Effect of Hydrogel Formation in IPN Type Inkjet Receiver Coatings on Print Quality and Storage Properties

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Abstract

Inkjet receiver coatings used in state of the art inkjet media are often constructed as water insoluble hydrogels. Hydrogel coatings formed from the dissolution of a water soluble and water insoluble polymer blend into a common carrier solvent shows a dramatic effect of morphology with the air temperature and drying rate used in the receiver coating drying process. The changes measured in the physical attributes of the inkjet receiver coating are shown to have a pronounced effect on the print quality of a typical inkjet print. Previously, little, if any, work has been published linking important phase structures of inkjet receiver coatings on print and image quality attributes. The author will present a model describing the mechanism of the hydrogel formation process and related information on observed print and image quality.

Introduction

Digital technology is revolutionizing the printing industry. The ability to print customized copies of materials with a variability of information at high speeds and in full color has caused new types of marking technology to replace traditional printing technologies in some market segments. Of the new types of digital printing, inkjet printing has shown tremendous promise because of its inherent low cost. As one might expect, with new printing technology comes requirements for new substrates and thus new surface coatings for these substrates.

Hydrogel coatings often are used to function as receiver coatings for inkjet inks. In a common solvent, a blend of water insoluble and water soluble polymers is made. Upon evaporation of the carrier solvent, a solid with very complex morphology remains. Within this paper we will show how two parameters, namely choice of solvent blends and drying temperatures effect the morphology of the hydrogel.

Experimental

Samples Preparation

Mixtures of variable poly(2-ethyl-2-oxazoline), a water soluble polymer, and variable poly(methylmethacrylate-*co*-hydroxyethylmethacrylate), a water insoluble polymer, were blended into a common carrier solvent. The carrier solvent was varied as one of the experimental variables, but is not discussed here. The fluids were then coated onto a PET substrate and dried under the rates and conditions described in the results and discussion to produce about a 12 µm film.

Instrumental

Differential scanning calorimetry (DSC) was carried out with a TA instruments DSC 2910. The T_g values reported are the 2nd run averages of three separate runs. Rheometry data was generated with a Rheometrics solids analyzer RSA II. Headspace analysis of retained solvent was done using a Perkin Elmer HS40 with a purge temperature of 135°C and wait time of 3 minutes for the analysis.

Results and Discussion

Summary of Physical Characterization

A miscible blend of a water soluble and water insoluble polymer may result in different morphology depending on the drying conditions used to prepare the solid blend. This phase structure can be probed with calorimetry, electron microscopy, rheometry, dynamic surface contact angle measurements and other techniques. Information from these techniques can be used to get a picture of the morphology of the inkjet receiver layer as it relates to the physical structure of the hydrophilic water-soluble (HWS) and hydrophilic water insoluble materials (HIS). As will be shown latter, the domain structure does influence the imaging and storage properties of the inkjet printing coatings. The influence of the phase behavior on some print quality attributes has been previously mentioned.[1]

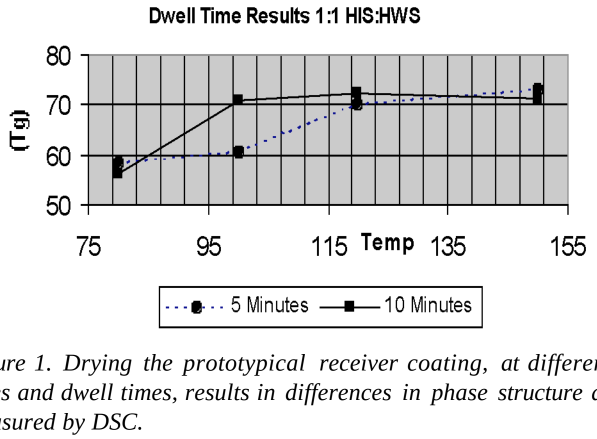

Figure 1. Drying the prototypical receiver coating, at different rates and dwell times, results in differences in phase structure as measured by DSC.

As shown in Figure 1, for a coating that is an equivalent mass of HIS and HWS, the heating temperature and dwell times show a marked influence on the resultant glass transition temperature of the IPN coating measured with thermal calorimetry. In no instance were two separate glass transition temperatures seen for this particular coating system. This information strongly suggests the presence of a single phase which differs in the geometry of the microstructure.[2]

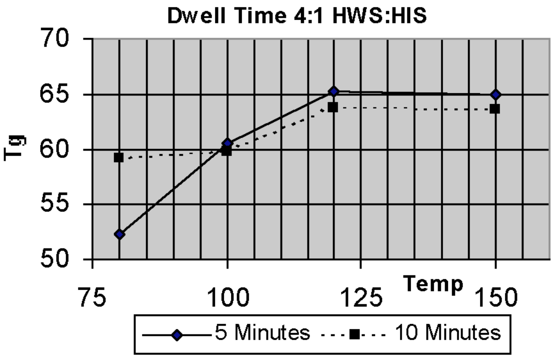

Figure 2. Drying a prototypical 4:1 HWS:HIS coating layer results in a morphology different than that of the 1:1 system.

As shown in Figure 2, changing the relative mass of the HIS and HWS components reduced the relative change in the drying rate dependence of the geometry of the IPN layer as measured with DSC. The overall magnitude of the change of T_g as a function of dryer dwell temperature is reduced as is the effect of the dwell time. In addition, the ultimate glass transition temperature obtained is approximately 10°C lower than for the 1:1 HWS:HIS layer. This is due to the differences measured in the simple T_g measured for the pure HIS component (110°C) and the HWS component (60°C).

Table 1. The E' data for the various 4:1 HWS:HIS films show a dependence on final temperature achieved in the drying process.

Temperature	Time	E' (100 rad/sec)
80	5	3.00E+09
120	5	5.00E+09
150	5	1.60E+10
80	10	3.00E+09
120	10	5.00E+09
150	10	1.80E+10

In addition to the thermal methods of characterization, mechanical methods can be used to probe the nature of the HIS:HWS blend. In this type of measurement, free standing films of the polymer layer needs to be prepared. As shown in Table 1, the relative differences in the modulus properties of the film do again depend on the rate of drying and also the ultimate final temperature that the film achieves. This data shows that harder films are produced for a material that achieve a higher final temperature of drying in the dryer process.

As with any polymeric material, the amount of retained organic solvent or water in the solid blend can have a dramatic effect on the measured physical properties. Small molecules are well known to act as simple plasticizers for many polymeric materials. In order to ascertain the overall effect to the measurements described above two separate experiments were carried out. In the first experiment the retained solvent content was measured by GC-Headspace analysis of the dried films. The data from the various film preparations is shown in Table 2 in percent weight of dry coating. The overall level of retained solvent is low for the various films characterized here.

To gauge the overall effect on the T_g measured for the films described here, a film was dried at 80°C for 30 minutes and the retained solvent and glass transition temperature was measured. As can be seen in Table 2, the level of retained solvent was dramatically decreased but the glass transition temperature measured was similar to other films dried at 80°C, measuring at 55°C. Therefore, it is the author's opinion that the effect of plasticizer on the system is a secondary factor in the observed differences in T_g and E' value. The primary influence is morphological.

Table 2. Retained solvent information for the materials prepared here.

Time	Temperature	Retained Solvent
5	80	2.5
5	100	1.9
5	120	0.7
5	150	0.1
10	80	2.5
10	100	1.5
10	120	0.4
10	150	0
30	80	0.1

Effect on Print Qualities

Drying the prototypical films at different rates, and final use temperatures, has been shown to produce materials with different morphologies. The second part of this experiment relates to the effect of the morphology on measurable print qualities like image coalescence, dot size and drytime for typical ink sets.

As shown in Figure 3, the coalescence of the prototypical inkjet media is indeed influenced by the different drying conditions used to prepare the samples. In general, worse coalescence is found for samples dried at higher temperatures and for longer times. This then means that worse coalescence is seen for samples that have measurably higher glass transition temperatures and E' values as measured with DSC (T_g) and Rheometry (E'). There is a large difference in the coalescence observed for the different component ratios of HIS:HWS. This is to be expected as the amount of water sorptive component increased.[3] However, the data clearly shows that within a series of materials the drying rate has a pronounced effect on this print quality attribute.

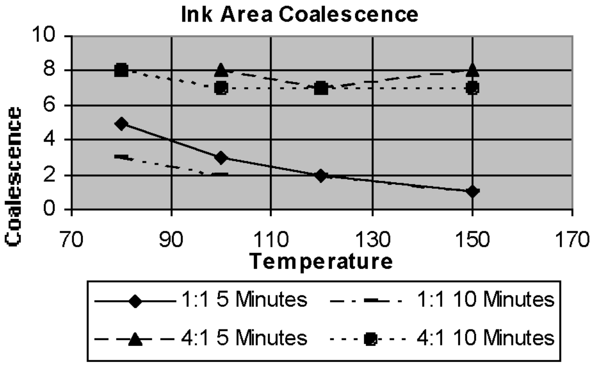

Figure 3. Qualitative coalescence results. The data suggest worse coalescence (lower numbers on the scale) as a function of increased temperature and dwell times.

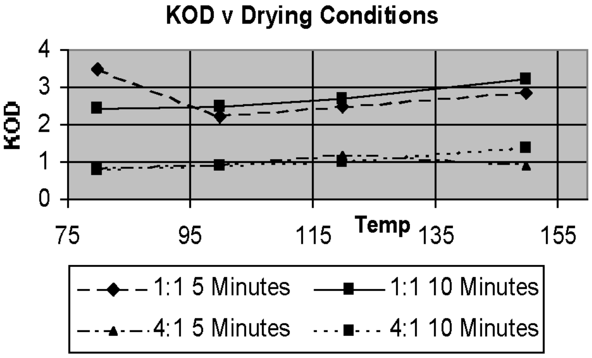

Figure 4. Black optical density (KOD), for pigment black ink, shows a dependence on weight ratios and dryer conditions.

Pigment ink area cracking was also found to be affected as a function of dryer rates and final settings. This is illustrated in Figure 4 below. In general a trend of higher black optical density for longer and hotter drying is observed. In addition, the differences in the blend ratios of the HWS to HIS component is again noted. One anomalous data point is that at 80°C, for 5 minute drying, the 1:1 HWS:HIS ratio had the highest pigment black optical density at around 3.6. This may be due to the much better black ink coalescence noted for that sample.

Qualitative Description of a Physical Model

Although, not enough information is presented to understand the root cause of the differences measured with the instrumental data completely; it is clear that the drying process has profoundly effected the morphology of the inkjet receiver coating. One possible explanation of the data is that the different dried films may have different levels of H-bonding between the different polymer components. The HWS component, having an amide structure, is capable of hydrogen bonding with the hydroxy groups of the HIS material. The degree of such hydrogen bonding interactions would be expected to influence the bulk properties of the materials greatly.[4] Many inkjet receiver coatings are comprised of H donor-acceptor pairs. It is anticipated that the morphology of many other systems will be equally complex.

Summary

Inkjet receptive coatings, for state of the art imaging applications, are often constructed of blends of water soluble and water insoluble networks. It has been demonstrated that the morphology of these networks is influenced by conditions that may be present in the industrial coating and drying process involved in manufacturing the inkjet media. The morphology of these materials has been demonstrated to have an effect on the basic imaging qualities. It is the authors hope that concepts like over dried or under dried can be tied back to the underlying morphology for a more quantitative understanding.

References

1. S. J. Sargeant, T. Chen, B. Parikh, B. *IS&T NIP 14*, 138-141, (1998).
2. Folkes, M. J. ed *Processing, Structure and Properties of Block copolymers*, Chapter 3.
3. Yuan, S.; Sargeant, S. J., Rundus, J., Jones, N., Nguyen, K. *IS&T NIP 13*, 413-417, (1997).
4. Olabisi, O., Robeson, L., Shaw, M. *Polymer-Polymer Miscibility*, pp 29-35.

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Biography

Steve Sargeant has been employed at Arkwright since 1993. His primary work involves the innovation, development and commercialization of new media for digital printing applications. He received a BS in chemistry from RIT and a Ph.D. in polymer chemistry from USC and was a postdoctoral researcher at Cornell University before joining the company. His current assignment at Arkwright is as Director of R&D.