

Coalescence and Film Formation Properties of Aqueous UV-Curable PUDs and Oligomers Prior to UV Light Exposure

*Ronald Obie
Wood Coatings Research Group, Inc.
High Point, USA*

Introduction

Coatings, particularly wood coatings, are typically utilized to provide beautification and protection to a substrate. Beautification is normally accomplished through adept color styling generally through accentuation of the wood grain with transparent stains and/or semi-transparent stains, or by application of an adeptly styled and designed opaque coating system, combined with a clear or opaque coating of excellent flow, leveling, clarity/patina, and appearance. Protection of the beautified article may be accomplished by the application of a clear or translucent coating system having physical properties such that environmental and or use stresses that the item may be exposed to are sufficiently resisted to maintain the beauty and functionality of the item. The coating protection property is dependent upon the coating having adequate and uniform film build, proper material or physical properties, combined with the longevity or durability of such physical properties. The coating beautification property is dependent upon the designed color and/or effect of the coating system, the coating having excellent flow and leveling, and, particularly for wood finishes, the coating system having excellent finish clarity or patina. Both the coating beautification and protection properties are highly dependent upon the quality of film formed.

Fundamentally, all coatings are composed of essentially four components: 1) a binder, 2) a carrier, 3) pigments, minerals, and/or dyes, and 4) additives. The binder component is the material that imparts most of the bulk physical properties to the coating. It is the component that is principally responsible for the protective and functional aspects of the coating such as viscosity, dry speed, hardness, toughness, adhesion, chemical resistance, etc.¹⁻³

The unique and advantageous material properties of binders, polymers, and films and the coatings made therefrom are a direct consequence of their chemical structure⁴ and large molecular mass^{5,6}. For water-based emulsion polymers, the ability to access the inherent high molecular weight built into the polymer by a film made therefrom is critically dependent upon proper coalescence of the polymer and film.

The film formation process of conventional thermoplastic solvent-based coatings is believed to be one in which coatings form a film by polymer chain entanglements as solvent evaporates. The film formation of latex based coatings has been studied by a number of investigators and is believed to take place by a multi-step process⁷⁻¹⁶. Conceptually, we may simplistically consider a latex polymer as comprised of relatively hydrophobic polymeric particles dispersed in water, ranging in solids content

from about 20% - 50% by weight, Figure 1a. Upon application in the form of a wet film, water and/or solvent evaporates primarily through vapor pressure control up to a solid content of roughly about 65%, at which point evaporation of water and/or solvent is believed to occur primarily through capillary action with the resulting capillary forces assisting to drive the particles into nearest neighbor distance and contact. The particles continue to come together and with sufficient mobility, deform to a honeycomb-like structure. Throughout this process, water and/or solvent evaporation is believed to occur through diffusion and evaporation. As the solids content approaches approximately 100%, particles are believed to continue to inter-diffuse and particle boundaries begin to break up and a rigid uniform film continues to form; this process is referred to as coalescence, Figure 1b – 1d. Evaporation of volatiles during this final process is diffusion controlled.

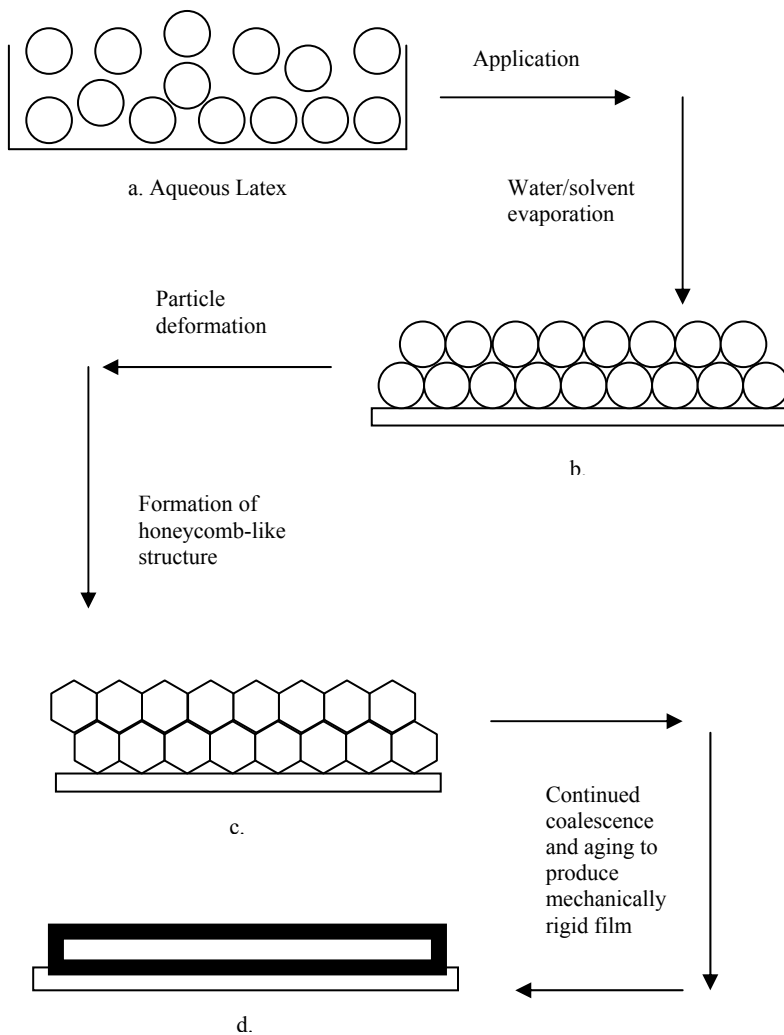


Figure 1. Conceptual Model of an Aqueous Latex and its Film Formation / Coalescence Process. a. Aqueous latex; b. Close packing of particles; c. Particle deformation; d. Mechanically rigid film

Most investigators agree that a key element in the coalescence process is the deformation and inter-diffusion of the polymer particle chains across boundary particles. It is expected that the greater the inter-diffusion, the better the final properties of the film. In order for the film formation process in latex systems to be energetically favorable, the forces which promote film formation must exceed the resistance of the polymer particles to separation, and deformation and flow (or coalescence)⁷. According to Hoy's particle coalescence theory¹³, the energy required for film formation (Q_{ff}), is the sum of the work required for concentration of particles and the work of compaction and coalescence, Equations 1- 3.

$$Q_{ff} = Q_{\text{concentration}} + Q_{\text{coalescence}} \quad (1)$$

Where $Q_{\text{concentration}}$ is the work (or energy) required for the concentration stage
 $Q_{\text{coalescence}}$ is the work (or energy) of compaction and coalescence

And

$$Q_{\text{concentration}} = \dot{\gamma} \int_{\Phi \rightarrow Kc} \partial \eta_{\text{paint}} \quad (2)$$

$$Q_{\text{film coalescence}} = G^*_{\text{film}} \Delta V_{\text{film } Kc \rightarrow 1} \quad (3)$$

Where

$\dot{\gamma}$ is the shear rate in the evaporative stage
 Φ is the polymer/filler volume concentration
 Kc is the onset of critical packing
 $\partial \eta$ is the change in viscosity

Where $Q_{\text{Coalescence}}$ is the work required to cause the polymer to coalesce and G^*_{film} is the complex modulus of the film or polymer. It is equal to complex shear modulus of the film at the temperature the film is being formed times the volume change in the film as volume fraction goes from Kc to 1(dry film)

- G^* can be thought of as the rigidity of the material
- Thus, the greater the rigidity, e.g., greater the T_g , the higher the energy barrier to coalescence

G^* can be modified by, (1) the compositional make-up of the polymer; (2) It can also be modified by the addition of filming or coalescent aids. The efficacy of a coalescent aid in sufficiently modifying the complex modulus of the polymer / film so that the coalescence process becomes more energetically favorable, is believed to be determined by^{7,12}

1) its distribution between the aqueous and polymer phases both initially and at the critical time of film formation, 2) its basic plasticizing efficiency for the polymer, and 3) its tendency to evaporate during and after film formation.

The compositional make-up of a polymer may be impacted by modification of polymer particle architecture and morphology, polymer molecular weight, and polymer glass transition temperature. Aqueous UV-Curable polymers offers an interesting opportunity to develop polymers that potentially easily coalesce with minimal addition of fugitive coalescents while simultaneously providing excellent film properties after exposure to UV radiation. Of necessity, removal of water from the polymer before exposure to the reaction chamber is required in order to obtain best film appearance and performance properties.

Experimental

Evaporative Dynamic Oscillation (EDOT)

Evaporative Dynamic Oscillation, (EDOT), was utilized to monitor complex viscosity, complex modulus, elastic modulus, viscous modulus, and film shrinkage of approximately 150 micron films. The EDOT technique has been described elsewhere^{17, 18}. Briefly, a liquid polymer or coating is applied to a substrate having a uniform well depth of 150 microns followed by leveling the surface of the coating. An EDOT probe is dipped to a controlled depth into the liquid. The probe is attached to a rheometer or some instrument that is able to impose a controlled strain or stress while simultaneously monitoring the response from the liquid imposed on the probe. In this study, a MCR 301 research grade rheometer from Anton Paar GmbH, Graz, Austria, was utilized. The response from the liquid imposed on the probe is monitored under essentially free-evaporative conditions at an air flow rate of 50L/hr. From the response, film properties such as complex viscosity, complex modulus, etc. are determined

Gravimetric Analysis

Gravimetric analysis of films was conducted as follows: Approximately 6 mil wet films were cast onto cleaned, pre-weighed, 8.89 cm by 18.42 cm glass plates, or aluminum panels from Q-Lab Corporation, with a 5.1 cm variable thickness film casting knife from BYK-Gardner. The film thickness setting was determined for each coating in advance by pre-casting films until a wet film thickness reading was obtained of 5 but not 6 mils as measured with a wet film thickness measuring gage from Paul N. Gardner. After the appropriate setting was obtained for the film casting knife, a test film was applied to the test panel, actual film thickness confirmed, and the coated glass or panel transferred to a constant temperature and humidity chamber equipped with a balance. Weight loss and visual dry of the test wet film were followed as a function of time.

Results and Discussion

Rate of Volatile Loss

Figure 2 displays weight percent volatile loss from an aqueous film consisting of a water-based UV-Curable polymer. The figure also displays calculated solids increase of the film as a function of time. The data indicates that there are at least three distinct phases to the drying process for this film as monitored by weight loss, (1) an initial linear volatile loss as a function of time; (2) a transition region

where volatile loss occurs as a function of reciprocal time; (3) a final region displaying extremely slow volatile loss from the film as a function of time. The initial linear region is where evaporation of volatiles occurs by a free evaporative mechanism. For this polymer, the free evaporative region occurs up to a solids content of about 52% solids, after which the rate of volatile loss slows dramatically. In this second stage, evaporation follows a reciprocal time mechanism from about 52% solids to about 84% solids. After reaching about 84% solids content, evaporation slows again to a negligible rate.

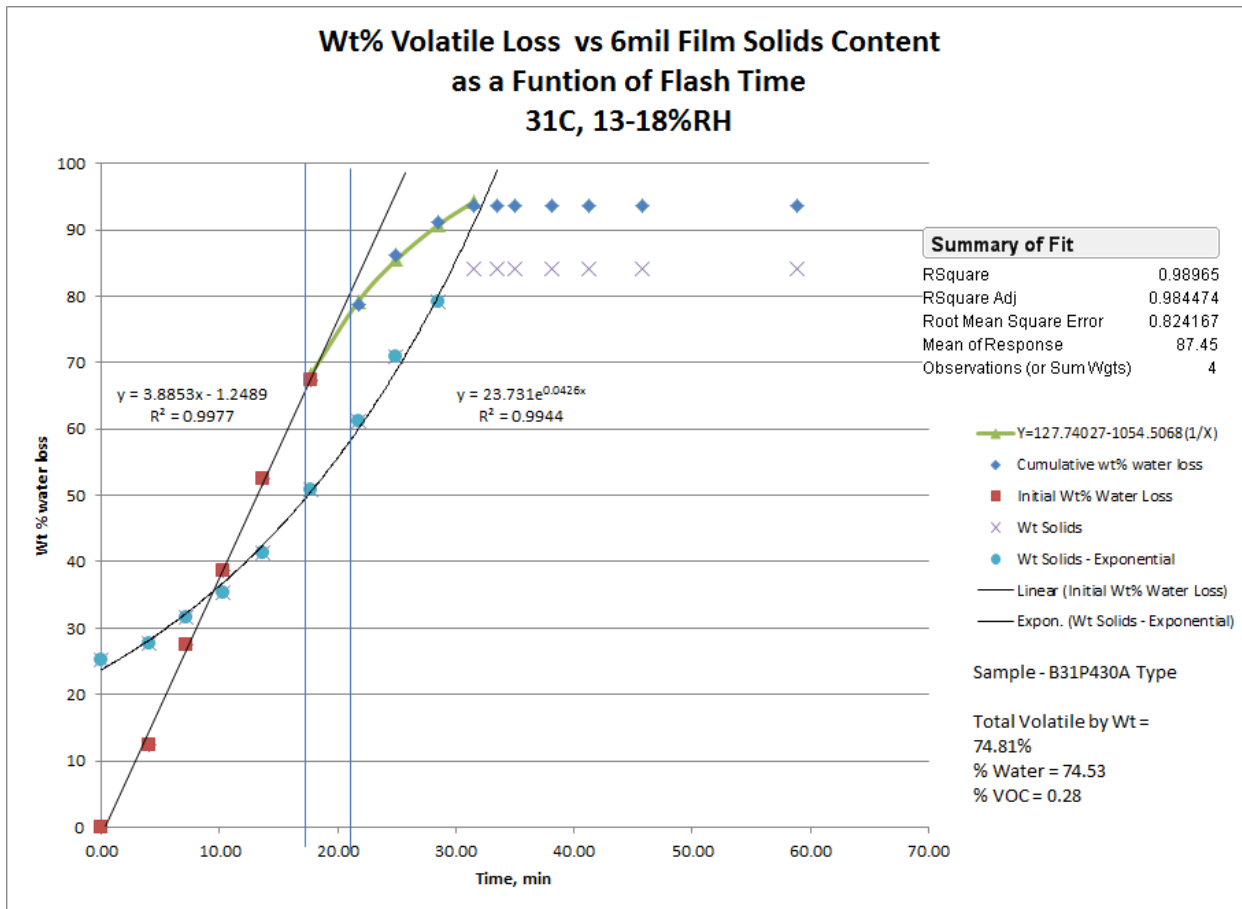


Figure 2. Comparison of Volatile Loss Vs Solids Content for Aqueous UV-Curable Polymer 1; Solids and Volatile Loss Parameters: 6 mil film on Plate Glass; Flash at 31 ° C, 12-18% RH; 100 L/hr. Air Flow into Environmental Chamber.

Figure 3 compares percent weight loss as a function of time for UV-Curable Polymer 1 and a second UV-Curable Polymer 2. The two polymers display similar evaporation phases with the following differences noted: (1) the linear evaporative dry phase of UV-Curable Polymer 2 occurs at a slower rate than that for UV-Curable Polymer 1; (2) UV-Curable Polymer 2 retains less final amount of volatile over the period tested.

Combined Gravimetric Analysis and Evaporative Dynamic Oscillation (EDOT Analysis)

Figure 4 displays weight loss, solids evolution, and complex modulus evolution of UV-Curable Polymer 1 as a function of time. The data shows an interesting correlation between the first inflection

area of the complex modulus curve and the linear-reciprocal transition in the weight percent volatile loss curve. Our hypothesis is that the linear-reciprocal transition represents the end of a purely vapor pressure controlled evaporation mechanism and perhaps the initiation of particles approaching nearest neighbor distance in the film formation process mechanism. The reciprocal / diffusion transition

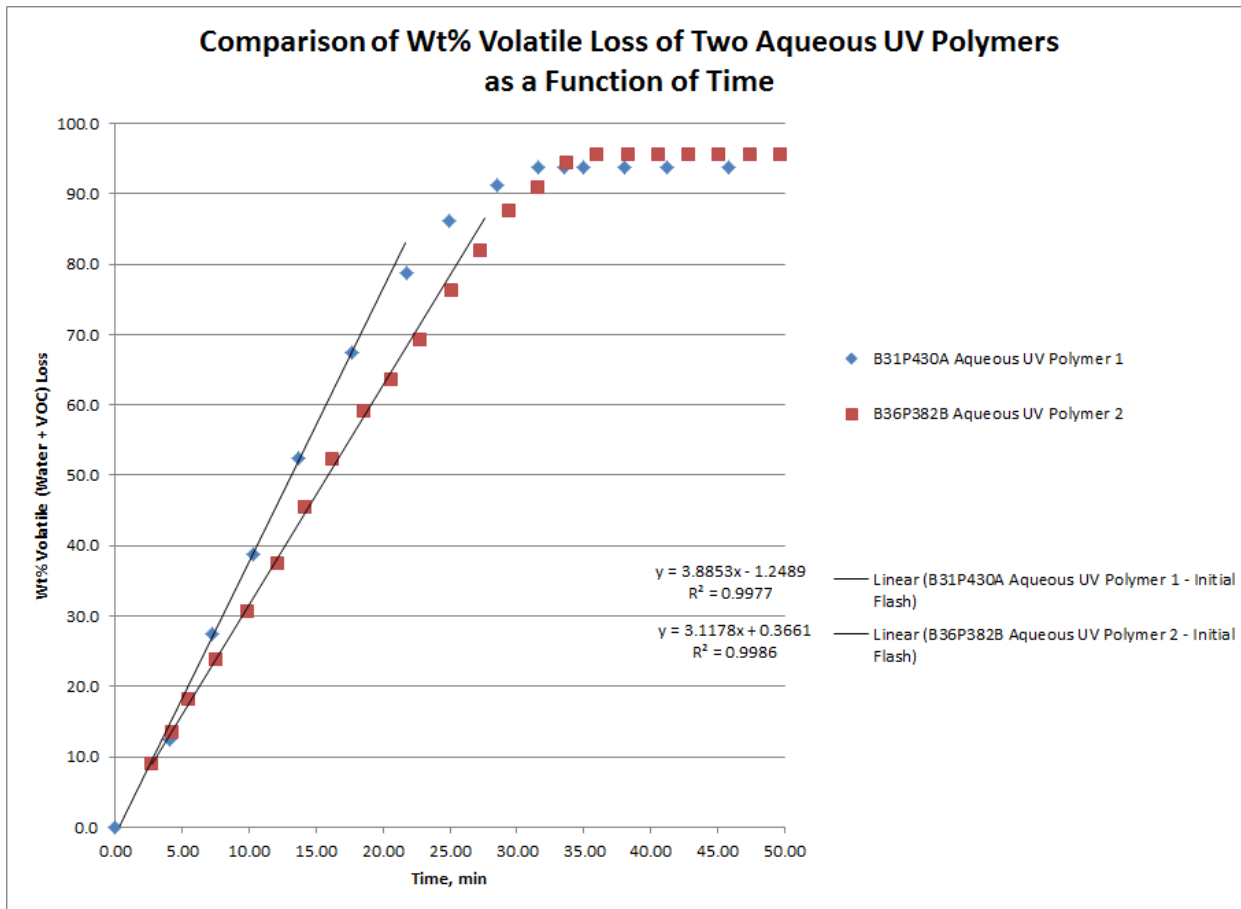


Figure 3. Comparison of Volatile Loss for Two Aqueous UV Polymers; Volatile Loss Parameters: 6 mil film on Aluminum or Glass Panel; Flash at 29 - 31 ° C, 12% - 18% RH;100 L/hr. Air Flow into Environmental Chamber.

is hypothesized to represent the nearest neighbor particle distance and the beginning of particle compaction, deformation, and coalescence. Figure 5 displays weight loss, solids evolution, and complex modulus evolution of UV-Curable Polymer 2 as a function of time. Table 1 summarizes the dry and film formation process differences between the two polymers. The data indicates that UV-Curable Polymer 2 reaches a higher non-volatile content and has a lower complex modulus than UV-Curable Polymer 1 in the dry stage before the polymers would be subsequently UV-cured. This may result in improved cure efficiency for UV-Curable Polymer 2 and subsequently improved film properties compared to UV-Curable Polymer 1. It is interesting to note that we found significantly improved MEK double rub resistance for UV-Curable Polymer 2 compared to UV-Curable Polymer 1.

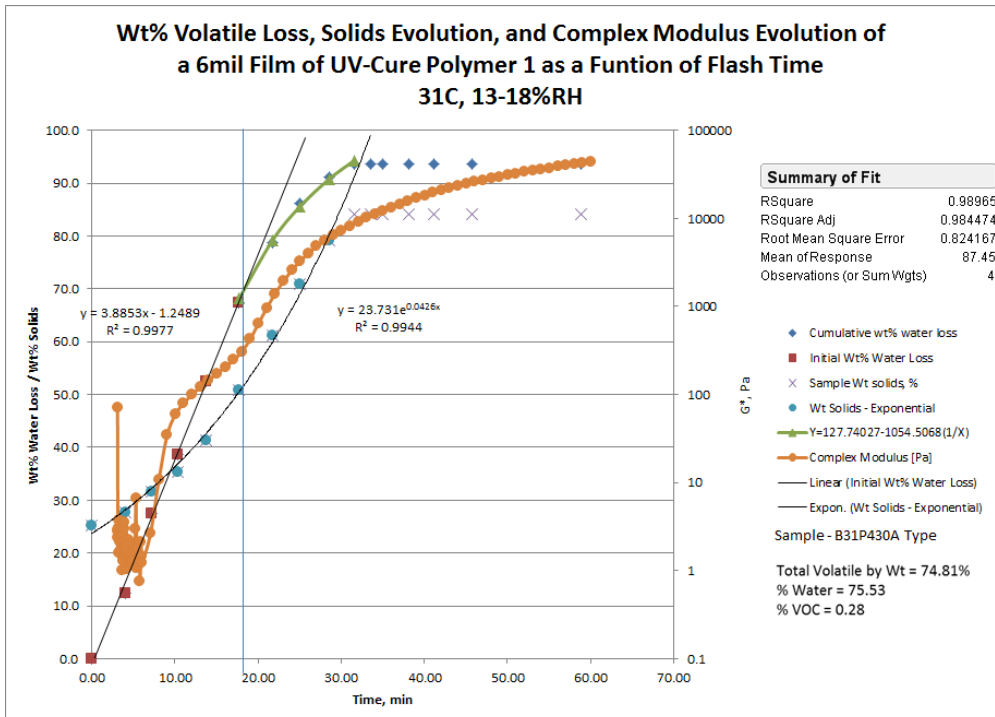


Figure 4. Comparison of Volatile Loss, Solids Evolution, and Complex Modulus (G*) for Aqueous UV Coating Polymer 1; Solids and Volatile Loss Parameters: 6 mil film on Plate Glass; Flash at 31 ° C, 12-18% RH; 100 L/hr. Air Flow into Environmental Chamber; G* Parameters: 150 micron Film Thickness, 30 C, 12%RH, 50L/hr Air Flow

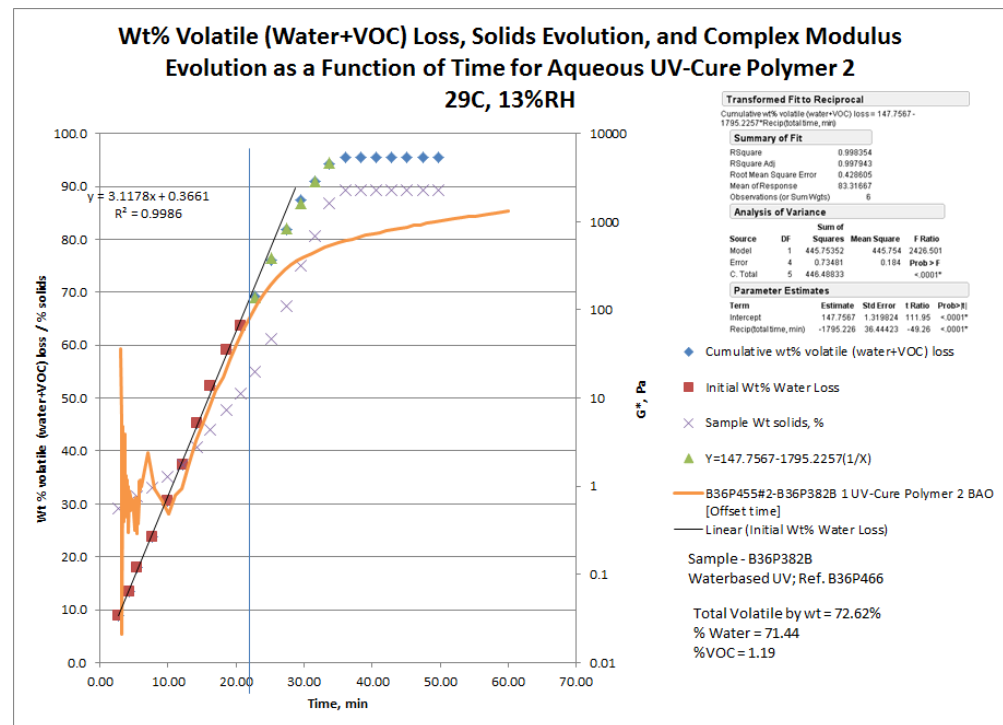


Figure 5. Comparison of Volatile Loss, Solids Evolution, and Complex Modulus (G*) for Aqueous UV Coating Polymer 2; Solids and Volatile Loss Parameters: 6 mil film on Plate Glass; Flash at 29 ° C, 13% RH; 100 L/hr. Air Flow into Environmental Chamber; G* Parameters: 150 micron Film Thickness, 30 C, 12%RH, 50L/hr Air Flow

Table 1. Comparison of Dry and Film Formation Differences Between UV-Cure Polymers 1 and 2 from Figures 3 - 5.

Polymer	UV-Curable Polymer 1	UV-Curable Polymer 2
Initial Dry Rate, grams volatile loss/min	3.89	3.12
Solids Content at Linear / Reciprocal Transition Region	≈52%	≈54%
Solids Content at Reciprocal / Diffusion Transition Region	≈84%	≈90%
Residual % Volatile Remaining at end of test period	≈6%	≈4.5 %
G* at Linear / Reciprocal Transition Region	≈308 Pa	≈56 Pa
G* at Reciprocal / Diffusion Transition Region	≈8229 Pa	≈607 Pa

Impact of Addition of Nepheline Syenite Mineral addition to UV-Curable Polymer on Pre-UV Light Exposure Properties

Figure 6 displays the impact of Nepheline Syenite addition on the complex modulus of a UV-Curable Polymer. Figure 7 is an overlay plot comparing the impact of 12.20% Nepheline Syenite addition on percent weight volatile loss, solids evolution, and complex modulus evolution for the UV-Curable Polymer. Table 2 summarizes the impact of Nepheline Syenite addition on dry and film formation properties as a function of pigment concentration.

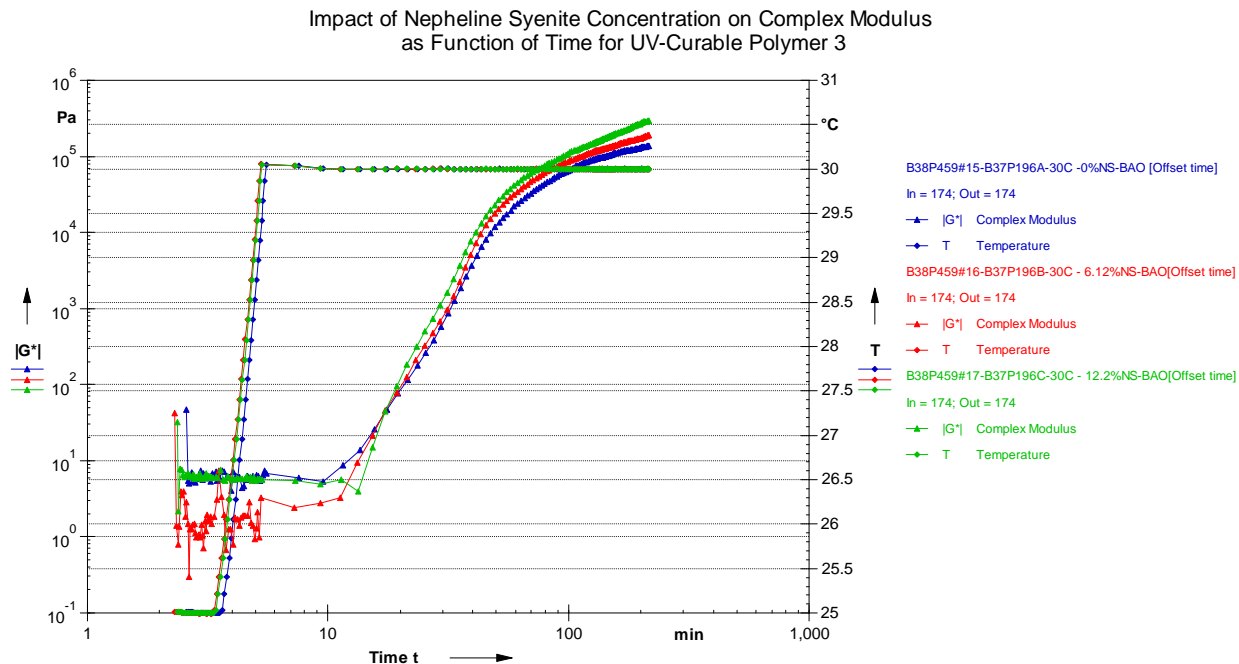


Figure 6. Impact of Nepheline Syenite (NS) Concentration on Complex Modulus Evolution of UV-Curable Polymer 3 as a Function of Time; Blue Curve – 0% Wt NS; Red Curve – 6.12% Wt NS; Green Curve 12.2% Wt NS on Total Resin Solids; G* Parameters: 150 micron Film Thickness, 30 C, 12%RH, 50L/hr Air Flow

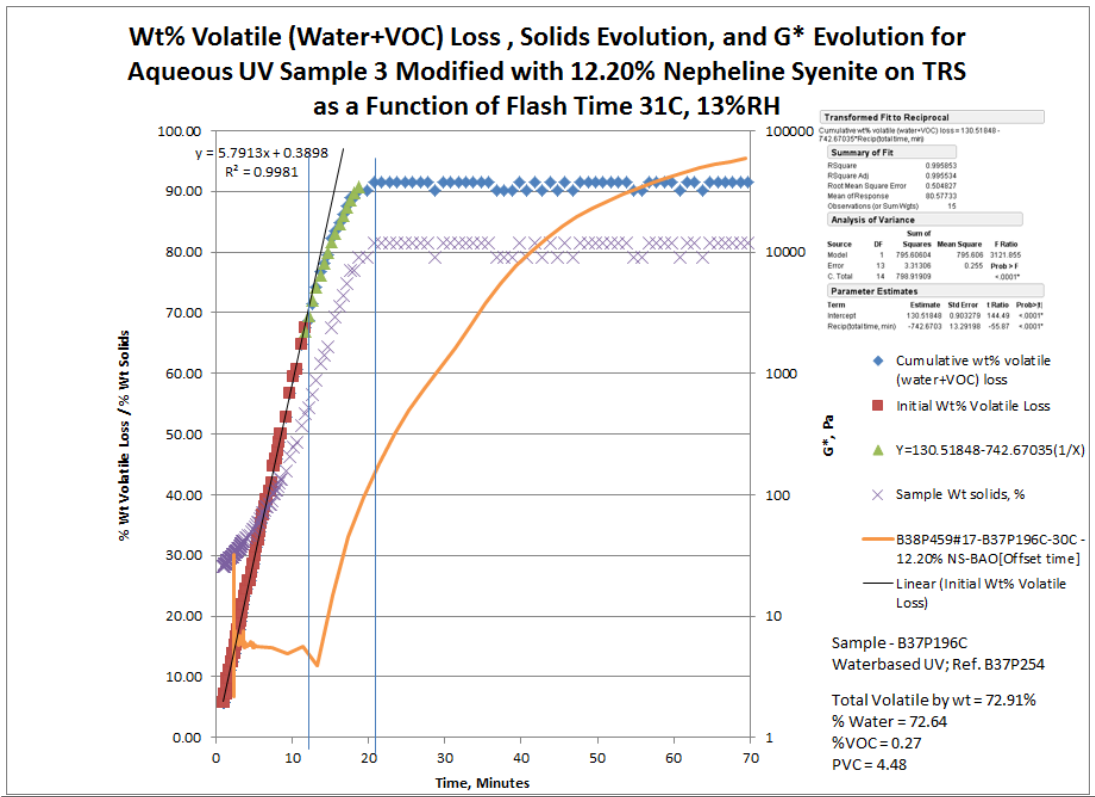


Figure 7. Comparison of Volatile Loss, Solids Evolution, and Complex Modulus (G*) for Aqueous UV Coating Polymer 3 Modified with 12.20% Nepheline Syenite on Total Resin Solids; Solids and Volatile Loss Parameters: 6 mil film on Aluminum Panel; Flash at 31 ° C, 13% RH; 100 L/hr. Air Flow into Environmental Chamber; G* Parameters: 150 micron Film Thickness, 30 C, 12%RH, 50L/hr Air Flow

Table 2. Impact of Nepheline Syenite Loading on Aqueous UV-Curable Polymer Dry and Film Formation Prior to UV Light Exposure	0	6.12	12.20
Nepheline Syenite Wt % on Total Resin Solids	0	6.12	12.20
Calculated Formula PVC	0	2.20	4.28
Initial Dry Rate, grams volatile loss/min	5.51	5.66	5.79
Solids Content at Linear / Reciprocal Transition Region	≈48%	≈46%	≈53
Solids Content at Reciprocal / Diffusion Transition Region	≈87%	≈81%	≈82
Residual % Volatile Remaining at ≈70 Min Dry Time	≈6%	≈8 %	≈8%
G* at Linear / Reciprocal Transition Region	≈9 Pa	≈3 Pa	≈6 Pa
G* at Reciprocal / Diffusion Transition Region	≈115 Pa	≈125 Pa	≈181
G* at ≈70 Min Dry Time	≈32520 Pa	≈45590	≈58910

The data of Figures 6 and 7 and Table 2 show that Nepheline Syenite has the net effect of increasing the rate of the initial evaporative dry of the sample while maintaining a lower complex modulus for a slightly longer time period. Further the data indicates that as Nepheline Syenite concentration increases, film formation modulus at the reciprocal / deformation / chain diffusion stage of the film formation process increases slightly as well. Finally, the data indicates that the final modulus (e.g., stiffness) of the film before UV exposure is increased as well (e.g., at approximately the 70 minutes time frame). The data seems to indicate that Nepheline Syenite incorporation results in the net effect of slightly increased amounts of residual volatile remaining in the film. It is interesting to compare the thermal response of the 0% and 12.2% Nepheline Syenite modified samples after the samples have aged 24 hours without UV curing. Figure 8 shows this comparison. The data indicates that addition of 12.2% Nepheline Syenite stiffens the polymer to the point that the product does not display an elastic-viscous transition, whereas the polymer without Nepheline Syenite does display this transition. Further, the 12.2% Wt Nepheline Syenite modified polymer displays a rubbery plateau region compared to a viscous flow region for the non-mineral modified sample. These results indicate that Nepheline Syenite has a significant stiffening effect on the pre-cure properties of the polymer.

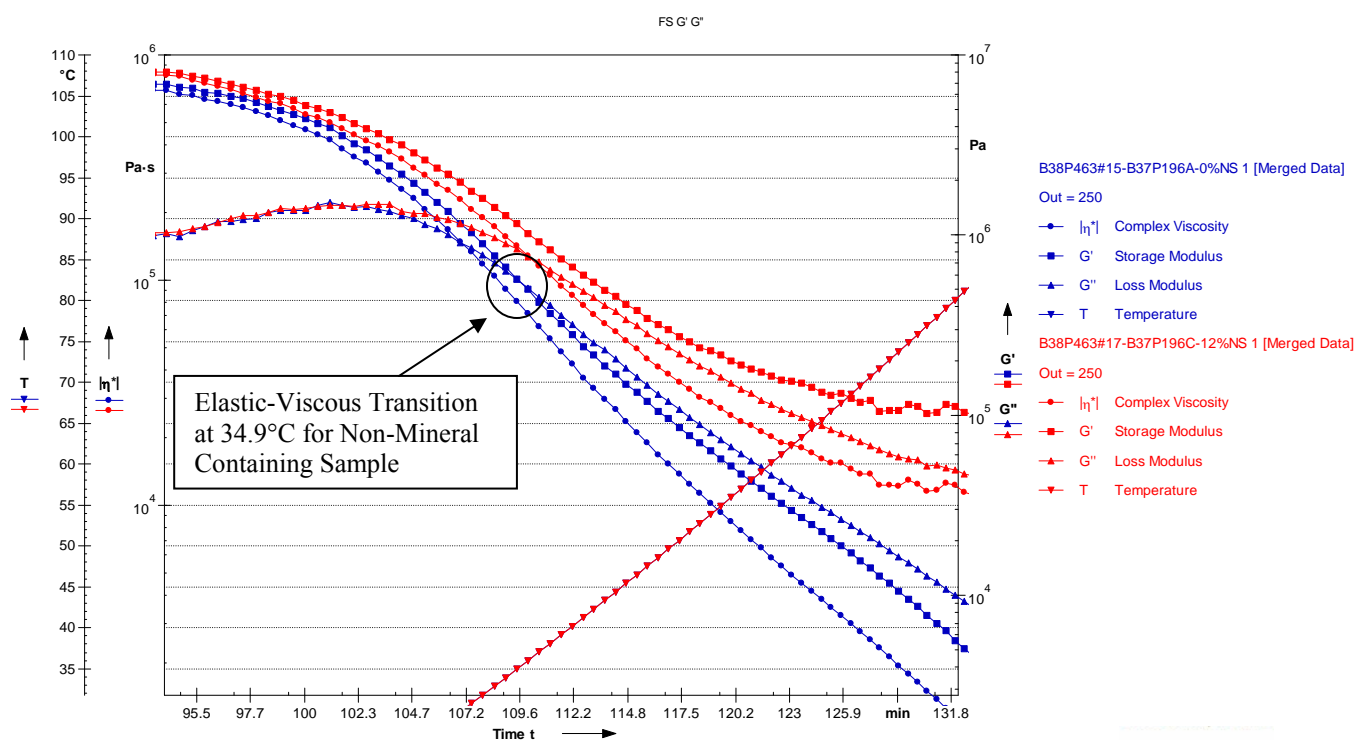


Figure 8. Pre-UV-Exposure Temperature Sweep Thermal Response Comparison between UV-Curable Polymer 3 Modified with 12.2% Nepheline Syenite (blue curves) versus Mineral-free Polymer (red curves) after Films aged 24 hours at 25C

Conclusions

It has been shown that Evaporative Dynamic Oscillation (EDOT) in combination with thermogravimetric techniques offer a powerful methodology to study film formation of aqueous UV-Curable Polymers with and without mineral modification. The results of this study show that aqueous

UV-Curable Polymers demonstrate a three-stage mass dry and film formation process; (1) free evaporation of volatiles represented by a linear weight volatile loss profile; (2) followed by a slower dry period represented by a reciprocal time dependency; and (3) a very slow drying final dry process that represents the compaction, deformation, and coalescence stage of the dry process. EDOT offers unique insight into the evolution of properties of the film as the film dries, and yields an indication of the energy required for coalescence. Finally, the results of this study indicate that addition of Nepheline Syenite to the aqueous UV-Curable Polymer moderately impacts film modulus during the early stages of dry and film formation, and more greatly impacts modulus at the later stages of film formation. Also, Nepheline Syenite mineral appears to greatly improve stiffness of the polymer before UV exposure to UV radiation.

Bibliography

1. Obie, R.T. "Applied Rheological Studies of a Coatings Chemist" Piedmont Society for Coatings Technology, Spring Mini Trade Show, Keynote Address, April 2009
2. Obie, R. T. "Novel Technology Tools for the Development of Low VOC Interior and Exterior Coatings and Stains with Solvent-Like Application and Performance Characteristics" AC Series, Coating Wood and Wood Composites – Designing for Durability, July 23 – 25, 2007; Seattle WA
3. Practical Wood Coatings Formulation and Application Course; Copyright, Wood coatings Research Group, Inc. <http://www.woodcoatingsresearchgroup.com/training.html>
4. Allcock, H. R.; Lampe, F. W. Relationship between Macromolecular Structure and Properties. *Contemporary Polymer Chemistry*; 2nd Ed.; Copyright 1990, 1981, Prentice-Hall, Inc. A Division of Simon & Schuster, Englewood Cliffs, New Jersey 07632, ISBN 0-13-170549-0, pp. 536-552.
5. Allcock, H. R.; Lampe, F. W. The Scope of Polymer chemistry. *Contemporary Polymer Chemistry*; 2nd Ed.; Copyright 1990, 1981, Prentice-Hall, Inc. A Division of Simon & Schuster, Englewood Cliffs, New Jersey 07632, ISBN 0-13-170549-0, pp. 1-20.
6. Wagner, H.L. The Mark-Houwink-Sakurada Equation for the Viscosity of Linear Polyethylene. *J. Phys. Chem. Ref. Data*. **1985**, *14*, 611-617.
7. Hoy, K., "Estimating the Effectiveness of Latex Coalescing Aids." *J. Coatings Technology*; Vol. 45, No. 579, 1973.
8. Vanderhoff, J. W. "Latex Film Formation", *Polymer News*, (1977), 3(4), 194 - 203
9. Mecurio, A; Kronberger, k.; and Friel, J.; "Aqueous Gloss Enamels", *J. Oil Col. Chem. Assoc.*, 1982, 65, 227 – 238.
10. Winnik, M. A.; Yang, Y.; Haley, F.; "Latex Film Formation at the Molecular Level: The Effect of Coalescing Aids on Polymer Diffusion." *J. Coatings Technology*, 64(811), 51 (1992).
11. Juhue, D.; Wang, Y.; Winnik, M.; Haley, F.; "Influence of a Coalescing Aid on Polymer Diffusion in Poly (butyl Methacrylate) Latex Film", *Makromol. Chem., Rapid Commun.* 14, 345 – 349 (1993).
12. *News on Oxygenated Solvents*, "Understanding Film Properties of Industrial Latexes Part I", Dow Chemical Technical Bulletin, April, 1996.
13. Hoy, K. "Coalescence and Film Formation From Latexes" *J. Coatings Technology*, 68(853), 1996.
14. Eckersley, S. T., Rudin, A.; "Drying behavior of acrylic latexes", *Progress in Organic Coatings*, 23 (1994) 387 – 402.
15. *News on Oxygenated Solvents Dow Chemical Technical Bulletin*, December 1992 "Using Coupling Index Values to Select Optimum Coupling Solvents for Water-Reducible Coatings."
16. Hazel, N. J.; "Water-based Coatings; A New Model For Coupling Solvents Part 1: Why is BGE So Good?" *Surface Coatings International*, 1994(5), Page 213.
17. Obie, R.T. "Evaporative Dynamic Oscillation, (EDOT), A Versatile Technique for Insitu Characterization of Polymers and Coatings" Proceeding American Coatings Conference, April 12 – 14, 2016 Indianapolis Indiana.
18. Patent Pending, Wood Coatings Research Group