

Cross-Linked Ink Jet Layers of Gelatin/Polyvinyl Alcohol Mixtures

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Abstract

In this study we investigated different types of gelatin with respect to compatibility with a water soluble polymer like polyvinyl alcohol, which is widely used as a component in ink receiving layers. The influence of conditions like concentration, composition, as well as pH level, on the phase behaviour were determined for different gelatin and polyvinyl alcohol (PVAL) types in solutions and in casted films using turbidity measurements and data from microscopic studies. A "compatible" system of PVAL and a chemically modified gelatine was described. Because of the importance of water resistance in ink receiving layers, we additionally focused on the cross-linking process of gelatin and a mixture of gelatin and PVAL with a common hardening agent. Cross-linking efficiency was rheologically determined using different temperatures and hardener concentrations.

Introduction

Gelatin is recommended as one component to be used in recording media^{1,2,3} mainly for high glossy ink jet materials. The binding capacity to solvents, pigments, and dyes, as well as its film forming properties and the ability to get cross-linked easily, are essential properties for imaging and ink jet applications.

Due to the requirements of ink receiving layers, complex formulations and multi-layer structions were recommended.⁴ Combinations of different water soluble materials are supposed to expand the spectrum of properties helping to perform all requirements of ink receiving layers. A problem arising from blending different polymers is the low tendency to form homogenous mixtures, which can be explained in thermodynamical terms. Incompatibility of different polymers can limit the suitability of promising blends, especially for glossy ink jet materials.

Polymer mixtures are normally heterogeneous however under certain conditions do not separate macroscopically, which is described as "compatible". Data of the phase behaviour of blended solutions and films in a system like PVAL and gelatin are rare.^{5,6} Some literature describes gelatin/PVAL blends (PVAL: grade of hydrolysis > 99%, MW 115.000 g/mol) as transparent and mechanically

compatible, but immiscible in a thermodynamical sense. A ternary phase diagram of the gelatin/PVAL/water system shows that phase separation occurs with polymer concentrations higher than 7.5% in water (PVAL: polymerisation degree 2.000, grade of hydrolysis 99,1%) in a fraction range of 0.05 - 0.95 PVAL/gelatin.

Results and Discussion

Due to the nature of gelatin properties often differ strongly with the type and pH level of the system. Table 1 shows different gelatin and PVAL used to make blends in this study.

Table 1. Physical data of gelatins and PVAL used for blending (IIP: isoionic point, A: acid processed, B alkaline processed, succ.: succinylated)

No. of gelatin	raw material	type of process	bloom* G	viscosity* mPa*s	IIP
1	pig skin	A, succ.	202	3.92	4.5
2	bone	B	289	3.80	5.1
3	pig skin	A	283	3.82	9.0
No. of PVAL	Degree of hydrolysis %		Average molecular mass g/mol		
4	88		14000		
5	88		130000		
6	98		125000		

*Gel Strength BS, ** at 60°C, 6.67 w/w %

Turbidity measurements were often used to describe the stability of dispersions.⁷ We measured the transmittance of glass supported films (thickness ca. 10 µm) of gelatine and PVAL casted from a 10 w/w % aqueous solutions at 60°C in different ratios and pH levels. These results in combination with visual interpretation indicate that films made from PVAL No. 4/gelatin No. 2 or 3 blends show low turbidity up to ratios of 0.4. The dependency of the turbidity on different pH levels is weak. If the PVAL is changed to a type with the same degree of hydrolysis but higher molecular mass films from blends out of gelatin No. 3 were

turbid (see Table 2). This behaviour also occurred with a PVAL of a higher degree of hydrolysis.

Table 2. Transmittance ($\lambda = 620$ nm) from films made of PVAL/gelatin of different ratios casted from 10 w/w % aqueous solutions at pH 8.

Gelatin No.	Transmittance, %					
	1			3		
	4	5	6	4	5	6
PVAL No:						
PVAL/Gelatin ratio w/w						
1	99	100	100	99	100	100
0.9	97	-	100	81	-	-
0.8	98	100	100	56	73	84
0.7	98	100	100	57	69	69
0.6	99	100	100	89	68	85
0.5	98	100	100	96	78	90
0.4	99	99	100	97	80	97
0.3	100	-	100	97	-	-
0.2	99	99	100	-	99	99
0.1	99	-	100	99	-	-
0	98	99	99	99	99	100

New aspects appear when investigating blends with chemically modified gelatin No. 1. All films were transparent (transmittance > 97 %), except when made from a solution at a pH level near the isoelectric point (at pH 5) and a low molecular weight PVAL (No. 4, Table 1). These results were verified by investigations of the films by means of microscope phase contrast images. If modified gelatine is mixed with PVAL No. 5 and 6 the turbidity of all solutions regardless of ratios does not rise (polymer concentration 10 w/w %). A microphase separation of the casted transparent films was not detectable under the microscope.

Table 3. Macrophase separation of blends of PVAL No. 4/gelatin No. 1 at different concentrations in water treated at 60°C for 4 h after mixing (+: disperse turbid, ++: coarse disperse)

Ratio PVAL/gelatin No. 1 w/w	amount of lower phase separated v/v %		
	10 w/w %	20 w/w %	30 w/w %
0.8	+	38	70
0.7	+	34	43
0.6	+	25	++
0.5	+	13	++
0.4	+	8	+
0.2	+	+	+

Films of PVAL No 4/gelatin No. 1 show phase separation. This behaviour strongly depends on the concentration of the polymers in the solution used for casting (see Table 3). Aqueous solutions of PVAL No.

4/gelatin No. 1 separate into two macrophases at concentrations > 10 w/w %. Below 10 w/w % they were turbid but films show transparent microphases (see Table 2). At 30% concentration we registered a decreasing tendency to separate into two macrophases at high PVAL/gelatin ratios, which might be caused by the increasing viscosity of the mixtures.

According to the described results, a hardening process of some PVAL/gelatin blends used in ink jet layers has to take place in a multiphase system. Parameters of the hardening process, well investigated^{8,9} for gelatin layers, has to be adapted. The cross-linking efficiency of various hardeners is known, but still, a simple hardening agent, formaldehyde, is used frequently. In contrast to most chemical reactions which accelerate with rising temperatures, the cross-linking process of homogenous gelatin layers shows a more complex behaviour. Regarding rheological data, e.g. the complex viscosity, η^* , after adding formaldehyde (20 ppm) to a 20 w/w % solution of gelatin at 50°C and raising the reaction temperature to different values, we observed, that the highest relative increase of η^* is detectable at lowest temperatures. Layers obtained under these conditions are cross-linked, which was proven by a frequency sweep of the gelatin solution at 50°C (see figure 1). The parallel lines of the storage modulus G' indicate their independence from the frequency, typical for cross-linked systems.

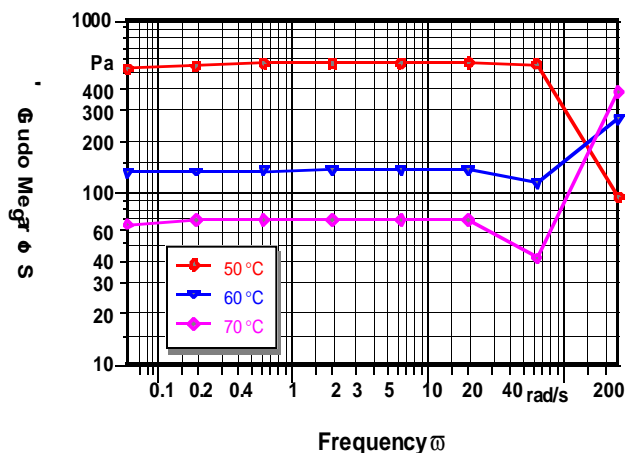


Figure 1. Frequency sweep of cross-linked aqueous gelatin No. 3 solution (20 w/w % at 50°C) treated for 1 h at different temperatures with 20 ppm formaldehyde.

As with the behaviour of the complex viscosity, we see that gelatin solutions treated at lowest reaction temperatures show highest storage moduli G' and consequently have the narrowest network. With regard to the swelling properties, it is important to know that not only the capacity of swelling is influenced by the degree of cross-links, it also has an effect on the initial velocity of swelling. The higher the temperature of the hardening process or the faster the cross-linking agent, the lower the rigidity of the gelatin layers and the higher initial swelling.¹⁰

Blends of PVAL/gelatin No 3 with ratios > 0.4 normally form a macroscopic two phase system. The cross-linking process differs with respect to the kinetics of hardening and the rigidity of the network (see Fig. 2)

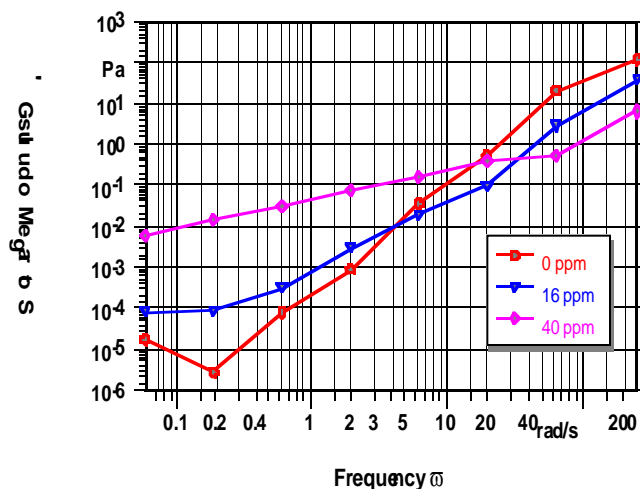


Figure 2. Frequency sweep of an aqueous blend (ratio 0.5) PVAL No. 4/gelatin No. 3 (polymer concentration 20 w/w % at 50°C) treated for 1 h at 60°C with different amounts of formaldehyde.

The rigidity of the aqueous blends investigated in Fig. 2 are lower than a solution of gelatin with the same concentration. The amount of hardener necessary for cross-linking is higher. From the decreasing slope of the curves at higher hardener concentration in Fig. 2, we see that networks keep flexible which might be positive for swelling speed and capacity.

Further investigations will show the influence of the rigidity of the heterogenous network on properties like swelling speed and swelling capacity.

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Biography

Dr. Ralf Pörschke studied Chemistry at the Rheinisch-Westfälisch-Technische Hochschule Aachen (Germany) and worked on the field of solid state polypeptide synthesis to become a Diplom Chemist in 1989.

At the Lehrstuhl für Makromolekulare Chemie and Textilchemie in Aachen under supervision of Prof. H. Höcker he completed his PhD studying the synthesis and properties of photo curable liquid crystalline polyesters. For a one year period he worked on different projects covering fibre chemistry and physics at the Deutsches Wollforschungsinstitut.

Since 1993 he has been a project manager of the Research and Development Department at the Deutsche Gelatine-Fabriken STOESS AG, Eberbach, being in charge with chemical modifications of protein materials.