Blends of Polyvinylalcohol with Collagen Hydrolysate: Properties of Water-Soluble Blown Films

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Summary: The study is focused on the effect of collagen hydrolysate and glycerol on properties of water-soluble polyvinylalcohol (PVA) blown films and blends. The experimental design method (DOE) was used in this study. Results from DOE show a strong effect of interactions between the blend components on resulting properties of the films. This fact was confirmed by means of the response surfaces of melting flow index, tensile strength and the content of insoluble fraction. It was concluded that the composition of PVA/CH blend must be precisely specified to avoid the processing complications.

Introduction

Collagen hydrolysate (CH) represents a mixture of oligopeptides originated of the enzymatic hydrolysis of collagen waste from leather industry. Kenawy et al1) prepared biodegradable PVA films modified with waste gelatine by coating process from water dispersion. The biodegradable films were crosslinked with dialdehyde. They confirmed that crosslinking is an effective way to extend the lifetime of films in the environment. Modification of PVA with CH gives the material with an improved biodegradability2). In addition, CH can affect the melt processing in the blow extruder and the product characteristics. Therefore, the objective of the present work is to examine selected processing characteristics as well as the final properties of the prepared films in a more complex way by using the experimental design method 3,4).

Results and discussion

The effect of CH, in combination with glycerol as plasticizer, on processing and properties of PVA blown films is difficult to study because of a number of variables present. Therefore, the 5 level two factors experimental design was chosen for investigation of the significance of all relevant parameters. Two weight ratios were defined as factors: x_1 = CH / PVA and x_2 = GL /

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(CH + PVA), where CH is collagen hydrolysate HYKOL E (Kortan, Czech Republic), PVA is polyvinylalcohol POVAL 205 (Kuraray, Japan) characterized by 12 mol% of residual acetate groups, 5 mPa viscosity of 4% water solution, and GL is glycerol of pharmaceutical grade (H.C.I. Chemicals, Slovakia). Stearic acid (S III, Setuza, Czech Republic) and SiO_2 is Sipernat 22S (S 22S Degussa, Germany) were used as additives in blends.

The conditions for experimental design and the compositions of individual blends are given in Tables 1 and 2, respectively.

Table 1. Conditions for experimental design

Factor No.	Factor	-1,414	-1	0	1	1,414	Step
x_1	CH / PVA	0,124	0,184	0,331	0,478	0,538	0,0147
x_2	GL/(PVA+CH)	0,130	0,155	0,215	0,275	0,300	0,0601

Table 2. Compositions of individual blends

	Coded levels of factors		Real levels of factors		Sample compositions [wt.%]				
Trial	x_1	x_2	x_1	x_2	PVA	CH	GL	SIII	S22S
1	-1	-1	0.184	0.155	73.1	13.5	13.4	0.31	0.31
2	1	-1	0.478	0.155	58.6	28.0	13.4	0.31	0.31
3	-1	1	0.184	0.275	66.2	12.2	21.6	0.28	0.28
4	1	1	0.478	0.275	53.1	25.4	21.6	0.28	0.28
5	-1.414	0	0.124	0.215	73.3	9.1	17.7	0.30	0.30
6	1.414	0	0.538	0.215	53.5	28.8	17.7	0.30	0.30
7	0	-1.414	0.331	0.130	66.5	22.0	11.5	0.32	0.32
8	0	1.414	0.331	0.300	57.8	19.1	23.1	0.28	0.28
9	0	0	0.331	0.215	61.8	20.5	17.7	0.30	0.30
10	0	0	0.331	0.215	61.8	20.5	17.7	0.30	0.30
11	0	0	0.331	0.215	61.8	20.5	17.7	0.30	0.30
12	0	0	0.331	0.215	61.8	20.5	17.7	0.30	0.30
13	0	0	0.331	0.215	61.8	20.5	17.7	0.30	0.30

The factor x_1 and x_2 were defined as follows. The range of CH content in blend PVA/CH was adjusted from 10 to 35 wt.% and the range of glycerol content in blend PVA/CH was adjusted from 10 to 25 wt.%. The very small contributions of the additives S III and S 22S to the ratios are neglected to simplify the use of the DOE method.

The blends in a dry form were prepared by using a planetary Brabender mixer. Each dry blend was characterized by melt flow index and by mechanical degradation evaluated from the torque curves, which were recorded by using a Brabender kneader operated at 230 °C, 50 rpm and load 5 kg.

The following parameters were evaluated from torque curves (Figure 1):

TQ_{min} – minimal value of torque [Nm] during kneading;

TQ_{t2} – time needed to increase the torque from a minimum value by 1 Nm;

TQ_{t3} – time needed to increase the torque from a minimum value by 2 Nm.

A rate of the torque increase $TQ_R = 1/TQ_{t3} - TQ_{t2}$ was evaluated as a slope of linear dependence between TQ_{t2} and TQ_{t3}.

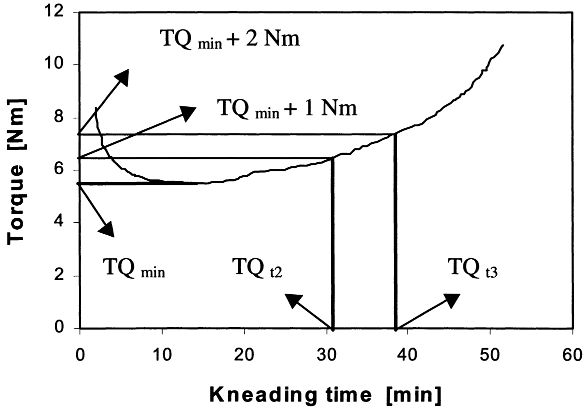

Figure 1. Schematic description of the parameters from torque curve

Melt flow index (MFI) measurements were carried out at 200°C under load 9kg and after 6 minutes of preheating.

Extruded tapes and blown films were prepared using a laboratory extruder with diameter 19 mm and L/D = 25. The compression ratio was 1: 3 and the temperature profile in extruder was 210, 220, 230 and 200 °C. All extruded samples were conditioned at the relative humidity 50% at 23 °C during 96 hours before the tensile strength measurements.

Table 3. The parameters evaluated using the experimental design method

Dry blends	Extruded tapes	Blown films
MFI /g /10min	Tensile strength / MPa	t_d /s*
TQ_{t2} / s		Up / wt%**
TQ_R /Nm/s		

***t_d** time to the first destruction measured as a time of the first defect observed after dipping the film in distilled water at 20 °C

****Up** insoluble fraction determined as a fraction filtered from 2 % solution prepared from blown film in distilled water

The experimental results obtained by using the DOE method are presented in a 3D-diagram form in Figures 2 to 8.

The response surface for melt flow index depicted in Figure 2 increases with increased both CH and glycerol content in the blend. A strong interaction activity of both factors is observed at higher concentration of both components. MFI increases along the diagonal from the point with the lowest concentration to the point with the highest concentration of both CH and GL in the blend.

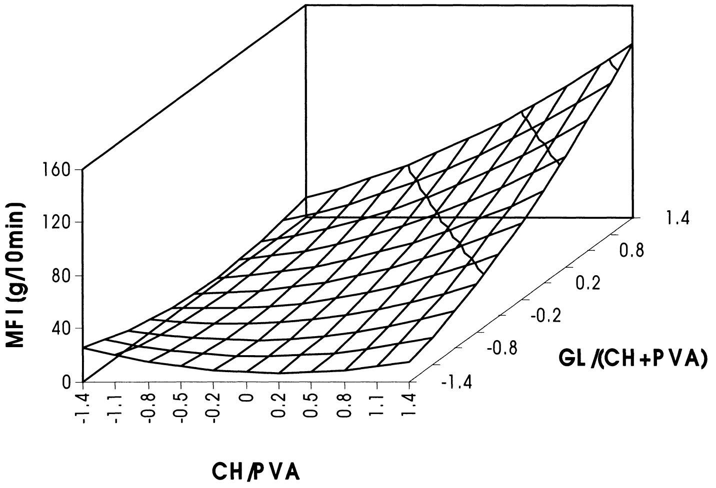

Figure 2. The response surface for the melt flow index

The dependence of torque minimal value (TQ_{min}) from both factors is shown in Figure 3. The effect of both factors obviously reflects the behavior of MFI. Both factors decrease TQ_{min} approximately in a similar extent. Torque minimal value is not affected by the interactions between CH and glycerol. This parameter decreases with rising the content of both collagen hydrolysate and glycerol content.

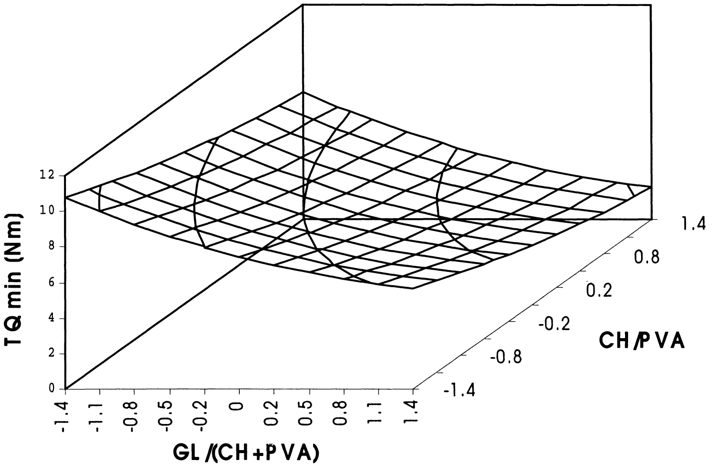

Figure 3. The response surface for torque minimal value (TQ_{min})

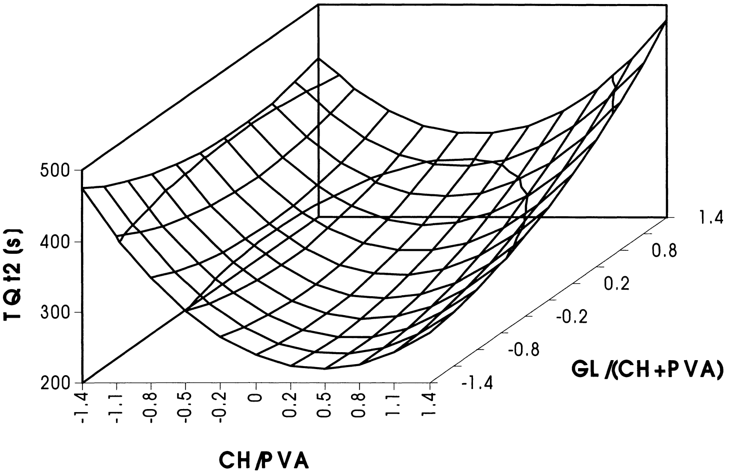

Figure 4. The response surface for torque TQ_{t2}

The response surface for parameter TQ_{t2} is shown in Figure 4. TQ_{t2} parameter characterizes a time when the torque starts to increase. Both factors have a strong effect on this processing characteristic. A higher collagen hydrolysate content in blend decreases TQ_{t2} and, in contrary, glycerol extends this time. The response surface along the collagen hydrolysate content achieves minimum for low as well as high glycerol content.

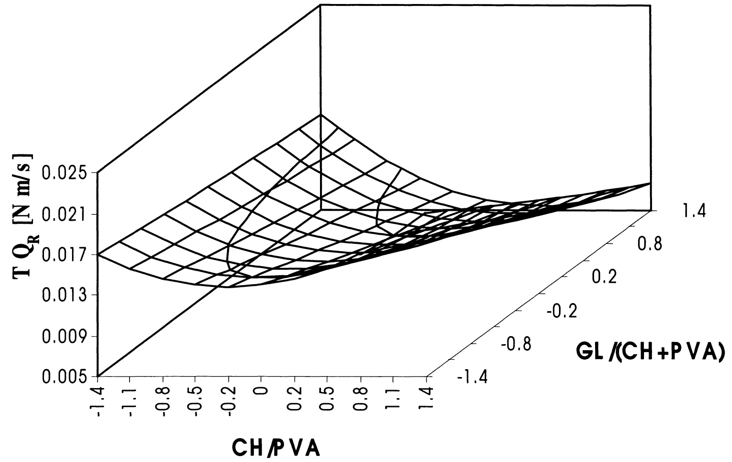

Figure 5. The response surface for rate of increase torque TQ_R

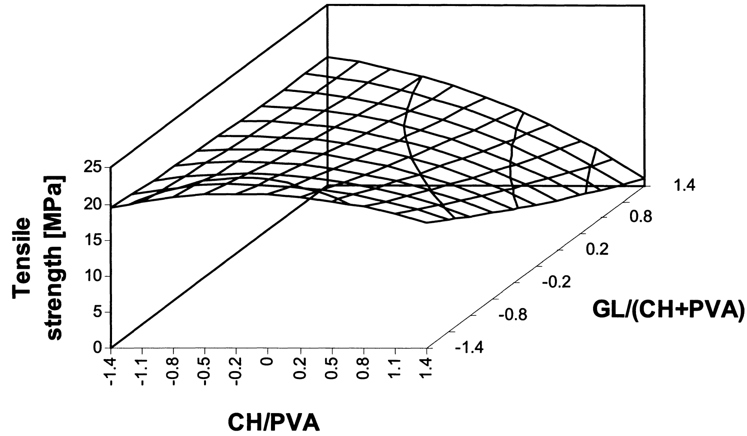

Figure 6. The response surface for tensile strength

Another important processing characteristic is the rate of the torque increase (TQ_R). Collagen hydrolysate content influences TQ_R quadratically. The effect of glycerol content is linear.

Decrease of TQ_R at higher collagen hydrolysate contents is more significant than at lower contents of collagen hydrolysate. This effect results from a significant interaction between both factors (Figure 5).

The extruded tapes were used for tensile strength measurements. The response surface for tensile strength is shown in Figure 6. Tensile strength at low glycerol contents reaches maximum when plotted against the collagen hydrolysate content. At a high glycerol content it is possible to see a quadratic decrease of tensile strength. The effect of glycerol addition is linear. Again, the interaction effect of both factors is clearly distinguished.

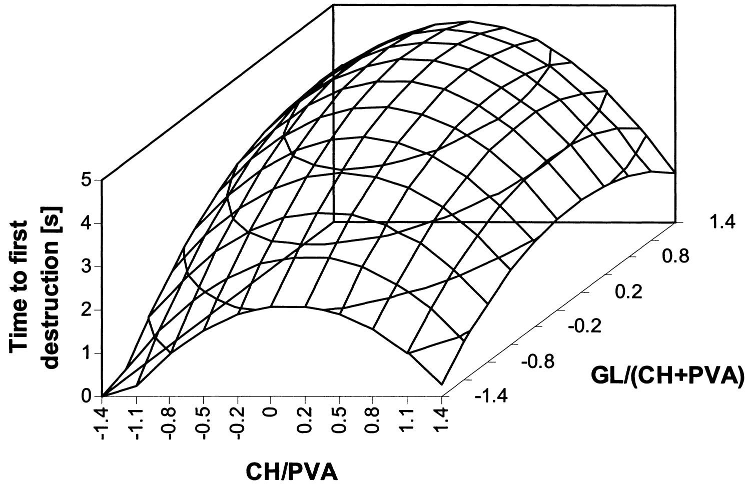

Figure 7. The response surface for time to the first destruction film

Time to first destruction (t_d) of films was evaluated using the designed solubility test. This parameter depends on both factors. An increase in glycerol content prolongs time to the first destruction linearly. The response surface reaches the maximum depending apparently on the first factor. Both factors play role independently and their mutual interaction is not significant (Figure 7).

An amount of insoluble fraction content determined in water solution (2 wt.%) depends on both factors (Figure 8). A contribution of glycerol to the final effect is evident. Insoluble fraction increases linearly with content of collagen hydrolysate. In contrary, glycerol content reduces this parameter. The effect of interaction between these two factors is reflected in a rapid increase of insoluble fraction content with decreasing the glycerol amount, and simultaneously with increasing the collagen hydrolysate content.

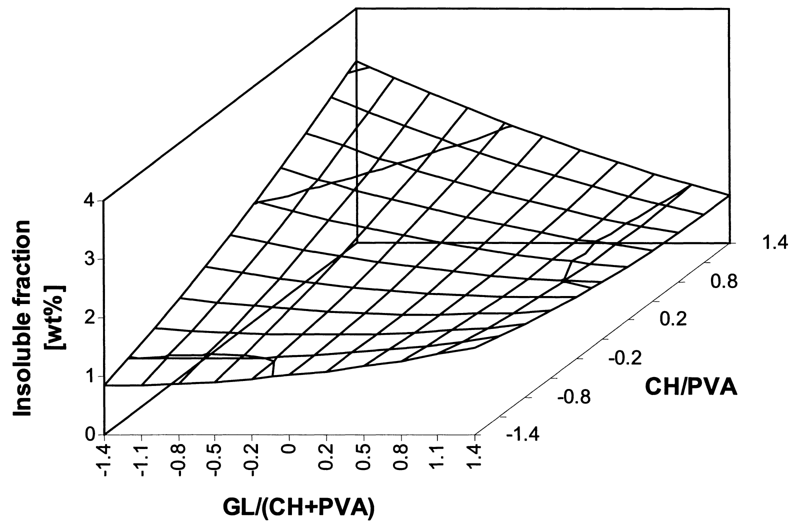

Figure 8. The response surface for insoluble fraction of blown films at 2 wt.% solution prepared in distilled water

Conclusion

All evaluated parameters are significantly influenced by collagen hydrolysate content described by factor CH/PVA as well as by glycerol content described by factor GL/(HC+PVA). TQ_{t2}, TQ_{min}, TQ_R parameters and time to the first destruction of film in water show extremes (maximum or minimum) on the response surfaces based on the collagen hydrolysate content. All these extremes lay -within the same concentration range of collagen hydrolysate (28-30 wt.%), which can be assumed as the critical concentration of CH in blend. A relatively strong interaction between collagen hydrolysate and glycerol is evident in case of the response surfaces of melt flow index, tensile strength and content of insoluble fraction.

The obtained results demonstrated in Figures 2 to 8 indicate a probability of the existence of chemical interactions between PVA and collagen hydrolysate, which influence processing properties of dry blend and properties of blown films as well. At the critical concentration range crosslinking reactions in PVA/CH blend start very fast. Due to this effect, blend with a higher content of collagen hydrolysate may become intractable. It can be concluded that composition of PVA/CH blend must be very precisely specified to avoid the processing difficulties for production on the industrial scale.

Acknowledgements

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