Approaches to Cross-linking Unique, Water Soluble Polymers Used in Inkjet Receptive Coatings

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Abstract

Ink receptive, water-soluble polymers are commonly used in inkjet coatings and applications. To render these coatings more resistant to water, cross-linking 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 cross-linking of 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), and poly(2-ethyl-2-oxazoline-co-ethyleneimine) (Aquazol®/PEI). Cross-linking chemistries to be explored will include commercial aziridine, epoxy, and melamine/formaldehyde cross-linking agents.

Introduction

Of the wide variety of materials employed in inkjet 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 inkjet 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 paper will focus on one environmental exposure issue: water resistance. One possible approach to forming water resistive inkjet materials from water-soluble polymers is via cross-linking during the process of film formation.[1-3] Such an approach can result in a single composition of cross-linked 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 inter-molecular fashion (XL). A semi-interpenetrating network (SPN) is comprised of an entanglement of a linear (or branched) polymer and a cross-linked polymer material. In this case, neither polymeric species is inter-molecularly bonded. An interpenetrating network (IPN) is comprised of two types of entangled cross-linked polymers that are entangled but not chemically bonded together. This paper will narrowly focus on cross-link architectures XL and SPN.

Experimental

PVP/DMAPMA/H_2SO_4 and VCL/DMAPMA/HEMA/HCL materials are available from International Specialty Products (ISP) under their respective trade names, ViviPrint™ 121 and ViviPrint™ 200. 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.[5] Polyfunctional epoxy Heloxy 67 is available from Resolution Performance Products, Houston, TX.[6] The melamine/formaldehyde Berset 2506 is available from Bercen, Cranston, RI.[7] 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 cross-linking, 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 grams per square meter. An inkjet 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 cross-linked and uncross-linked prints are placed side-by-side for visual, comparative purposes. Proposed chemical reaction mechanisms presented in this paper are determined spectroscopically from solutions of samples prepared in similar fashion, but with much higher levels of cross-linker. In some cases, model compounds were employed. These particular experimental details are beyond the scope of this paper.

Results and Discussion

Polymeric solutions of the polyfunctional aziridine CX-100 and VCL/DMAPMA/HEMA/HCL were prepared as indicated in Table 1. These solutions were pH adjusted to pH~9 using concentrated ammonium hydroxide in order to stabilize the polymer cross-linker solution.

To determine the suitability of this particular cross-linker with the polymer, gloss measurements were performed. Please refer to Table 2.

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

Table 1. Sample Composition for VCL/DMAPMA/HEMA/HCL terpolymer and CX-100

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	CX-100 (g)	% Cross-linker
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 2. Gloss for Composition of VCL/DMAPMA/HEMA/HCL terpolymer and CX-100

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

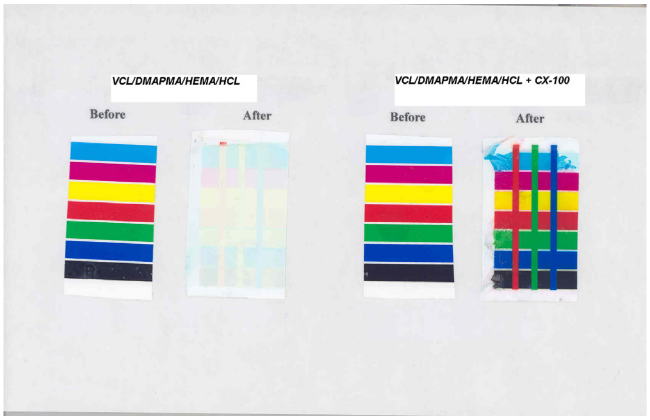

Figure 1. Comparative water submersion test results for uncross-linked and cross-linked VCL/DMAPMA/HEMA/HCL.

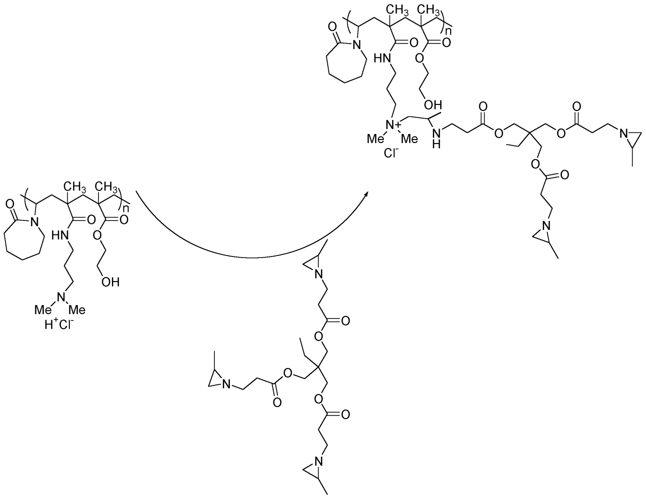

Figure 2. Proposed Cross-linking mechanism for CX-100[8] and VCL/DMAPMA/HEMA/HCL.

A representation of a possible cross-linking reaction between the monomeric constituent DMAPMA and aziridine is presented in Figure 2. The partially free proton, present via neutralization of the polymer with hydrochloric acid, enables the activation of the 3-membered aziridinic ring via protonation. Upon ring opening, the resulting carbanion rapidly attacks the nitrogen of DMAPMA, resulting in formation of a cross-linked network structure. Interestingly, such a reaction is desirable for inkjet printing because the cationic nature of the film is further enhanced by the quaternization, formed from the carbanion's new covalent bond to the DMAPMA nitrogen. The resulting network structure in this system is primarily XL.

Polymeric solutions of the polyfunctional epoxy Heloxy 67 and Aquazol®-PEI were prepared as indicated in Table 3.

To determine the suitability of this particular cross-linker with the polymer, gloss measurements were performed. Please refer to Table 4.

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

The cross-linking reaction between the ethyleneimine moiety of Aquazol®-PEI and epoxy is presented in Figure 4. In this system, Aquazol®-PEI behaves essentially as a co-reactive 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.[9,10] The final network structure in this system is primarily XL.

Polymeric solutions of the melamine/formaldehyde Berset 2506 and VP/DMAPMA/H_2SO_4 were prepared as indicated in Table 5. Note that in this experiment, the polymer pH was reduced by further addition of phosphoric acid.

Table 3. Sample Composition for Aquazol®-PEI copolymer and Heloxy 67

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	Heloxy 67 (g)	% Cross-linker
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)

Table 4. Gloss Properties for Composition for Aquazol®-PEI copolymers and Heloxy 67

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

Table 5. Sample Composition for VP/DMAPMA/H_2SO_4/H_3PO_4 copolymers and Berset 2506

Product	Polymer Solution (g)	% Solids	Polymer Solids (g)	Berset-2056 (g)	% Cross-linker
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 3. Comparative water submersion test results for uncross-linked and cross-linked Aquazol®-PEI.

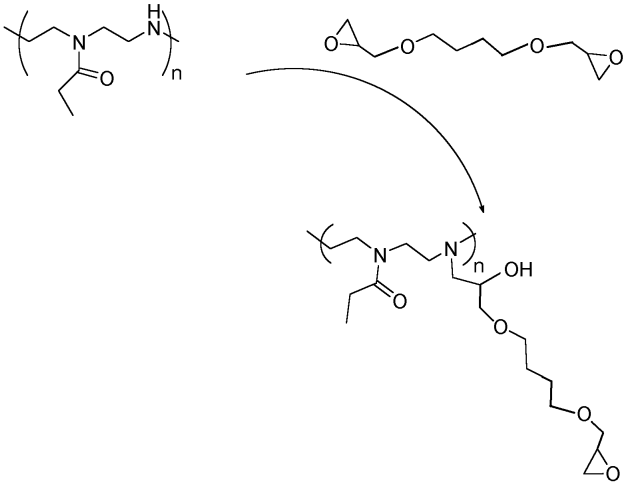

Figure 4. Proposed cross-linking mechanism for Heloxy 67 and Aquazol®-PEI.

Table 6. Sample Composition for VP/DMAPMA/H_2SO_4/H_3PO_4 copolymers and Berset 2506

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

To determine the suitability of this particular cross-linker with the polymer, gloss measurements were performed.

Results of 30-minute, agitated, water submersion tests are presented in Figure 5. The neat film is an excellent film former. Upon cross-linking, an improvement to the water-soluble polymer's ability to resist water is observed.

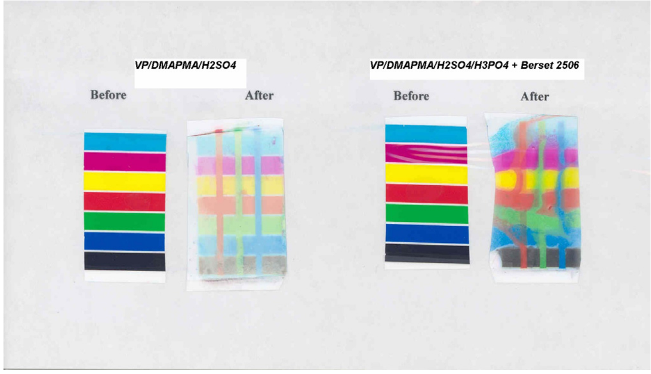

Figure 5. Comparative water submersion test results for uncross-linked and cross-linked VP/DMAPMA/H_2SO_4.

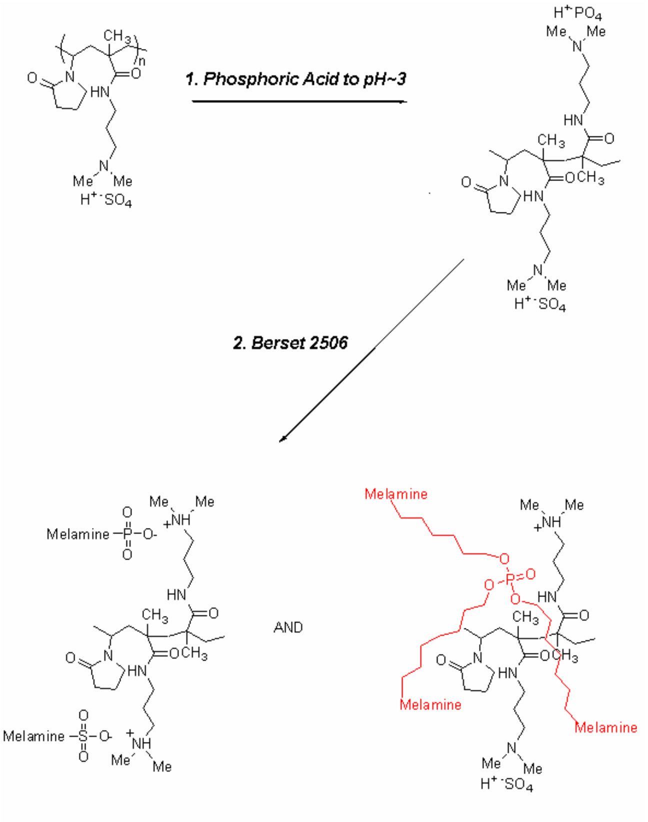

Figure 6. Proposed Cross-linking mechanisms for Berset 2506 and VP/DMAPMA/H_2SO_4/H_3PO_4.[11]

A representation of a possible cross-linking reaction between the monomeric constituent DMAPMA and melamine/formaldehyde is presented in Figure 6.

Possible cross-linking reactions between the DMAPMA and melamine formaldehyde are presented in Figure 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 XL and SPN type networks are formed in this system.

Conclusions

A variety of cross-linking chemistries have been explored. Polymers comprised of N-[3-(dimethylamino)propyl] methacrylamide (DMAPMA) are capable of being cross-linked by polyfunctional aziridines. Interestingly, such polymers, when neutralized with polyprotic acids are also capable of cross-linking with melamine/formaldehyde crosslinkers. Polymers comprised of un-substituted amines are capable of cross-linking with polyglycidyl crosslinkers. In all cases, the resulting films exhibit enhanced water resistance, without sacrificing gloss, and are inkjet printable.

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Biography

David K. Hood earned his B.S. degree in Chemistry in 1990, M.A. degree in Chemistry in 1992, and Ph.D. in Applied Science (Polymer Chemistry) in 1996, all from the College of William and Mary in Williamsburg, VA. Upon completion of a Visiting Assistant Professor in Chemistry position, also at William and Mary, he joined International Specialty Products (ISP) in Wayne, NJ in 1999. His current work is primarily focused on the development materials and technical coating solutions for the inkjet and printing industries. He is a member of ACS, PMSE, and the APS-SoR.