

Role of Media Polymer Chemistry on Dye / Polymer Interactions and Light Stability of Ink Jet Graphics

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Abstract

The chemical environment within the receiving layer(s) is known to influence the permanence of dye-based ink jet graphics. A correlation was observed between dye light fastness and the concentration dependence of UV / VIS absorption in dyed acrylamide and polyvinyl pyrrolidone polymers. This has been interpreted as a consequence of media influenced dye aggregation. Computer modeling of dye polymer interactions supports this interpretation in the case of the polyvinyl pyrrolidone and acrylamide polymers, but suggests other factors can also play a role in the favorable photo stability of polyvinyl alcohol images. The validity of the computer models and dyed polymer techniques employed in understanding dye photo fade are addressed.

Introduction

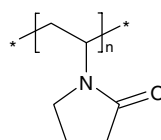
Image photo stability of dye based ink jet prints is an ongoing area of study. Many factors may influence this, but it is known that interactions between dye and media play a large role.¹ More specifically, the degree of dye aggregation within the receiving media has been reported to influence dye photo stability.² The more strongly a dye aggregates, the more it behaves like a micro pigment and will therefore be more photo stable.

The solvating ability of the environment should impact the amount of dye aggregation. There will be a smaller amount of dye aggregate in highly solvating media than expected in poorly solvating media. The solvating ability of different media will obviously vary greatly depending on the polymers employed and the structure of the specific dyes involved.

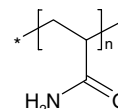
Computer simulations can be used to obtain theoretical interaction energies of a dye and polymer network. Essentially, an energy value can be obtained that reflects the likelihood of uniform dispersion of dye within the polymer. Dyes in systems with less favorable dye / polymer interactions will be more poorly dispersed and have a greater tendency to form aggregates.

Evidence for dye aggregation can be obtained by comparing the UV/Vis spectra of the dye at different concentrations in the polymer. For an aggregated dye, a change in λ max is expected at higher concentrations. In an aggregate, strong electronic interactions occur which cause the individual molecules to act as a single entity. The effect of these electronic interactions can also be seen as a change in the absorption profile of the dyes.³

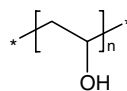
In the present work, model calculations were used to predict the likelihood of Acid Yellow 23 aggregation in commercially available polymers, namely polyvinyl pyrrolidone (PVP), polyacrylamide (PAM) and polyvinyl alcohol (PVOH). Spectral analysis (UV / Vis) of films cast from formulations of the individual polymers containing different concentrations of the dye confirmed the validity of the computer model in predicting aggregation tendencies of this dye.



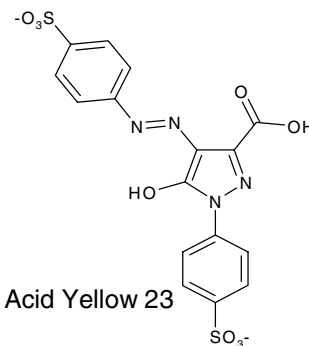
Polyvinyl Pyrrolidone (PVP)
K90 grade
Aldrich



Polyacrylamide (PAM)
Glascosol W13
Ciba Specialty Chemicals



Polyvinyl Alcohol (PVOH)
Gohsenol KH-20
Nippon Gohsei



Acid Yellow 23

Figure 1. Structures of polymers and dye.

The relationship of aggregation to photostability was determined by accelerated aging of these films in a xenon weatherometer. Dye loss was conveniently measured by loss of UV / Vis absorption. By using dyed films, the dye / polymer chemistry could be explicitly evaluated, negating other factors relating to the printing process that may have confused the results.

As final verification of these methods, films of the polymers in question were cast, dried and printed on using a HP ink set and printer. The printed images were exposed under exactly the same conditions as the dyed polymer films and dye degradation was measured in terms of optical density loss.

While increased dye aggregation was consistent with the improved photopermanence of the dye in PAM vs PVP, results showing good stability in PVOH without significant dye aggregation suggest the importance of other stabilizing mechanisms.

Experimental

Computational Details

Simulated interaction energies were estimated via a molecular dynamics method using the condensed phase force field COMPASS.⁴ Models of amorphous polymer (typically 20mers), dye, and polymer/dye blends were constructed as a cubic cell of roughly 20 Angstroms/side using a Monte Carlo procedure which is a combination of that described by Theodorou² and Meirovitch³. Each cubic cell was packed at the experimental density (or a reasonable approximation thereof) and subsequently equilibrated via constant temperature molecular dynamics, with periodic boundary conditions, for at least 50 ps. Production runs of 100 ps followed, during which "snapshots" of the systems were collected every 5 ps. The cohesive energies of each sample were calculated⁴ and averaged over the entire production run. Energies of mixing at a specified composition (5% by volume of dye) were calculated as described by Case and Honeycutt.⁵ All simulations were done within the Materials Studio software of Accelrys, Inc.

The computer model was initially verified by comparisons with values for solubility parameters obtained in the literature.

Table 1. Calculated Hildebrand Solubility Parameters – Comparison to Experiment

Compound	Calculated δ (J/cm^3) ^{1/2}	Experimental δ
Water	48.5	47.9
Ethylene Glycol	34.8	32.9 – 34.9
Triethylene Glycol	27.8	26.3 – 29.1
Polyvinyl alcohol	26.8	25.8 – 29.1
Polyacrylamide	27.5	23.1 (N-isopropyl)
Polyethylene oxide	22.0	20.4

Dyed Polymer Details

Acid Yellow 23 was dissolved into aqueous solutions of PVP, PVOH and PAM at two concentrations of 0.5% and 2.0% weight per dry weight of polymer.

Coatings were applied onto 1.5" diameter quartz discs using a Headway Spin Coater Model EC 101DT-1790. Rotation speed and duration were adjusted to achieve film thicknesses of 10 microns and 2 microns. UV/Vis spectra of the resultant discs were taken using a Perkin Elmer Lambda 9 Spectrophotometer. The discs were then exposed in an Atlas Ci65 Weatherometer, installed with a Xenon arc lamp and inner and outer borosilicate filters, for 48 hours. The exposure conditions were power = 0.35 Wm^2 , relative humidity = 50% and temperature = 50°C. After exposure, final UV/Vis spectra were taken using the Lambda 9.

Printed Polymer Details

Aqueous solutions of PVP, PVOH and PAM (all at 10% NV) were drawn down onto a clear polyester substrate using a Meyer bar so that a 20-micron coating thickness was obtained after oven drying.

Yellow, magenta and cyan color blocks were printed on the samples using a HP 970 Cxi desk jet. Initial optical density measurements on the color blocks were taken using an X-Rite TR938 Spectrophotometer. The resultant prints were exposed in an Atlas Ci65 Weatherometer, installed with a Xenon arc lamp and inner and outer borosilicate filters, for 48 hours. The exposure conditions were power = 0.35 Wm^2 , relative humidity = 50% and temperature = 50°C. After exposure final optical density measurements were taken with the X_rite Spectrophotometer. The percent loss in optical density ((initial-final/initial) x100) is reported.

Results and Discussion

The computational results show that the dye has a good affinity for the vinyl pyrrolidone and vinyl alcohol homopolymers but not for the acrylamide homopolymer since less mixing is expected for the higher interaction energies. This implies that the dye is more likely to aggregate in the polyacrylamide than in the polyvinyl alcohol and polyvinyl pyrrolidone. It is interesting to note that the polyacrylamide has the best affinity for water and polyvinyl alcohol the best affinity for triethylene glycol of the three examined.

Table 2. Calculated Energy of Mixing (J/cm^3) and Solubility Parameters (J/cm^3)^{1/2}

Polymer	δ	----- dE_{mix} ----- Triethylene		
		H2O 40%	Glycol 20%	A.Y. 23 5%
PAM	27.5	-19.1	14.3	51.8
PVP	19.8	-21.0	35.6	-1.0
PVOH	26.8	-118.1	0.2	0.0

These results were borne out by the UV / Vis spectra of the dyed polymer films, Figure 2. Acid Yellow 23 in PVP did not exhibit the concentration dependence of λ_{\max} seen in the PAM sample indicating dye aggregation in PAM but not in PVP.

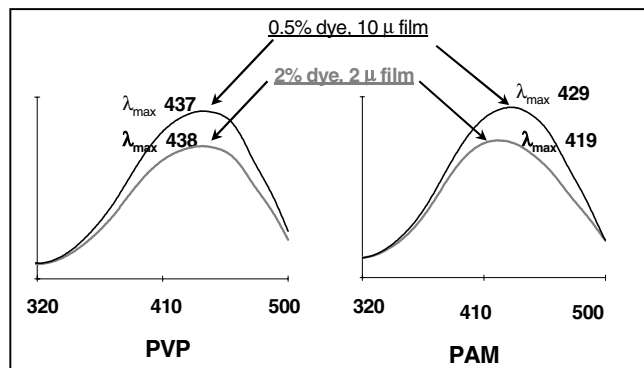


Figure 2. Concentration dependence of dye absorption in PVP vs. PAM

Comparing the amount of dye degradation after exposure to the Xenon source, we find that the PVP and PAM dyed polymer film samples behave very differently, Figure 3. After a 96 hour exposure, the dye was completely lost in the PVP film but remained intact in the PAM film. Taken together with the above results, this appears to offer a correlation between dye aggregation and photo stability.

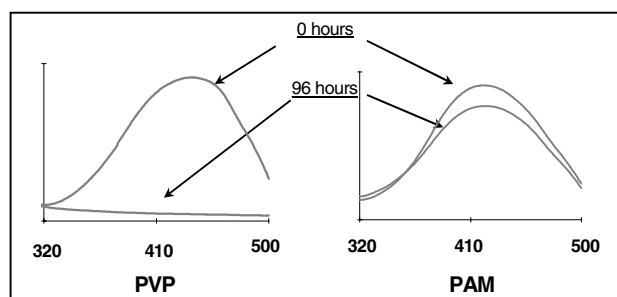


Figure 3. Loss of Dye from PVP and PAM films, 2% dye concentration.

Xenon exposure of the printed films shows the same trends in dye stability, substantiating the application of dyed film studies to printed articles.

It can be concluded that theoretical and experimental evidence has been obtained that dye aggregation occurs in PAM and not in PVP. Additionally, experimental evidence confirms that the extent of dye degradation in PVP is more severe than in PAM. This holds true for both dyed polymer and printed polymer films. This infers that aggregation does play a role in stabilizing the dye against irradiance.

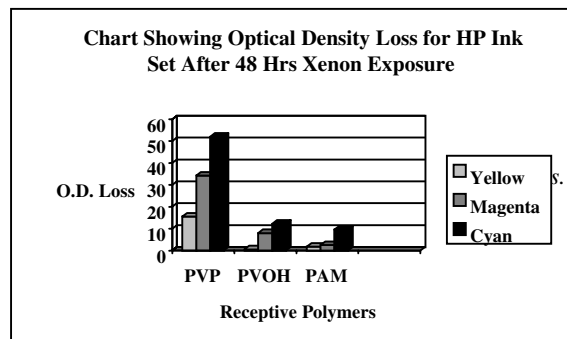


Figure 4. Photo stability of Printed Polymer Films

The case for polyvinyl alcohol, however, appears dramatically different. Theoretical and preliminary experimental information suggests that Acid Yellow 23 does not aggregate in this polymer yet the printed polymer samples are extremely stable towards Xenon exposure. Consequentially, it is suggested that factors other than dye aggregation can be responsible for enhanced dye photo stability. In the case of PVOH, for example, a large hydrogen bond network involving both dye and polymer creates the possibility for more rapid deactivation of the excited dye. It should be noted that more experimental evidence is required to substantiate this hypothesis.

Conclusion

The computer modeling and experimental tools used in the study indicate that dye aggregation can influence dye photo stability in the case of Acid Yellow 23. With respect to this dye in polyvinyl pyrrolidone and polyacrylamide, the computer model successfully predicts photo stability in terms of aggregation effects, aggregation is both predicted and seen, and photo stability increases.

The situation for polyvinyl alcohol and Acid Yellow 23 appears different. The computer model does not predict dye aggregation in this polymer and preliminary experiments substantiate the prediction. Thus, it is suggested that although aggregation effects can provide extended photo permanence other mechanisms such as hydrogen bonding between the dye and polymer can be as equally effective.

References

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Biography

Andrew Naisby is a Scientist in the Applications Laboratory of Ciba Specialty Chemicals Corporation in Tarrytown,

New York (USA). Supervising Ciba's ink jet media laboratory his primary line of work is developing photo stable polymers for ink jet. He previously spent nine years with Rexam Graphics in both the UK and USA where he was involved in the formulation of media coatings and printing inks.

Mr. Naisby holds an Honours Degree in chemistry from the Bristol, England university