

**EFFECT OF ZIRCONIUM INSOLUBILIZERS ON
SILICA COATING RHEOLOGY**

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ABSTRACT

Zirconium species are used in inkjet coatings to improve the waterfastness of the coating and print quality by reducing the ink spread and excessive ink migration into the coated layer. We investigated the effect of two anionic zirconium complexes, ammonium zirconium carbonate (AZC) and potassium zirconium carbonate (KZC), on the rheology of a gel-silica/PVOH inkjet coating. Both zirconium species had an influence on the rheological properties of the coating and its components. The interactions between the zirconium salts and the coating were found to be weak and lessened as the shear rate increased. The viscous modulus was higher than the elastic modulus indicating more fluid like behavior.

INTRODUCTION

The ink jet market is fast growing because ink jet printing can provide special consumer needs such as high image quality and photographic quality at relatively low cost (1). The printing technology as well as the specialized ink (2-5) and the substrate (6-9) are all necessary for this high quality printing. The inks used contain relatively high amounts of water (1), approaching 65% to 90%. Water based inks are inexpensive, and, more importantly, do not plug the print head (1). Water containing inks require substrates that have a high and open surface porosity so that the ink can be held on the surface and dry quickly due to fast absorption right beneath the substrate (6). These requirements are met with special coated papers (6-14). A typical inkjet coating formulation includes silica-based pigments, polyvinyl alcohol binders, and additives. Silica-based pigments are unique in structure and provide the paper substrate an open, porous structure (10-15). Polyvinyl alcohol is a strong enough binder to hold silica pigments with high surface area on the substrate, providing the best ink holdout along with silica-based pigments (15). Additives are also used to improve print quality and water fastness (16). Among the additives, ammonium zirconium carbonate is widely used (16-19). (Is potassium carbonate widely used in inkjet applications?) Unfortunately, these coating formulations have special rheological problems (17) that cause problems and defects during the coating's application; some problems are shear blocking during the screening process and film splitting at the exit nip of the size press. Studies are continuing to explore the

rheology of silica/polyvinyl alcohol-containing ink jet coatings, and significant progress has been achieved in regards to silica and polyvinyl alcohol coatings (20,21).

BACKGROUND

Inkjet Coating Additives

Zirconium compounds are frequently used as additives or insolubilizers in coating formulations. They are used in inkjet formulations to improve dot resolution and water fastness. The improvement results from the association interactions between the additive and the ink. As a result, a bleed-free, water resistant colorant forms without too much absorption into the substrate (17)

Ammonium zirconium carbonate (AZC) and potassium zirconium carbonate (KZC) insolubilizers are commonly used in paper and paperboard coatings because they offer various advantages over other commercial insolubilizers. First, they give good results in anionic coatings and have a broad tolerance to pH changes since they are anionic in nature. Second, they do not require a long cure time. Curing starts and is completed very quickly when the coating formulation applied on the substrate surface starts drying; it does not require a high temperature. Third, they provide excellent water resistance to paper coating binders, improve printability of the paper, and reduce print mottle (16,18,19).

Zirconium is a widely distributed element and is ranked 18th in abundance in the earth crust (22). It is in Group IV in the Periodic Table. It has a valence of 4, a small ionic radius, and a high coordination number. Because of the high charge to ionic radius ratio, the aqueous chemistry of zirconium is characterized by hydrolysis and the presence of anionic species. Zirconium can form cationic, anionic, or neutral polymeric

complexes in the presence of some ligands such as hydroxyl, phosphate, carbonate, sulfate, and nitrate ions. Zirconium in these complexes is found in the form of hydroxy-bridged polymers (23). The chemical structure of AZC's is shown in **Figure 1**.

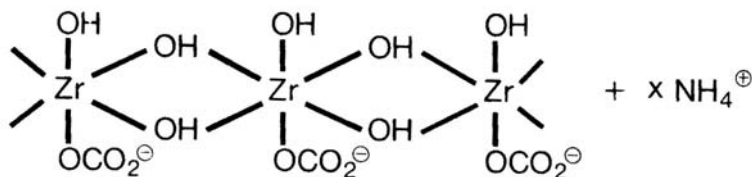


Figure 1: Chemical Structure of Amonium Zirconium Carbonate

Zirconium complexes contain oxygenated sites, and this enables them to react with oxygen-containing organic polymers as well as carboxylated latexes (24). Zirconium can crosslink with organic polymers containing carboxyl and/or hydroxyl groups (24,25). These crosslinking reactions are what permits the polymers to form water resistant structures and insolubilize in water. When added to paper coating formulations, zirconium complexes crosslink with paper coating binders containing either carboxyl or hydroxyl groups. The result is modified coating rheology, and a water resistant coating film on the substrate after drying (24). The reaction mechanism of AZC with hydroxyl groups and carboxyl groups are shown in **Figure 2** and **Figure 3**, respectively.

Bonds formed between carboxyl groups on organic polymers, such as carboxyl-methylcellulose, and zirconium ions, are strong and durable. However, reaction conditions should be controlled to achieve optimum efficiency and to avoid precipitation and gellation. On the other hand, bonds formed between organic polymers with hydroxyl

groups, such as starches, polyvinyl alcohol, and cellulose derivatives, and zirconium ions are through a hydrogen bonding mechanism (23). This type of interaction may result from very weak to fairly strong bonding depending on the polymer solution of zirconium species. Thus, the choice of zirconium species depends on the coating system (23). Zirconium compounds exist in aqueous and solvent solutions as polymeric species, and polymerization is through hydrogen bonding at oxygen sites on the zirconium. The chain length of zirconium species can be varied by altering temperature, pH, or chelating agent; all of these can have a significant effect on the crosslinking reaction (26).

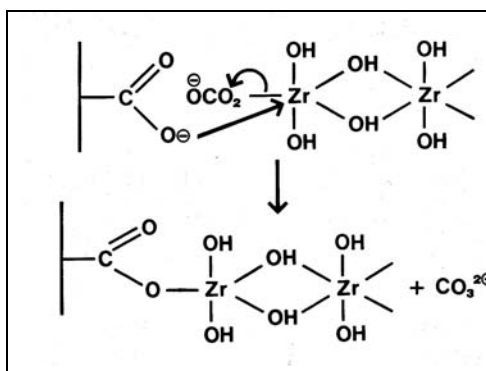


Figure 2: Carboxylic bonding Mechanism.

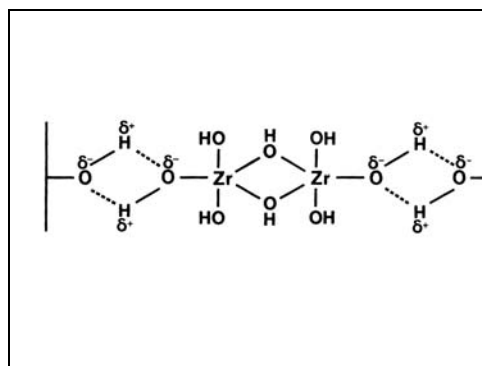


Figure 3: Hydrogen Bonding Mechanism.

Zirconium complexes used as insolubilizers for paper/paperboard coating pigments are extremely sensitive to pH and temperature changes (27). Dilution initiates rapid polymerization, hydrolysis, and the precipitation of hydrous zirconia. These unwanted reactions can be observed as increased viscosity or hazy solutions. Therefore, it is important to adjust the coating formulation's pH as close as possible to the zirconium species used in the formulation. Also, the affinity of zirconium for oxygenated paper coating components does not show any preference for specific components and will interact with any chemical that has the proper reactive sites. Therefore, the order of

zirconium addition into paper coatings is important. If it is added first or midway into the preparation of a formulation, premature bonding may result at undesired sites, leading to less available reactive zirconium. It is better to add the zirconium salts to the coating formulation last to avoid these undesired interactions (27).

AZC is the most widely used insolubilizer in paper coatings because of its versatility (16,28). It works best under alkaline conditions and is very compatible with alkaline coating pigments, such as CaCO_3 and satin white commonly used in the paper industry, while other commercial insolubilizers such as glyoxal and aldehydes require acidic conditions to produce catalytic condensation reactions with coating binders. AZC is an alkaline salt of zirconium and is used as an aqueous solution. There are ammonium cations, anionic hydroxy-bridged zirconium polymers that contain carbonate in the zirconium solution. Excess carbonate ions in the solution are also present to improve the stability of the solution; the concentration of carbonate ions can be varied to modify the molecular size distribution and properties of the AZC solution. Carbonate ions are very sensitive and unstable to dilution, pH changes, and temperature changes. They require an alkaline environment and are stable at a pH of 9-10. If the solution is excessively diluted, the pH changes, or the temperature changes, then carbonated hydrous zirconia may form that appears as a gelatinous solid. Stability of the solution can be improved by the addition of tartrate ions that act as chelating ligands (16,28).

If AZC decomposes in the presence of organic binders, reactions occur between the reactive sites on the zirconium and the functional groups on the binders (16). As water evaporates from the AZC solution, CO_2 from CaCO_3 and ammonia are released from the solution; the resultant chemical is an insoluble, carbonated hydrous zirconia of

variable composition. This is dependent on the drying conditions. If this occurs, reactive sites form on the zirconium that can enter into crosslinking reactions with the functional groups of the paper coating binders; the result is crosslinked binders that are insoluble in water (16).

AZC in solution generally does not react with functional groups of coating binders because of its preference for carbonate ions in the solution (23). However, any condition that causes AZC to decompose may result in interactions of zirconium with the coating components in the formulation mostly due to hydrolyses of oxygenated zirconium species. Those interactions are mostly weak and are due to hydrogen bonding generated on zirconium by hydrolyses. This, of course, influences the rheology of the coating formulation; the rapidity of the reaction may produce structural changes in the coating. At low shear rates, a viscosity increase may be observed. But, these interactions are weak and easily broken at higher shear rates (23).

The crosslinking reaction of AZC with coating binders upon drying are dependent on the functional groups in the binder, the conformation of the polymer chains, and the rate of decomposition of the AZC (23).

The chemistry and reaction mechanisms of KZC with coating binders and coating components are very similar to that of AZC. The ammonium cations are replaced by potassium cations in the zirconium complexes to produce ammonium-free, odorless insolubilizers.

Ryu et al. (17) studied AZC, zirconium ammonium acetate (ZAA), and poly-DADMAC in a typical silica/PVOH inkjet formulation, investigating their effect on coating rheology and print quality. They reported steady shear viscosity and yield stress

increase with the addition of all 3 additives; AZC had the smallest effect, while poly-DADMAC had the highest affect. They concluded that this is the result of the cationic structure of poly-DADMAC and ZAA. This causes functional groups of each additive to react with either the oxygen of the surface siloxane or the silanol groups in the silica network to enhance viscosity more readily than AZC. AZC is anionic in nature, and therefore does not interact as much with the silica/PVOH structure as the cationic poly-DADMAC or neutral ZAA. If the increase in viscosity is significant, there could be a need to lower the solids content of the formulation, leading to coating quality problems and higher drying costs. They also found a significant increase in the elastic modulus of the inkjet coatings where the 3 additives are added into the coating formulation. An increase in the elastic modulus for a coating formulation is not desired since that may cause coating application problems like scratches, skips, and stalagmite formation. The elastic modulus of each coating was higher than the viscous modulus, suggesting gel-like behavior of silica/PVOH sample. Gel-like behavior is more pronounced with all 3 additives, poly-DADMAC giving the highest gellation. They also investigated the effect of additive addition level on the rheology of the inkjet coating and concluded that the initial addition level (0.2 parts on dry pigment) increased the elastic modulus drastically, while this increase was constant, but at a lower rate for poly-DADMAC (What?). On the other hand, there was a slight increase in elastic modulus of the coatings for increasing addition amounts of AZC and ZAA in the formulation, after a drastic increase in their initial addition level.

The objectives of this study were:

- a. to determine the effect of zirconium-containing insolubilizers on rheology of inkjet paper coatings,
- b) to establish a methodology to determine the optimum addition level of zirconium containing insolubilizers from the rheological perspective, and,
- c) to determine if the type of zirconium complex influences the rheological behavior of a silica-based inkjet coating formulation.

EXPERIMENTAL DESIGN

Coating Preparation

A 30 % by weight, highly hydrolysed, low molecular weight, cold-water soluble polyvinyl alcohol solution (Airvol-203S) was prepared by adding dry PVOH into 40- 45 °C distilled water under agitation. Mixing was continued for one hour. The speed of the mixer was adjusted to maintain a slight vortex without incorporating air. There were no defoamers or antifoams used during the preparation because of their possible effect on the rheology of the PVOH; still an excessive amount of foam was present in the solution. To eliminate the foam from the solution, the PVOH solution was kept overnight and the foam accumulated on the top of the solution was collected and discarded the next day. The resultant solution was clear and foam-free. AZC (Bacote 6200) and KZC (ZirmelM) were added into smaller batches of PVOH solution at six different addition levels under low agitation. The pH of the solution was maintained at 6.0 after the preparation of the solution. Addition levels of these cationic additives ranged from 5 to 10 % of dry binder weight, with a 1 % difference at each level. Before the addition of AZC and KZC, the pH of the solution was maintained in a slightly acidic side, since any adverse effect of the insolubilizer on the binder or strong interactions between the additive and PVOH would

be observed most dramatically at alkaline conditions. The highest practical solids content was 30% for this particular PVOH, and the same concentration of solution was prepared for coating make up as well.

The gelled silica pigment was dispersed into 25 °C distilled water with a high-speed disperser. Dispersing under high shear rate was continued for 40 minutes. The solids content of the silica gel pigment slurry (Grace, SyloGel P612) was 25 %, which is about the critical solids content for this particular pigment. AZC and KZC were added into small batches of the gelled silica slurries at six different addition levels under agitation. The pH of the slurry was not adjusted prior to crosslinker addition. The addition levels of AZC and KZC were determined on the basis of dry binder content in a typical inkjet formulations and ranged from 5 to 10 %, at 1 % increments.

One inkjet coating formulation was prepared by mixing 40 parts PVOH into 100 parts gelled silica under agitation, and AZC and KZC were added in the above amounts in small batches. (EXPLAIN WHY)

Characterization of Rheological Properties

The viscosity and viscoelastic parameters of the coating were characterized by a Brookfield RVT viscometer (#3 spindle, 20 rpm) and a Rheometrics dynamic stress (controlled-stress) rheometer (DSR5000), respectively.

To distinguish the effect of the cationic additives on the PVOH and the silica, rheological studies were also performed on them separately. Prior to Brookfield and rheometrics measurements, all samples were left under agitation. Agitation prevented the silica pigment from settling out; the same shear protocol was used with the PVOH solutions, ink jet coatings, and silica slurries.

Steady and dynamic oscillatory rheology measurements were performed using a Rheometrics dynamic stress rheometer (DSR5000). Double couette geometry was used for the measurement of silica, PVOH, and the coatings, because the double wall couette geometry enabled the lowest shear rates along with the most sensitive measurements. Although addition levels of AZC and KZC 5 to 10 %, at 1 % increments, and rheometrics tests were performed for each addition level, 5%, 8% and 10 % addition levels were included in figures (What are you trying to say?).

Initial tests were performed to determine the strain percents of each sample before performing the dynamic stress sweeps. All the samples were pre-sheared at 10% strain with creep tests for 90 seconds. Then, all the samples were tested with the same pre-shear history. While a 5-minute test delay was used for the PVOH and the coating for loading history following the preshearing, a delay time was not used for the silica suspension because of the rapid settling of particles in the slurry. Following the pre-shearing and test delays as described, steady-shear experiments were performed to determine shear rate dependent viscosity and oscillatory measurements to determine the microstructure of the tested samples.

RESULTS AND DISCUSSION

Figure 4 shows representative Brookfield viscosity (what is shear rate?) curves as a function of insolubilizer type (AZC or KZC), and additive addition level for a 23% gel-silica/PVOH inkjet coating formulation. While the Brookfield viscosity did not significantly change and remained constant for all addition levels of KZC, it significantly increased (~15%) with increasing addition levels of AZC. **Figure 5** shows representative steady shear curves for PVOH solutions containing different addition levels of AZC and

KZC insolubilizers. The steady shear viscosity curves exhibited a slight increase as the addition level of AZC increased. As the addition levels of KZC increase from 5% to 10% on dry binder weight, the increase in steady shear viscosity is steeper and more apparent than that of AZC addition. At the lowest addition level of KZC (5% in dry binder weight) and for all AZC addition levels, the low steady shear viscosity for PVOH remained essentially constant with increasing stress. In other words, the drops in steady shear viscosity with shear stress for the given additives and their addition levels were fairly small. At the highest KZC addition level (10% on dry binder weight), steady shear viscosity is initially considerably higher. As the applied shear stress increases, the decrease in viscosity is considerable for this solution. There seems to be a yield stress behavior for the PVOH +10% KZC solution at about 0.2 dyne/cm^2 suggesting a structure breakdown of the solution at the given stress value. This behavior may be true for all other solutions in the stress range between 0.1 dyne/cm^2 and 0.2 dyne/cm^2 . All the viscosity curves at low shear rates indicate, pseudoplastic flow of the PVOH regardless of the additive type and the addition level of the additive.

Critical stress (yield stress) values, where a viscosity curve exhibits a sharp change with increasing shear rate and/or shear stress, were not completely apparent at addition levels below 10%, indicating additive type and addition level did not influence the structure of the PVOH solution significantly at these addition levels.

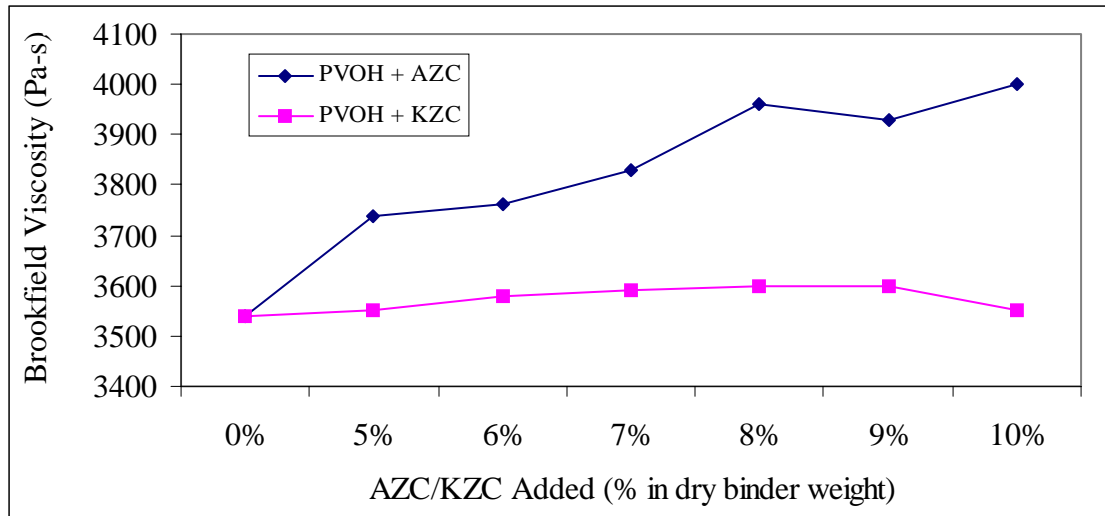


Figure 4. Brookfield Viscosity (shear rate?) of PVOH at Different Addition Levels of AZC & KZC.

Figure 6 and Figure 7 show the viscous and elastic modulus of PVOH solutions at different addition levels of AZC and KZC as a function of shear stress where frequency is constant at 1 s^{-1} . The viscous modulus was 100x higher than the elastic modulus, suggesting a fluid like behavior. Further tests as a function of frequency were not needed for this reason. Because the samples exhibited a fluid like behavior, the structure recovery from the elastic component of the material could not be observed for these samples. Both elastic and viscous moduli of the samples were constant and not influenced by the insolubilizer type or addition amount.

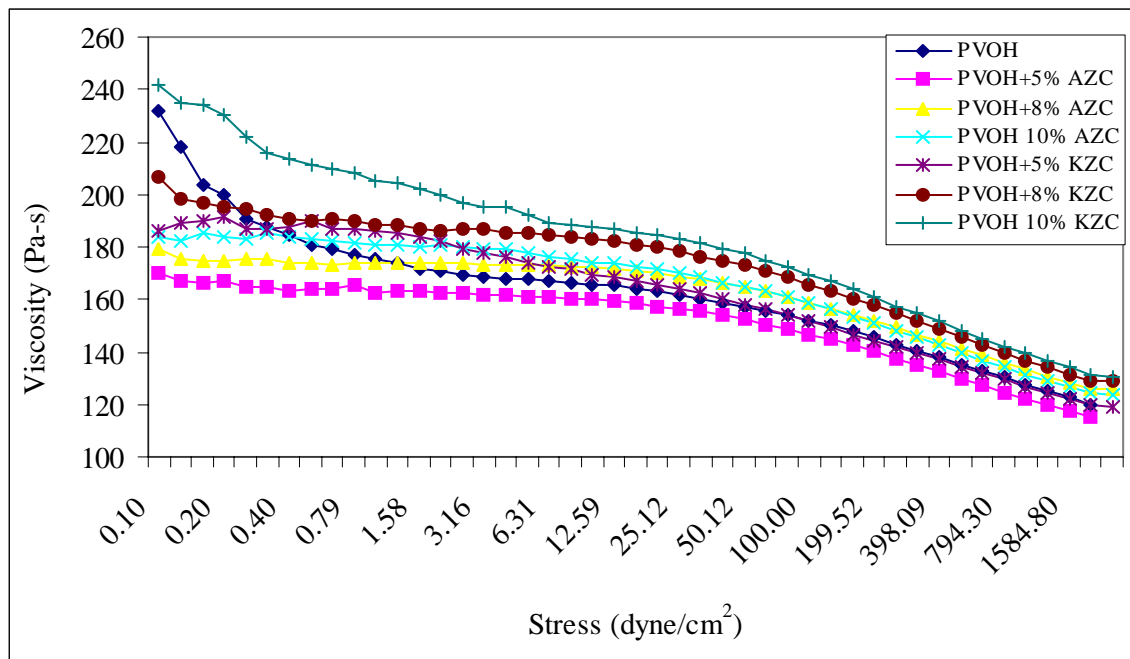


Figure 5. Steady Shear Viscosity of PVOH as a function of shear stress at Different Addition Levels of AZC & KZC.

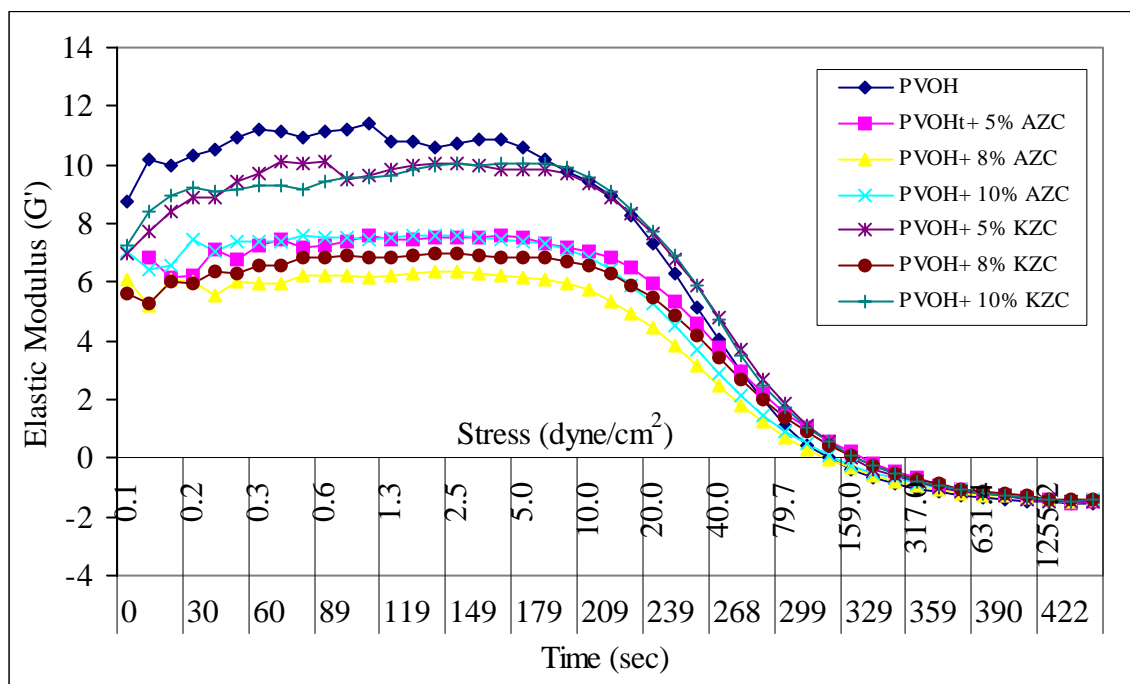


Figure 6. Elastic Modulus of PVOH at Different Addition Levels of AZC & KZC.

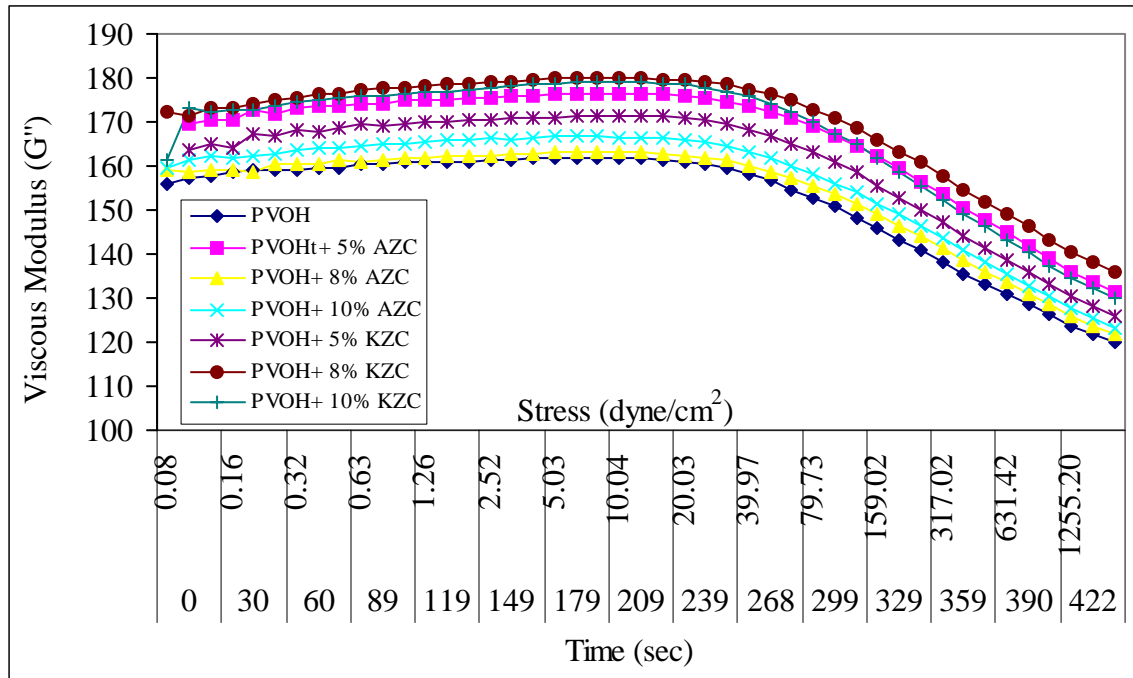


Figure 7: Viscous Modulus of PVOH at Different Addition Levels of AZC & KZC.

The change in viscous modulus as the addition level of the added insolubilizers increased exists but can be considered insignificant. Changes in the elastic modulus of the PVOH +AZC/KZC solutions also exists and can again be considered as insignificant since the elastic modulus values over the measured region are small and already indicate a fairly weak solid like structure. Therefore, it can be concluded that the lowest and the highest addition levels of AZC and KZC did not have a significant effect on the solution structure. This indicates that neither the AZC nor KZC interacted strongly with the PVOH solution to cause structural changes (What about the 10% KZC case?). This is desired in solution prior to coating application. If there were strong interactions in solution between the pronounced coating components and the zirconium species, any structural change in coatings would affect the coating application negatively, possibly

causing scratches, skips, etc., during application. The desired interaction between zirconium species and the coating binders should start after the coating application when drying starts.

The addition of both AZC and KZC somewhat contribute to the viscous and elastic modulus of a PVOH solution. At the highest addition of KZC, the effect is more pronounced. This is probably due to the weak interaction between the zirconium species and the hydroxyl functional groups on the PVOH binder.

The Brookfield viscosity (shear rate?) of the silica suspensions decreased at the lowest addition levels of AZC and KZC; increasing addition levels did not have any significant effect on Brookfield viscosity (**Figure 8**). The silica suspension (**Figure 9**) started with a higher viscosity at low shear stress values, and then at the higher values silica with AZC and KZC caught up with the silica without additives. It should be noted that this difference in viscosity between the silica slurry with no additives and the silica slurry with AZC/KZC additives is very small (from 1 to 4 Pa-s) and can be considered as insignificant. However, the different steady shear response curves observed for the silica with and without zirconium species suggests an interaction between oxygen sites of the zirconium and the silanol and/or siloxane groups on the silica. Zirconium species might have acted as dispersants for silica and might have had a stabilizing effect by reducing the charge interaction between silica particles or agglomerates by bonding their reactive oxygenated sites if the two viscosity curves given are interpreted together.

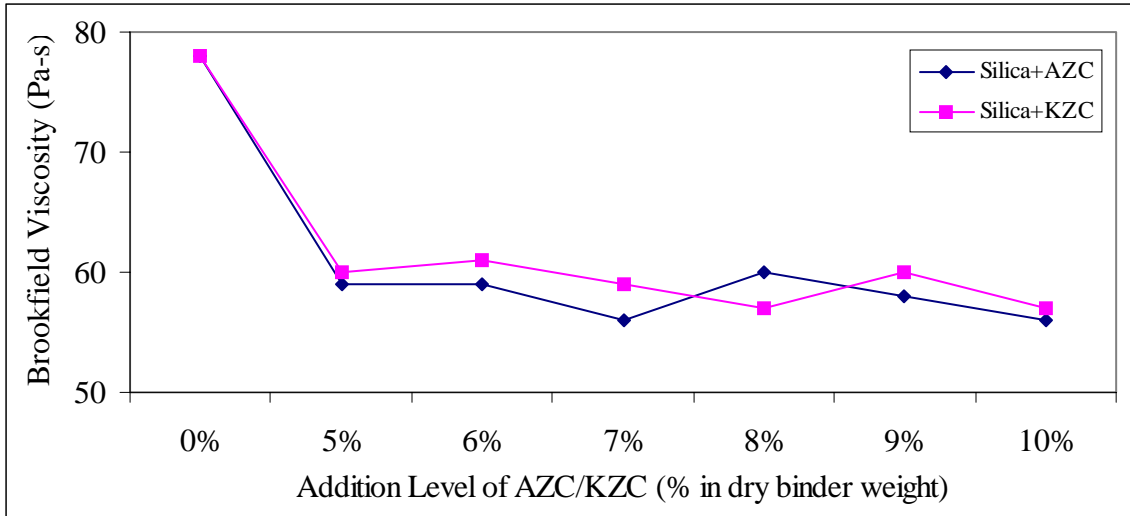


Figure 8. Brookfield Viscosity (shear rate?) of Silica at Different Addition Levels of AZC & KZC.

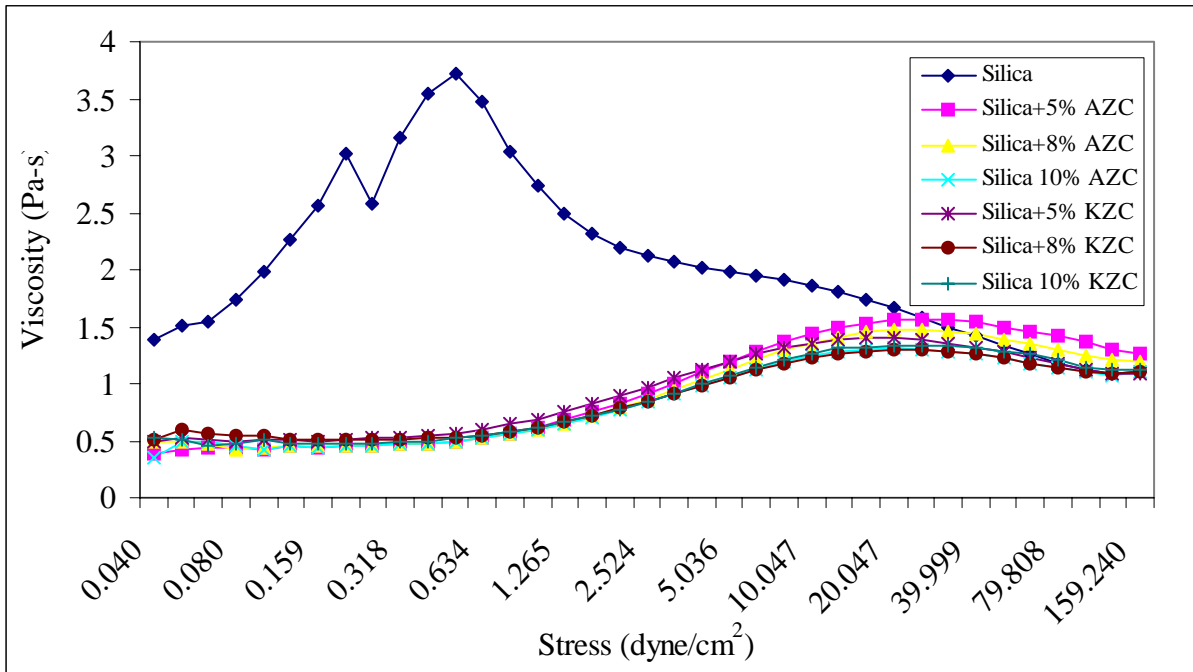


Figure 9. Steady Shear Viscosity of Silica at Different Addition Levels of AZC & KZC.

Is the dip in the silica curve at .318 reproducible?

Dynamic stress sweep tests for silica suspensions with and without the two-zirconium species at different addition levels at constant frequency (1 s^{-1}) were run. Since the silica slurries were low concentration suspensions, negligible elastic values were obtained. Also, no apparent linear region was found in the viscous modulus curves (Figure 10).

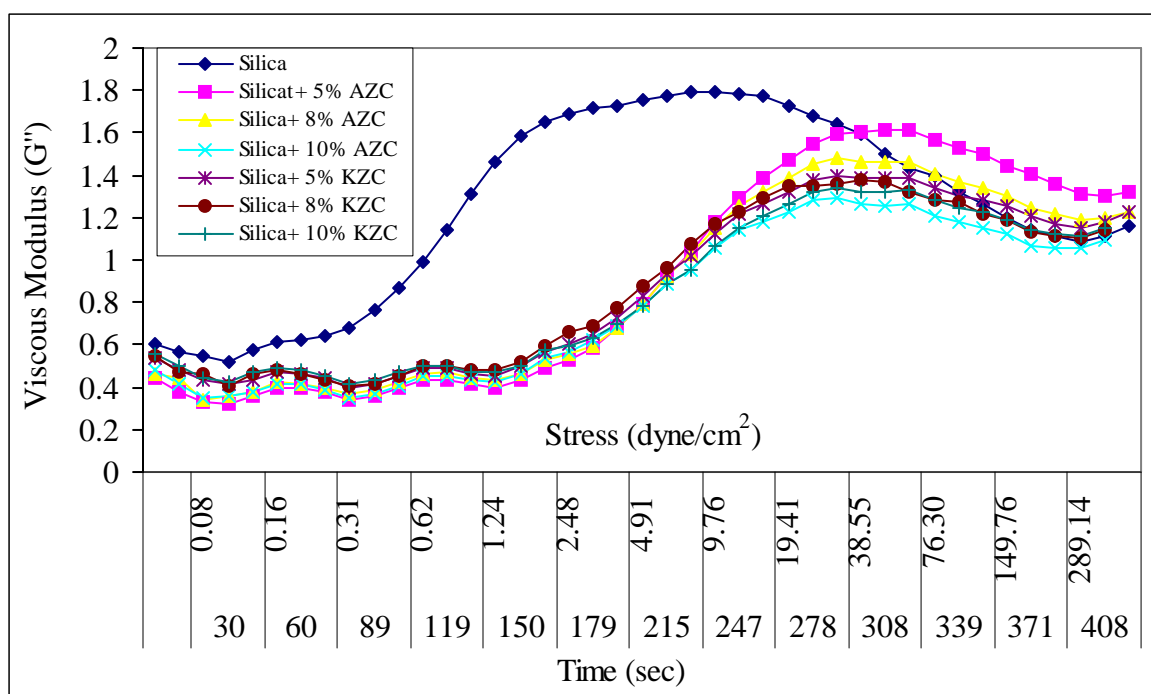


Figure 10: Viscous Modulus of the Silica at Different Addition Levels of AZC & KZC.

Inkjet Coating

As shown in **Figure 11**, the Brookfield viscosity of the inkjet coating formulation exhibited a significant increase with the addition of both AZC and KZC. The viscosity

was also dependent on the addition level of the zirconium species in the coating formulation.

The Brookfield viscosity (shear rate?) of the inkjet coating was slightly influenced by KZC addition; increasing addition levels of KZC increased the viscosity. The low shear, steady viscosity curves for the inkjet coatings are shown in **Figure 12**. An increase in viscosity was observed at low shear rates for the inkjet formulations containing AZC or KZC. At higher shear stress values (2-3 dyne/cm²) the viscosity of the inkjet coatings with AZC, and KZC approached the viscosity of the inkjet coating formulation without additives. This indicates that both AZC and KZC interact weakly with the oxygen sites (hydroxyl groups) of PVOH and/or silanol and/or siloxane groups of silica pigments that are easily broken down with increasing shear rates (stresses).

Dynamic stress sweep tests to determine viscous and elastic moduli of the inkjet coatings with and without zirconium species as a function of shear stress at constant frequency (1 s⁻¹) were also made. The elastic modulus values of all coatings were fairly low, and no linear region was obtained. Plots in the elastic modulus – shear stress exhibited a typical dilution polymeric solution behavior (10). This is interesting because the solids content of the coating formulation prepared was 23%, which is not considered as a dilute solution for inkjet coatings due to the high surface area and internal pore structure of the gelled silica. Viscous modulus curves barely exhibited a linear region, but still were significantly higher than the elastic modulus, indicating a liquid-like behavior. Zirconium added into the coating formulation, together with the addition level, had an influence on the viscous modulus of the coating formulation. Viscous modulus

values were higher for the coating formulations where KZC is used, and increasing. Both AZC and KZC addition levels increased the viscous modulus (**Figure 13**).

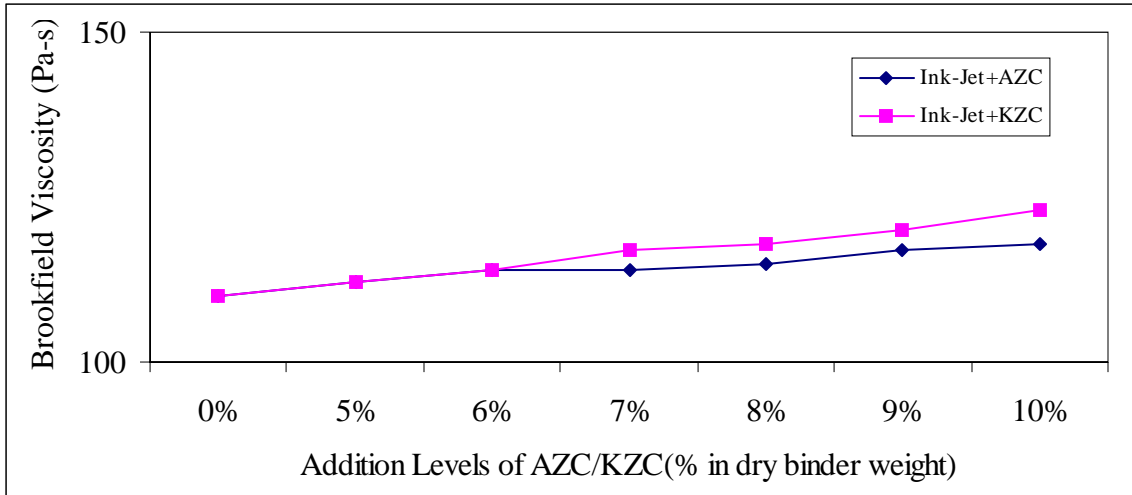


Figure 11. Brookfield Viscosity (shear rate?) of Inkjet Coating at Different Addition Levels of AZC & KZC.

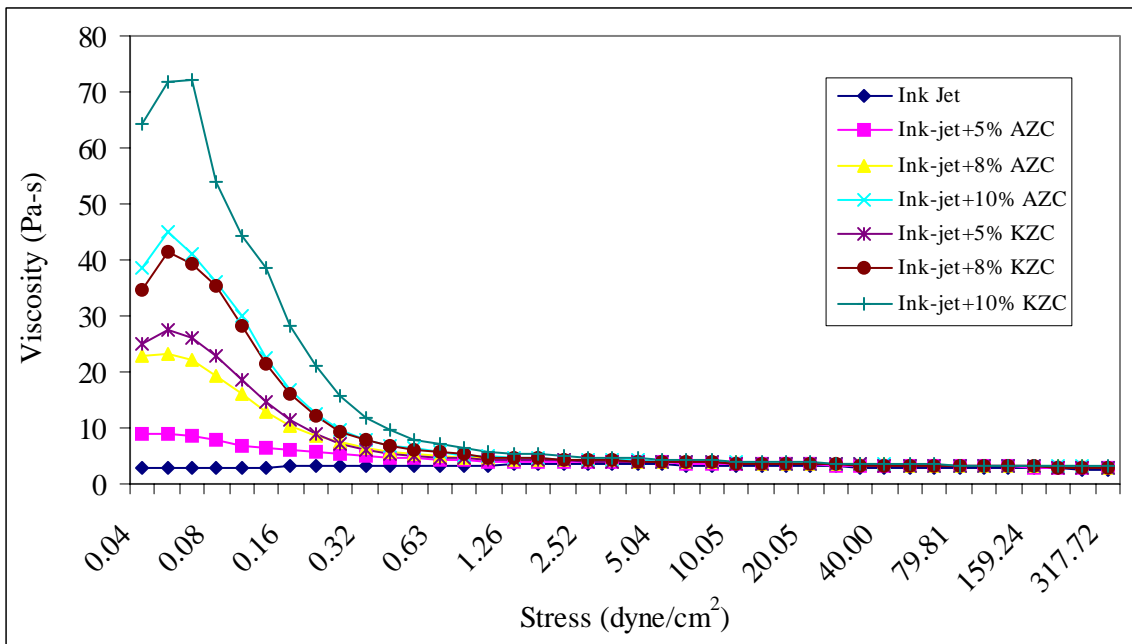


Figure 12. Steady Shear Viscosity as a function of shear stress for Inkjet Coating at Different Addition Levels of AZC & KZC.

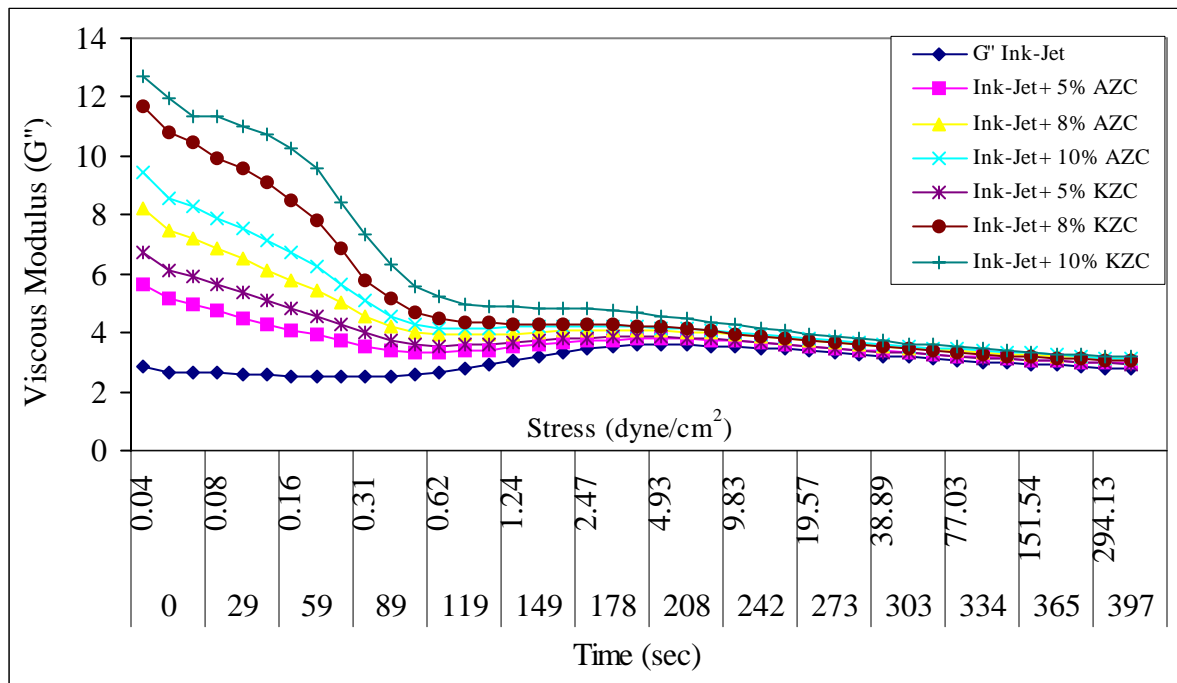


Figure 13. Viscous Modulus of the Inkjet Coating at Different Addition Levels of AZC & KZC.

CONCLUSIONS

Anionic zirconium species of AZC and KZC added to inkjet coatings had some influence on the rheology of the coating formulation, KZC giving a little higher viscosity. Both zirconium species interacted with the silica and the PVOH in suspension, solution, and coating. However, these interactions were weak and easily broken down at higher shear rates, while these additives increased the viscosity of the PVOH and decreased the viscosity of the silica pigments (unclear?). Both AZC and KZC probably worked as secondary dispersants with the silica pigments with charge repulsion between pigments preventing agglomeration. Since the viscous modulus was much larger than the elastic modulus and exhibited more fluid-like behavior, no problems in high-speed paper coating applications are expected. Addition levels of the AZC and KZC were not found to greatly influence the rheology of the final coating composition and coating components. Thus, from a rheological viewpoint, there is no limitation on the amount of anionic zirconium species that can be used in inkjet coating formulations, within the range of experimented addition levels (from 5% to 10% in dry binder weight).

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