A Comparison of the Physical Properties of Different Gelatine Types for Inkjet Applications

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Abstract

Within the last years gelatine has become, among the usage in classical Photographic materials, also a very important component for glossy Inkjet media. This can be deduced to the combination of gelatine properties like high light /ozone stability, high gloss of the surface, high color densities of the printouts and reasonable dry times.

Besides these classical quality parameters for glossy Inkjet media, which were examined and presented in detail for different gelatine types in the past, also other gelatine properties are crucial with respect to the usage in Inkjet coatings.

The knowledge of differences in swelling capacities and kinetics, surface tensions and the rheological behavior of gelatine solutions is also important for the production of Inkjet media and were studied in detail for different gelatine types.

In the present paper the results of these measurements for different gelatine types will be shown and compared.

From the results it can be concluded that these properties, in contradiction to the above mentioned quality parameters (light stability etc.) are different for the investigated gelatine types. This could lead to an optimized usage of gelatine in the production of Inkjet materials.

Introduction

Light Stability, Gloss, Dye Fixation

As already presented in the past the light stability of gelatine containing glossy Inkjet coatings is superior compared to porous papers.[1] The reason for this behavior is that gelatine forms a closed film and protects the Inkjet dyes against UV-radiation, oxygen and ozone.

Figure 1 shows the light stability of two commercially available papers from Canon compared to a standard coating with Imagel MA – similar results were found for other glossy papers.[1]

Besides the light stability also the gloss levels and the high color densities of the printouts, which can be achieved by the usage of gelatine, are advantages of gelatine. Comparisons of commercially available papers and simple Imagel coatings showed that the gloss levels/color densities of the Imagel coatings reached at least the quality of the papers in the market.

Detailed studies regarding the gloss and the color densities are in preparation and will be published in the future.

Both the light stability and the gloss do not depend on the gelatine type – the results are comparable for all Imagel types.

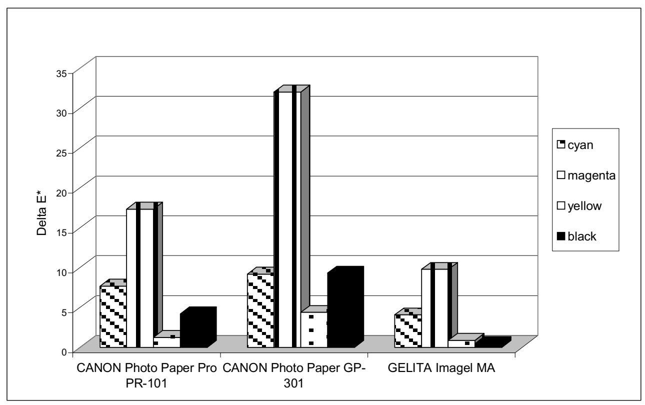

Figure 1. Light stability of an Imagel MA coating in comparison to commercially available glossy Inkjet papers from Canon (printed on Canon BJC 8200, exposition time = 24 h with 710 W/m²).[1]

In contradiction to this the dye fixation of pure gelatine coatings depends on the type of gelatine and the pH. Due to the different Isoionic Points (IIP) of the Imagel types the total charge of the gelatine molecules is influenced by the pH. This leads to a dependence of the gelatine type and the pH, at which the coating solutions are prepared, on the dye fixation.[2]

All investigations described above focused on these parameters and described properties, which are crucial for the quality of finished glossy Inkjet papers.

Besides these properties also the knowledge of rheological data, surface tensions and swelling capacities is quite important for the choice of a suitable gelatine type and an optimized usage in production.

Therefore the first investigations regarding these properties were performed and will be discussed in the present paper.

Due to the fact that the aim of this paper was the introduction of additional properties, we focused on the presentation/discussion of the results and tried to limit the theoretical background to a minimum. In the future further detailed studies regarding the different properties have to be done and will be published together with a comprehensive theoretical background.

Experimental

Gelatine Types Used for this Study

An overview about the gelatine types, which were used for the measurements is given in table 1. Imagel AP is a high Bloom, high viscous acid processed pigskin gelatine with an Isoionic Point (IIP) of ~ 9. Imagel BP and NP are both limed bone gelatines, which differ in the gel strength and the viscosity. For both types the IIP is ~5,1.

Imagel MS is a modified pigskin gelatine with a degree of modification of ~95%. The modification is done with Succinic Acid Anhydride. Due to the modification the IIP is ~ 4,5.

Imagel MA is also a modified pigskin gelatine – this type was modified with an alkyl-derivative of Succinic Acid Anhydride and especially designed for Inkjet applications.[3] The degree of modification for this type is ~ 40%.

Table 1. Overview of the Different Gelatine Types Used for All Measurements (see text).

Type	Process	Gel Strength (Bloom) g	Viscosity mPas	pH	IIP
Imagel AP	pig skin A	295	5,4	5,4	9,0
Imagel BP	bone B	280	5,3	5,8	5,1
Imagel MA	pigskin A, Mod.	235	6,0	6,5	5,2
Imagel MS	pigskin A, Mod.	205	4,0	5,3	4,5
Imagel NP	bone B	140	3,5	5,4	5,1

Preparation of the Gelatine Solutions

All gelatine solutions, which were used for the measurements, were prepared in the following manner.

First the gelatine was allowed to swell in the desired amount of water for 30 minutes to avoid gel blocking. Afterwards the pre-swollen gelatine particles were dissolved under slow stirring by heating the solution to 50°C. In general the water content of the dried gelatine (~ 10%) was neglected during the preparation of the solutions.

Rheological Measurements

For all 5 gelatine types the gelation process was obtained by determining the complex modulus of shear G* in a rheological experiment. From this complex modulus the viscosity and the storage modulus G´ (=network strength) as a function of time is received during gelation.[4] All measurements were performed on a rheometer from Physica (MCR 300 equipped with PP50). For the detection of the complex modulus G* of shear a sample volume of 1ml was placed onto the rheometer plate and the measurement was started. After keeping the temperature for 2 minutes at 60°C the samples were cooled down to 20°C within 5 min. Afterwards this temperature was kept at 20°C for 17 hours - data were taken every 10s. All measurements were carried out at a constant frequency of 1 Hz and a deformation of 1% to ensure linearity of the deformation.

Measurements of the Optical Rotation

The optical rotation measurements were performed on a polarimeter from Perkin Elmer (model 343 plus), equipped with a heatable cuvette. After the preparation of the 6,67% gelatine solutions and a pre-heating of the cuvette (60°C) the solution was transferred into the cuvette and placed in the cell holder. Then the samples were cooled to 20°C within 2 minutes by using a second cryostat and the measurement was started. The optical rotation at a wavelength of 589 nm was detected once a minute over a time period of 17 hours (=1020 minutes). Although conditions like humidity and outside temperature cannot be controlled by this device, measurements on different days showed a good reproducibility of the measurements.

Measurement of the Surface Tension

The surface tensions of the diluted gelatine solutions were determined with a contact angle measuring device from Data Physics using the pendant drop method. In principle this device detects (with a CCD-camera) the shape of a drop of a gelatine solution, which is formed at the lower end of syringe needle. The shape of the drop depends on the relation between two forces. The weight force pushes the drop in the vertical direction, whereas the surface tension creates a force to minimize the surface of the drop and acts therefore perpendicular to the weight force – due to this the spherical shape of the drop is kept. In the equilibrium state the shape of the drop is characteristic of the surface tension of the solution and can be calculated by the Young-Laplace equation.

After the syringe was filled with the solution to be tested and the drop was formed the measurement was started and 16 data points were taken within 320 sec.

Measurements of the Swelling Capacity/Kinetics

In order to measure the swelling properties of the different gelatine samples the time dependent water uptake per gram gelatine was measured. 5 g gelatine were put in a graduated cylinder and 100 ml water were added under slow stirring. After 2, 4, 6, 8, 10, 15, 20, 25, 30 and 40 minutes the swollen gelatine particles were separated from the water by a sieve and weighted. Water on the surface of the gel particles, which was not taken up by the gelatine, was removed by compressed air. For every time dependent measurement a new sample of 5 g gelatine and 100 ml water was prepared. All measurements were performed at room temperature.

Results/Discussion

Rheological Measurements

Figure 2 shows the results of the rheological experiments for all Imagel types. A comparison with the values for the gel strength (see table 1) shows that this method, with the exception of Imagel MA, is suitable to describe the gel strength at least qualitatively by means of a rheological experiment. In addition to this the storage modulus G´ of all gelatine types changes rapidly within the first 3 hours of the experiment. This time dependence differs strongly for all gelatine types and might be very interesting for the handling in production, because usually the first minutes/hours during gelation are quite important (before drying of the coating).

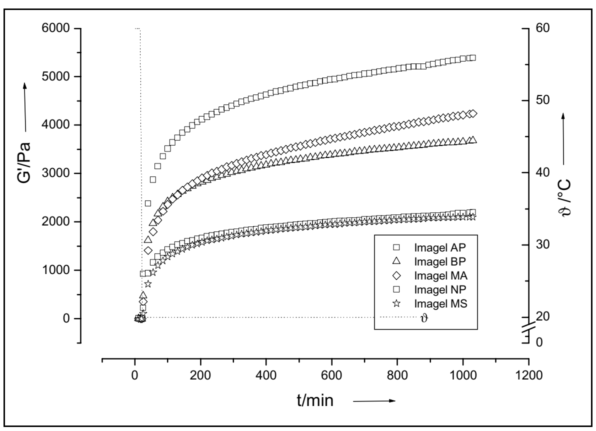

Figure 2. Time dependent storage modulus G´ of the different Imagel types.

Afterwards a slower gelation takes place, which is still ongoing after 1020 minutes (=17 hours), but very close to a plateau region, in which the storage modulus G´ remains constant. The small difference between the rheological curves of Imagel MS an Imagel NP can be deduced to the measuring temperature of 20°C – measurements at lower temperatures showed clearly that the differences become larger if the temperature is decreasing.[5]

In contradiction to the other types the rheological curve of Imagel MA cannot be correlated with the gel strength (see table 1). The reason for this is still not clear at the moment, but might be deduced to the unique pH-dependent properties of Imagel MA. This pH-dependence can be explained by the introduction of a large alkyl chain as a side group during modification. Due to this side group effect parameters like gel strength, viscosity and turbidity become pH-dependent for Imagel MA. As an example the turbidity of Imagel MA solutions is decreasing if the pH of the solution is raised.

Optical Rotation

Figure 3 shows the optical rotation of all Imagel types as a function of time. The optical rotation is a suitable measurement for the detection of single, double and triple helices in the gel, which are formed by the gelatine. Due to the fact that the junction points of the gelatine network consist of triple helices, the detection of the amount of these helices can be used to detect the part of the gel strength, which is caused by triple helices as junction points. The higher the change of the optical rotation during the gelation, the more helices are formed and the more junction points in the network exist.

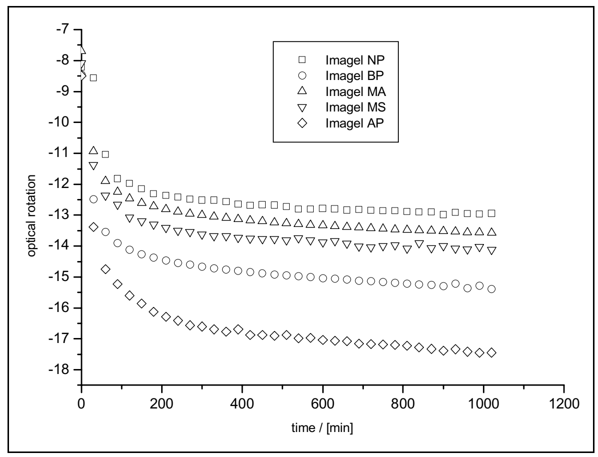

Figure 3. Optical rotations of the different gelatine types.

In accordance to the measurements of the shear modulus the optical rotations of all types except Imagel MA can be correlated at least qualitatively with the gel strength. Also for the optical rotation Imagel MA shows a unique behavior – on the basis of the results for the storage modulus less helices than expected are formed – the reason for this has to be deduced to the sterical demanding alkyl chains.

These side groups suppress the formation of helices partly during gelation. The reason that Imagel MA shows an optical rotation, which is comparable to Imagel NP, but a very high storage modulus indicates clearly the formation of other junction points than triple helices.

Due to the large alkyl chains of Imagel MA it is quite obvious that these junctions points are entanglements, but the nature of these crosslinks has to be proved and will be part of the next investigations.

Surface Tension

Figure 4 shows the results of the surface tension measurements of all Imagel types due to the pendant drop method. The solutions of all types showed similar pH-values (from 5,3 – 5,8) but large differences in the IIP (see table 1).

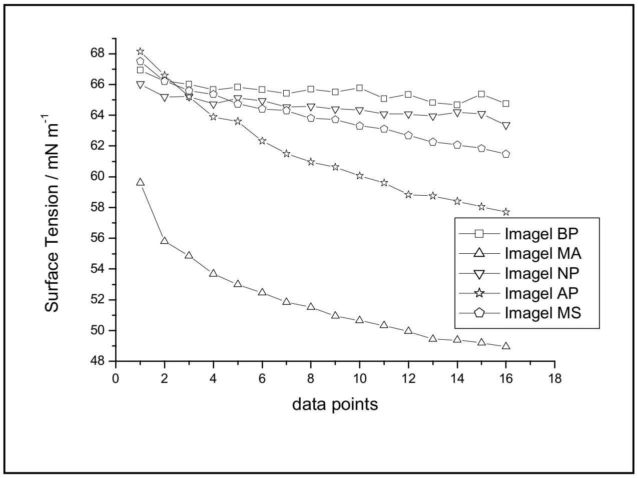

Figure 4. Surface tension of the different gelatine types (0.5%, RT, pH not adjusted,pendant drop method), for comparison: pure water = 73 mN/m.

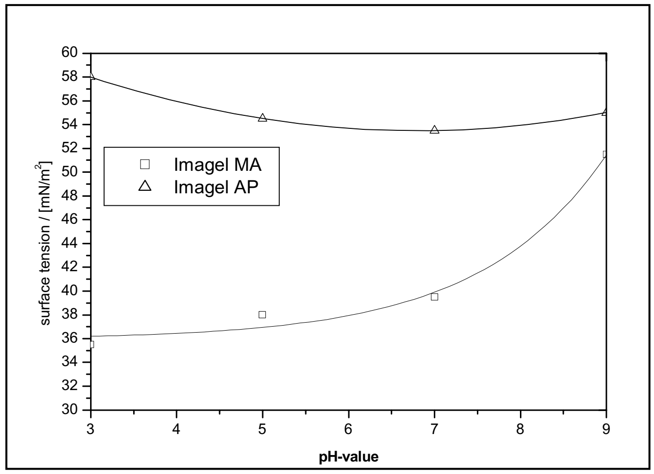

Figure 5. pH-dependence of the surface tension of Imagel MA and Imagel AP (1%, RT, Lecomte-de Nouy-ring method).

The fact that the surface tension for all 5 types decreases slightly during the measurements cannot be deduced to a shrinking of the drop (caused by the evaporation of water) and thus a change of the shape of the drop. The reason is that we observed stable values for pure water, although the water drop was also shrinking slightly.

It is also unlikely that a pure concentration effect is responsible for the observed time-dependence. Due to the decrease of the drop size the gelatine concentration is raised slightly during the measurement. This would lead to a time-dependence of the surface tensions of the samples, but we would expect that this decrease does not depend on the different gelatine types, because the shrinking of the drop and therefore the increase of the concentration was the same for all samples.

For that reason we developed a model, by which the observed results can be explained.

For Imagel AP, BP, MS and NP the resulting surface tension after 20 seconds (data point 1) can be correlated with the IIP. For similar pH-values the IIP of the types is an indication for the total charge of the gelatine molecule. As a result it can be concluded that an increase of the total charge of the gelatine molecule leads to an increase of the surface tension of gelatine solutions at least for the types AP, BP, MS and NP. For these types the surface tension can be adjusted by changing the pH of the solutions.

From figure 5 it becomes apparent that a higher gelatine concentration leads to a lower surface tension (1% solution in figure 5 compared to 0,5% solution in figure 4). Therefore the decrease of the surface tension during the measurement is caused by an enhancement of the gelatine concentration in the surface layer by diffusion and not only by an increase of the total gelatine concentration in the drop.

Furthermore we observed the largest decrease of the surface tension during the measurement for the gelatine types with the highest charge on the molecule (Imagel AP followed by Imagel MS). Imagel MA shows a similar time-dependence but a lower surface tension at the beginning of the measurement as it was expected on the basis of the IIP-pH relation. In figure 5 the pH-dependant surface tensions of Imagel MA and AP are compared.[7]

Imagel AP shows, in accordance to the comments above, a minimum of the surface tension close to the IIP of ~9 at which the gelatine molecules are nearly uncharged. In contradiction to AP the surface tension of Imagel MA shows the lowest values at a pH of ~3 and increases with increasing pH-values – no minimum is found in the range of the IIP. The reasons for this behavior are not clear at the moment. We just started to investigate this in detail and will publish the results in the future.

It can be concluded that the surface tension depends in the first place on the relation between the pH-value and the IIP of the respective gelatine type, if parameters like concentration and temperature are constant. The time dependence of the surface tensions can be explained assuming that a diffusion of gelatine molecules into the surface layer of the drop takes place. Nevertheless further measurements have to be done to verify this model.

Swelling Capacity/Kinetics

Figure 6 shows the swelling curves at room temperature of all 5 Imagel types. It becomes obvious that the different types show large differences in their swelling behavior, which cannot be correlated with single parameters like gel strength, IIP etc..

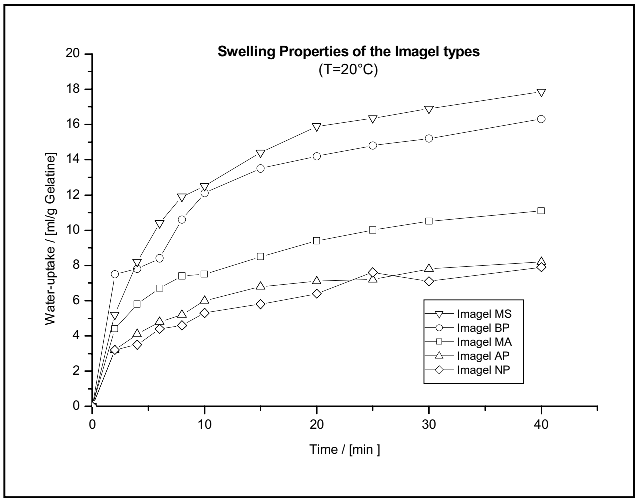

Figure 6. Swelling properties of the different gelatine types.

The reason for that is the fact that the swelling behavior of polyelectrolytes depends on a variety of different parameters like network parameters, total charge of the molecules, interaction parameters between the polyelectrolyte and the solvent etc.. Therefore it is difficult to explain the differences in swelling for all gelatine types at the moment. A complete review about all those influences of different parameters on the swelling behavior is given in the literature.[7-9]

The influence of the gel strength can be used to explain the differences in swelling between Imagel BP and NP. The higher the gel strength the higher the swelling capacity will be. The poor swelling of Imagel AP has to be correlated with a lower interaction parameter to the solvent, because the gel strength is higher than Imagel BP and due to the high IIP Imagel AP shows a higher total charge on the gelatine molecule at a pH of 5,3 – 5,8 (compared to BP).

From the curves of Imagel MS and MA it becomes apparent that a modification of the gelatine molecule leads to a higher swelling capacity.

It can be summarized that the measurements show large differences for the swelling capacity of the different Imagel types. These differences can be partly deduced to parameters like gel strength or pH-IIP relation, but details have to be studied more in detail in the future.

Conclusion

In contradiction to parameters like light stability, gloss, color densities and dye fixation, which were studied in detail in the past and are very important for the quality of Inkjet papers, the investigation of other properties like rheological behavior, surface tensions and swelling capacities showed large differences between the Imagel types.

The measurement of the storage modulus of the different gelatine types showed that the gel strength can be correlated at least qualitatively with the rheological curves for all types except Imagel MA. The largest differences were obtained within the first 3 hours of the experiment.

The measurements of the optical rotation of all types confirmed the results of the rheological experiment. Also for this method Imagel MA showed a different behavior. From both methods it could be concluded that the formation of helices for Imagel MA is at least partly suppressed and therefore the high storage modulus (compared to the gel strength) has to be caused by other junction points (e.g. entanglements).

The measurements of the surface tension showed the influence of the charge of the gelatine molecule and therefore also to the IIP-pH-relation. Therefore the surface tension of the different gelatine types can be varied by adjusting the pH. In addition to this a time dependence of the surface tension was observed for all types, which can be explained assuming a diffusion of gelatine molecules into the surface layer of the drop during the measurements.

Also for the swelling capacity the types showed large differences, which could be partly explained by parameters like the gel strength and the IIP. In general the swelling capacity depends on a lot of different parameters, which have to be studied in detail in the future.

The purpose of this paper was to introduce the above mentioned parameters and present the results/differences between the different Imagel types. The knowledge of such properties might be useful for the optimization of the production of Inkjet media.

It was shown that the different Imagel types cover a broad range of properties regarding the applied methods.

Due to the fact that the observed differences between the types cannot be correlated completely with standard parameters, further detailed studies have to be done and will be presented in the future.

Acknowledgements

The author wishes to thank Mrs. B. Strobl, Mrs. B. Steck, Mr. P. Reiter and Mr. S. Frömmel for performing the experimental work.

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Biography

Dirk Kisters studied Chemistry at the Gerhardt-Mercator-University of Duisburg (Germany). For his Doctoral Thesis he worked on the field of: "Characterization of Thermo-reversible Gels by means of Analytical Ultra-centrifugation" and received his PhD in Chemistry in the department Applied Physical Chemistry (head: Prof. Werner Borchard) in Duisburg in January 2001. In August 2000 he joined GELITA PHOTO Europe, a department of the DGF Stoess AG in Eberbach, Germany. Since July 2001 he is project leader of the Inkjet Group of GELITA PHOTO. e-mail: dirk.kisters@gelita.com.