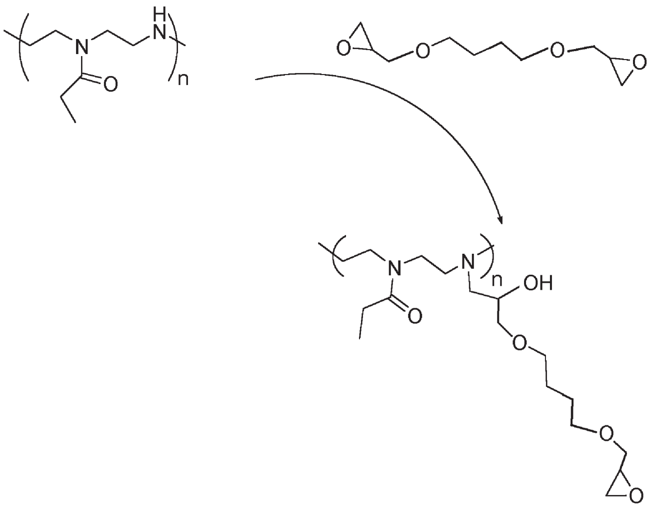

Figure 4. Proposed crosslinking mechanism for Heloxy 67 and Aquazol®-PEI.

former. Upon crosslinking, an improvement to the water soluble polymer's ability to resist water is observed.

A representation of a possible crosslinking reaction between the monomeric constituent DMAPMA and melamine/formaldehyde is presented in Fig. 6.

Possible crosslinking reactions between the DMAPMA and melamine formaldehyde[7] are presented in Fig. 6. The initial neutralization of DMAPMA comonomer with sulfuric acid conceivably neutralizes two DMAPMA moieties with one, polyprotic acid group. Further addition of phosphoric acid serves to free some acid functionalities, sulfuric and phosphoric acid, enabling ionic bonding of the melamine/formaldehyde system to DMAPMA ligand. Some acid may be free from the polymer, resulting in the formation of poly(melamine/formaldehyde). Thus, both crosslinked and semi-penetrating type networks are formed in this system.

TABLE VI. Sample Composition for VP/DMAPMA/H_2SO_4/H_3PO_4 Copolymers and Berset 2506

Product	Gloss (60°) Uncrosslinked	Gloss (60°) Crosslinked
VP/DMAPMA/H_2SO_4/H_3PO_4	90.9	91.0

The use of crosslinking can provide important insight to polymer architecture. To explore this concept further, the features of the studied coating structure will be described in detail. First, the crosslinkable polymer to be employed is HEMA/DMAPMA. Neutralization of HEMA/DMAPMA with hydrochloric acid yields quarternization of DMAPMA, similar to the DMAPMA monomer structure featured in Fig. 2. Again, the presence of the partially free proton on DMAPMA enables activation of the aziridine ring, resulting in a crosslinked type of network. The aziridine crosslinker employed for this example was XAMA-7.

The polymer architecture to be studied was PVP. PVP is not generally receptive to aziridine based crosslinking. Blending PVP K90 into the HEMA/DMAPMA/HCL yields an semi-penetrating network coating structure, where the linear, completely water soluble PVP polymer is entangled with the crosslinked HEMA/DMAPMA/

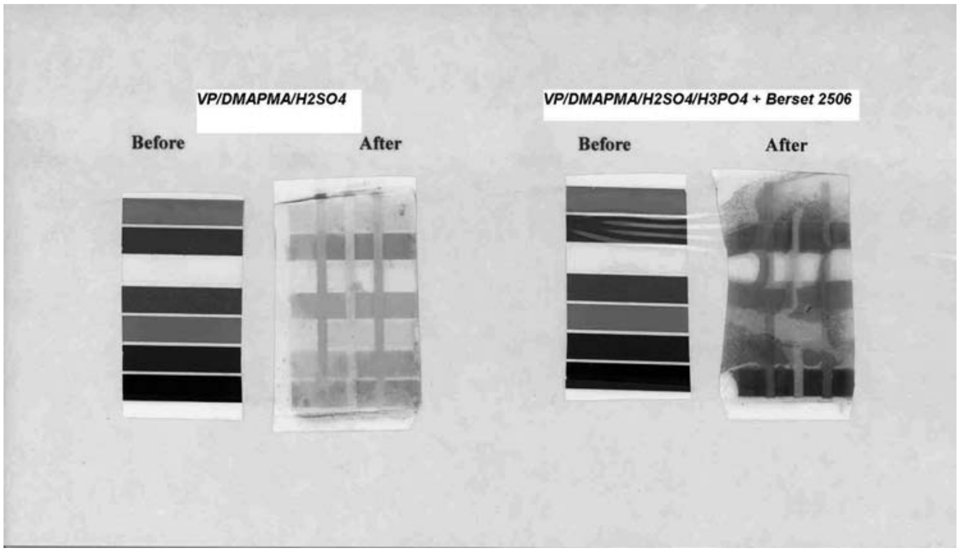

Figure 5. Comparative water submersion test results for uncrosslinked and crosslinked VP/DMAPMA/H_2SO_4.

TABLE VII. Sample Compositions for HEMA/DMAPMA/HCL/PVP and HEMA/DMAPMA/HCL/MCPVP and XAMA-7

Product	HEMA/DMAPMA/HCLPVP (10.3% solids) (g)	K90 or MCPVP Solution (10% solids) (g)	Polymer Solids (g)	XAMA-7 (g)	% Crosslinker
HEMA/DMAPMA/HCL/PVP SPN	1.6	13.6	1.53	0.02	1.3
HEMA/DMAPMA/HCL/MCPVP Modified SPN	1.6	13.6	1.53	0.02	1.3

Note: Crosslinker level for these compositions was not optimized. Percent Crosslinker = XAMA-7/(XAMA-7 + polymer solids)

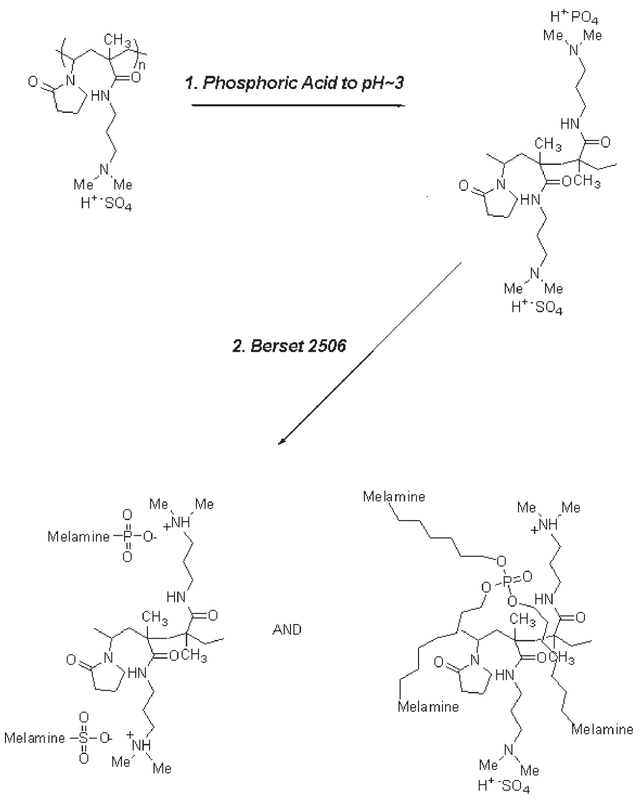

Figure 6. Proposed Crosslinking mechanisms for Berset 2506 and VP/DMAPMA/H_2SO_4/H_3PO_4.[11]

HCL structure. One unusual variation on PVP is the molecular composite PVP (MCPVP).[8] In broad terms, MCPVP is comprised of water soluble PVP K~90 and nanoscale PVP insoluble particles. Once again, the blending of MCPVP into HEMA/DMAPMA yields a modified semi-penetrating network coating structure, where the soluble PVP is entangled with the crosslinked HEMA/DMAPMA/HCL and the nanoscale particles are physically bound in the same crosslinked network. An idealized representation of these structures is presented in Fig. 7.

Specific components of these coatings are presented in Table VII.

The water resistive performance of these two, different coatings are presented in Fig. 8. As expected, the PVP can disentangle itself and re-solubilize. The result of this effect is presented in Fig. 8 (top), where the sky exhibits substantial coating failure. Conversely, MCPVP (Fig. 8 (bottom)) is largely intact due to the ability of the SPN coating structure to retain the MCPVP nanoscale particles in the film structure.

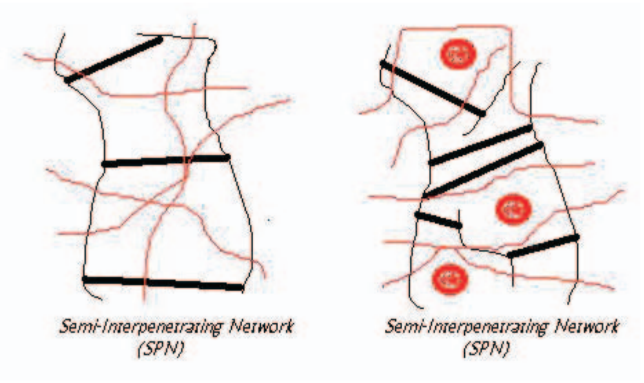

Figure 7. Idealized Representations of a HEMA/DMAPMA/HCL/**PVP** SPN (left) and HEMA/DMAPMA/HCL/**MCPVP** Modified SPN (right).

Figure 8. 40 minute, water agitated submersion results for HEMA/DMAPMA/HCL/PVP K90 SPN (top) and HEMA/DMAPMA/HCL/MCPVP Modified SPN (bottom).

Conclusions

A variety of crosslinking chemistries have been explored. Polymers comprised of N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA) are capable of being crosslinked by polyfunctional aziridines. Interestingly, such polymers, when neutralized with polyprotic acids are also capable of crosslinking with melamine/formaldehyde crosslinkers. Polymers comprised of unsubstituted amines are capable of crosslinking with polyglycidyl crosslinkers. In all cases, the resulting films exhibited enhanced water resistance, without sacrificing gloss, and are ink jet printable. Valuable polymer architecture insight can be gained from simple studies of blended crosslinkable and uncrosslinkable ink jet receptive polymers.

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