Properties and Application of a Radiation Curable, Inkjet Receptive Polymer

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Abstract

A cationic, water-soluble, free-radically UV curable polymer suitable for inkjet receptive coatings is described. Specifically, poly(vinylcaprolactam-co-N-[3-(dimethylamino)propyl]meth acrylamide-co-hydroxyethylmethacrylate) neutralized with hydrochloric acid, modified by glycidyl methacrylate (VCL/DMAPMA/HEMA/GMA/HCL). The structure and properties of this novel material are presented. In addition, some formulation strategies for inkjet receptive coatings are discussed and examples presented.

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Introduction

Water-soluble polymers continue to contribute many important properties to the final, inkjet receptive coating product performance. Coating properties that often benefit from the use of water-soluble polymers include film formation, dye fixation, gloss, and fluid management of print ink. As the industry trend to extend these products into more extreme environments continues, where exposure to water, UV radiation, and ozone can be severe, cross-linking of these materials becomes an increasingly essential requirement of the water-soluble polymer.[1]

Cross-linking of water soluble materials is not without challenges. From identification of appropriate cross-linkers, determination of required amounts of cross-linker, stabilization of requisite pot-life of cross-linker in coating formulation (*if possible*), to safe handling of such materials for plant personnel, the implementation of cross-linking technology can be a challenge. One potential approach to addressing many of these issues is the implementation of UV coating technology.

Radiation coating technology, or more specifically UV coating technology, has a rich history. One distinct advantage to this technology is that properly designed coating solutions are unlikely to change in the absence of appropriate light. This provides production personnel with the potential to have greater control of the coating components and process.

Commercial, UV coating applications can be found in use today on a variety of substrates such as wood, metal, paper, plastics, ceramics/glass, and textiles. As Thalacker wrote back in 1990, in addition to the performance attributes radiation curable coating are capable of providing, such technology can be attractive when reduction in energy costs and elimination of solvents (VOC content) are desired.[2] Now some twenty years later, those comments are even more powerful in the face of ever rising energy costs and increasing pressures to improve the environmental footprint of many manufacturing processes. More recently, in 2006 an executive summary from the SGIA encouraged members of the graphic arts community to achieve energy reduction via radiation curing technology to enhance the sustainability of graphic related products.[3]

This paper will focus on a novel technique for cross-linking a cationic, water soluble, inkjet receptive polymers: specifically, poly(vinylcaprolactam-co-N-[3-(dimethylamino)propyl]methacryl amide-co-hydroxyethylmethacrylate)neutralized with hydrochloric acid, modified by glycidyl methacrylate (VCL/DMAPMA/HEMA/ GMA/HCL). The structure and properties of this novel material are presented. In addition, some formulation strategies for inkjet receptive coatings are discussed and examples presented.

Experimental

VCL/DMAPMA/HEMA/HCL material is available under the trade name ViviPrint™ 200 from International Specialty Products (ISP) located in Wayne, New Jersey. The preparation of VCL/DMAPMA/HEMA/GMA/HCL is presented elsewhere and beyond the scope of this paper.[4] Triethylene glycol divinyl ether is available under the trade name Rapi-Cure™ DVE-3 from ISP. 2-Hydroxyethyl methacrylate (HEMA, 97% purity) and ammonium hydroxide (ACS Reagent Grade) were purchased from Aldrich Chemicals, located in Milwaukee, Wisconsin. UCECOAT 6558 is an aliphatic urethane acrylate solution in water available from Cytec Surface Specialties, located in Drogenbos, Belgium. CN963B80 is an aliphatic polyester based urethane diacrylate oligomer blended with 20% SR238, hexane diol diacrylate (HDDA), available from Sartomer Company, located in Exton, Pennsylvania. Darocur 1173 is 2-hydroxy-2-methyl-1-phenyl-1-propanone and is available from Ciba Specialty Chemicals located in Tarrytown, New York.

To test the UV curable VCL/DMAPMA/HEMA/GMA/HCL polymer, a coating solution is prepared. This coating solution is drawn onto clear, DuPont-Teijin Melanex polyester film with a #40 Meyer rod. The resulting wet film is placed in to a Fusion UV LC-6B bench-top conveyor equipped with F300S/SQ lamp system. The belt speed was set for 1-5 ft/min to achieve full cure. The final dry coating weight was approximately 10 grams per square meter. An inkjet test pattern was printed onto the film using the Hewlett-Packard HP 5650, in Plain Paper Mode (Palo Alto, CA). Optical density was measured using a Gretag Macbeth D19C Densitometer (Regensdorf, Switzerland). Gloss was measured at 60^o using a BYK micro-TRI-gloss meter (Model 4430; Geretsried, Germany) when coating was applied to white Melanex film. The printed film was allowed to stand for a minimum of 24 hours. Portions of the printed film were also subjected to distilled water, agitated 15 minute submersion test.

Results and Discussion

Previous work demonstrated the excellent print receptivity of the VCL/DMAPMA/HEMA/HCL polymer couple to strong water solubility.[1] For many print applications, suitable cross-linking was required to achieve suitable moisture resistance for this polymer.[5] To render the polymer suitable for UV cross-linking, a free acrylate moiety is now incorporated into the polymer. A representation of the proposed structure for VCL/DMAPMA/ HEMA/GMA/HCL is presented in Figure 1.

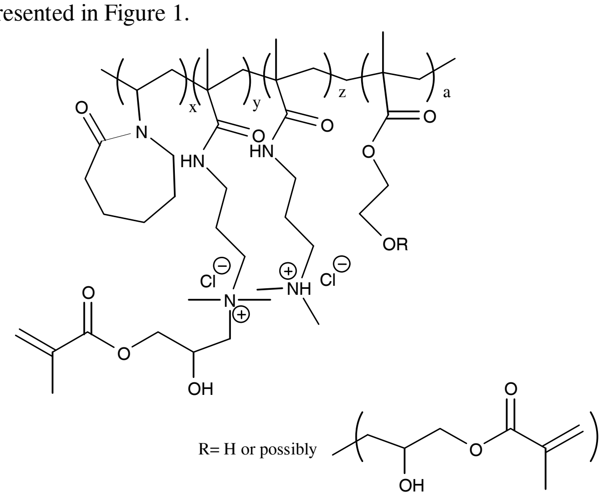

Figure 1: Proposed Structure of VCL/DMAPMA/HEMA/GMA/HCL UV Curable polymer

The physical properties of the VCL/DMAPMA/HEMA/GMA/HCL polymer are presented in Table 1. In general, the polymer is a low viscosity material that exhibits a reasonably high T_g. The polymer exhibits some brittleness but continues to be very print receptive providing for high gloss, transparency, film forming, and good dye fixation properties.

Table 1: Physical Properties of VCL/DMAPMA/HEMA/GMA/HCL UV Curable polymer

Property	Data
Viscosity (cPs)	~100 at 15% solids in water
Molecular Weight (g/mol)	115,000
T_g (°C)	159

Aqueous Based UV Coating

An aqueous, prototype glossy coating formulation was developed and is presented in Table 2. The basic compositional strategy for this coating was to flexibilize the VCL/DMAPMA/HEMA/GMA/HCL polymer with the UCECOAT 6558 urethane acrylate. The urethane acrylate imparts additional water resistance to the coating due to the inherent hydrophobicity of the polyurethane. HEMA monomer was employed to provide some additional softening to the cross-linked network, enabling the coating composition to receive the ink more efficiently while also enabling a minimization of solution viscosity. The ammonium hydroxide was employed to enhance the mixing and compatibility of the solution components. Darocur 1173 was employed to initiate the free radical polymerization. As a result, the coating yields good print receptivity, gloss, and transparency.

As a general overview to coating preparation, ingredients were combined in the following manner. First, VCL/DMAPMA/HEMA/GMA/HCL and de-ionized water are combined. The ammonium hydroxide and HEMA are added. Finally, UCECOAT 6558 and Darocur 1173, to initiate the free radical polymerization, are added. During all stages of formulation construction, the fluid was thoroughly mixed. Specific coating compositional details are presented in Table 2.

Table 2: Prototype Aqueous Based UV Curable Coating

Product	Mass (g)	Percent Solids	Dry Mass (g)	Wt% Dry Film Composition
Water	3.8			
VCL/DMAPMA/ HEMA/GMA/HCL	3.8	30	1.14	70.6
UCECOAT 6558	0.5	50	0.25	15.5
Ammonium Hydroxide	1.45			
HEMA	0.2	100	0.2	12.4
Darocur 1173	0.025	100	0.025	1.5
Total	9.775		1.615	100

The general properties for the prototype coating and coating solution are presented in Table 3. The general solution properties are suitable for a variety of commercial application methods, such as knife, slot-die, rod, roll, blade, and gravure coating processes.

Table 3: Properties of Aqueous Prototype UV Curable Coating

Property	Data
Solution Solids (%)	~16.5
Coating Solution Viscosity (cPs)	103 (Brookfield LV III, #62, 100 RPM)
Coat Weight (grams per square meter)	10.2
Appearance	Transparent
Gloss (60°) (White Melanex)	75

Print test results for the prototype coating are presented in Table 4.

Table 4: Print Properties of Aqueous Prototype UV Curable Coating

Color	Optical Density Before Water Exposure	Optical Density After Water Exposure	% Change
K (Black)	3.3	2.93	-11
C (Cyan)	0.55	0.54	-1.8
M (Magenta)	0.57	0.67	18
Y (Yellow)	0.89	0.59	-14

In general, results presented in Table 4 suggest good dye fixation properties, particularly for cyan and magenta. Some black and yellow ink was lost as a result of the water submersion test, but the relative fixation was good for an inherently water soluble, polymeric material employed in this simple prototype coating.

100% Solid, Non-aqueous Based UV Coating

A non-aqueous, prototype glossy coating formulation was developed and is presented in Table 5. The basic compositional strategy for this coating was to flexibilize the VCL/DMAPMA/HEMA/GMA/HCL polymer with the CN963B80 polyester based urethane diacrylate blended with hexane diol diacrylate. The urethane diacrylate/HDDA solution imparts additional water resistance to the coating due to the inherent hydrophobicity of this system. HEMA and DVE-3 monomers were employed to provide some additional softening to the cross-linked network, enabling the coating composition to receive the ink more efficiently while also enabling a minimization of solution viscosity. Darocur 1173 was employed to initiate the free radical polymerization. This coating also yields print receptivity, gloss, and transparency.

As a general overview to coating preparation, ingredients were combined in the following manner. First, VCL/DMAPMA/ HEMA/GMA/HCL and HEMA are combined during gentle warming. The DVE-3 and CN963B80 are added. Finally, Darocur 1173 initiator was added. During all stages of formulation construction, the fluid was thoroughly mixed. Specific coating compositional details are presented in Table 5.

Table 5: Prototype Non-Aqueous Based UV Curable Coating

Product	Mass (g)	Percent Solids	Dry Mass (g)	Wt% Dry Film Composition
HEMA	1.04	100	1.04	52.3
VCL/DMAPMA/ HEMA/GMA/HCL	0.3	100	0.3	15.1
CN963B80	0.43	100	0.43	21.6
DVE-3	0.15	100	0.15	7.5
Darocur 1173	0.07	100	0.07	3.5
Total	1.99		1.99	100

The general properties for the prototype coating and coating solution are presented in Table 6. The general solution properties are suitable for a variety of commercial application methods, such as knife, rod, slot-die, and blade process. Other process, such as gravure, may require some additional compositional modifications to present a more appropriate solution viscosity.

Table 6: Properties of Non-Aqueous Prototype UV Curable Coating

Property	Data
Solution Solids (%)	100
Coating Solution Viscosity (cPs)	9600 (Brookfield LV III, #64, 50 RPM)
Coat Weight (grams per square meter)	60
Appearance	Transparent
Gloss (60^o) (White Melanex)	84

Print test results for the prototype coating are presented in Table 7.

Table 7: Print Properties of Non-Aqueous Prototype UV Curable Coating

Color	Optical Density Before Water Exposure	Optical Density After Water Exposure	% Change
K (Black)	3.16	2.51	-20.5
C (Cyan)	0.69	0.31	-55
M (Magenta)	0.55	0.31	-44
Y (Yellow)	0.88	0.28	-68

In general, results presented in Table 7 suggest dye fixation properties. However, the magnitude of % change after water submersion reveals some hardness to the coating surface. To overcome the coating hardness, the coating weight was increased, admittedly an undesirable approach, to demonstrate general application utility. Other possibilities for coating improvement include increasing the VCL/DMAPMA/HEMA/GMA/HCL polymer contribution or application of coating as a thin surface coating to a more absorptive sub-layer.

Conclusions

We have successfully developed and demonstrated a free radically curable, cationic, inkjet receptive polymer. Properties of this novel polymer were presented. Aqueous and non-aqueous prototype coatings have been developed and the general formulation strategies discussed.

Acknowledgement

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References

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Author 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. He is currently Manager – North American Technical Service and Development for ISP Performance Chemicals. He is a member of ACS, PMSE, and the APS-SoR.*