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Blends of Polyvinylalcohol with Collagen Hydrolysate: Thermal Degradation and Processing Properties

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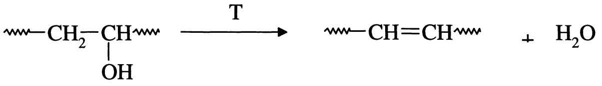
Summary: The blends of polyvinylalcohol with collagen hydrolysate were studied from the point of view of the effect of collagen hydrolysate on thermal degradation and processing properties. Elimination of deliberated acetic acid in reaction with NH_2 groups of CH can protect PVA against acidic catalysis of degradation. Using talc instead of silica can eliminate the crossliking effect in PVA-CH-silica blend when silica is used as antiblock agent. The obtained results make possible to use PVA/CH blends for blowing of biodegradable films with CH content up to 30 wt.%.

Introduction

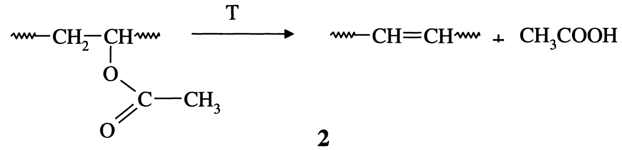
Polyvinylalcohol (PVA) is water soluble biodegradable polymer. Processing of PVA using the blow extrusion technology exhibits some specificity due to its relatively high sensitivity to thermal degradation at processing temperatures. It is commonly known that PVA in the first stages of thermal loading deliberates the low molecular weight product, water, and double bonds are formed in polymer chain (reaction **1**). Cross-links can be formed in the next step via the double bonds system.



$$\sim CH_2-\underset{OH}{CH}\sim \xrightarrow{T} \sim CH=CH\sim + H_2O$$

1

Acetic acid can be released from residual acetate groups of PVA (reaction **2**).



$$\sim CH_2-\underset{O-C(=O)-CH_3}{CH}\sim \xrightarrow{T} \sim CH=CH\sim + CH_3COOH$$

2

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The first stage of PVA degradation can be catalysed by acidic environment as it was described in the work[1)]. Both reactions together with acidic catalysis lead to crosslinking which causes an increase in the melt viscosity and makes the melt intractable. From this point of view, the addition of compound with basic groups seems to be suitable for improving the thermal stability of PVA. Collagen hydrolysate (CH) from enzymatic hydrolysis of leather waste may represent such a compound since it contains free basic NH_2 groups. Therefore we used CH as a modifier for PVA blow extruded films[2,3)]. This natural low molecular weight mixture of oligopeptides enhances the biodegradability of modified PVA films. We found that this modification also improved other properties (solubility, mechanical properties) of the films. Based on the FTIR spectroscopy measurements it was concluded that CH reacted with PVA during blend processing. However, the additional data showed[4)], that CH caused problems during processing (melt viscosity increasing) if used at higher concentrations (more than 15 wt-%). The objective of this work is to study in more detail the effect of CH on thermal stability and processing of PVA/CH blends.

Degradation of blends studied by thermogravimetry

Since the first stage of PVA degradation is associated with deliberation of the low molecular weight products, thermogravimetry (TG) was chosen to study the thermal stability of PVA. The characteristic curve for PVA is shown in Figure 1. The most important part of TG curve represents the temperature range between 150 and 200 °C, which corresponds to the processing temperatures of PVA blends during blow extrusion. This part of TG curve can be approximated by a linear fit and the rate of deliberation of low molecular weight products, *i.e.* the rate of degradation, can be estimated as the slope of this fit. The compositions of the model mixtures used for TG analysis are listed in Table 1. All mixtures were blended in the Brabender kneader (30 cm^3) at 230 °C during 5 minutes under 5 kg loading at ambient atmosphere and at 50 rpm. DERIVATOGRAPH 1500 D (MOM Budapest, Hungary) was used for TG analysis at the heating rate 5 °C and 100 mg sensitivity. The TG curves for pure CH, pure PVA (Blend No 1) and blend PVA/CH = 80/20 (Blend No 5) are shown in Figure 2.

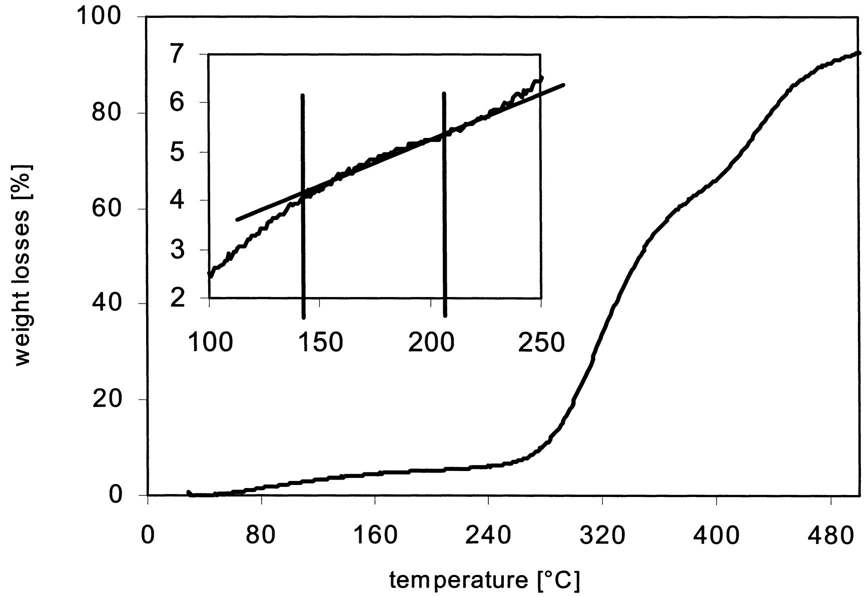


Fig. 1. The characteristic TG curve for PVA POVAL 205 (12% of acetate groups, viscosity of 4 % water solution 5 mPa.s at 20 °C, Kuraray, Japan).

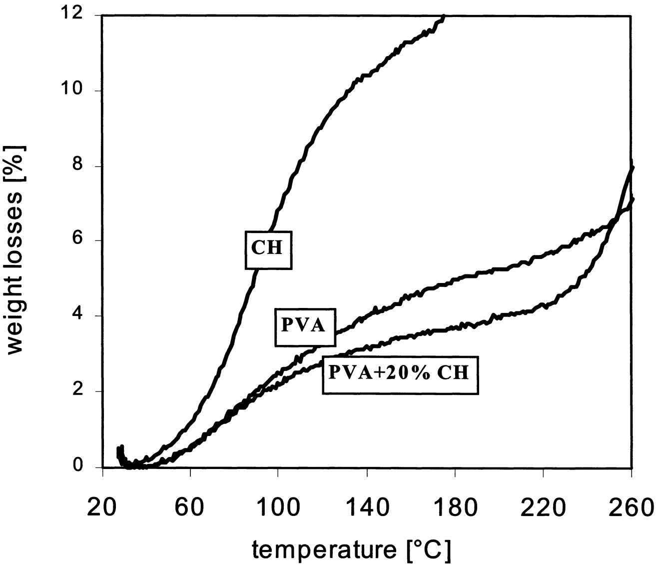


Fig. 2. TG curves for pure CH, pure PVA and blend PVA/CH = 80/20 by weight.

Table 1. Composition of mixtures for TG analysis

No	1	2	3	4	5	6
POVAL 205 wt-%	100	95	90	85	80	70
HYKOL E wt-%	0	5	10	15	20	30

PVA – POVAL 205, 12 % acetate groups, viscosity of 4 % solution 5 mPa.s, Kuraray, Japan
CH – HYKOL E, 14 wt-% of nitrogen, $M_w \cong 10\,000$, Kortan Hrádek n/Nisou, Czech Republic

It is interesting that the curve for PVA/CH blend does not lay between the curves for pure components. These results confirm interactions between PVA and CH, because the blend curve shows less weight losses than it can be expected based on the additive rule. The slope of linear fit between 150 and 200 °C was evaluated as the degradation rate for all prepared blends. The results are shown in Figure 3 as the dependency of evaluated slope on CH content for the measured samples as well as for calculated values according to the additive rule. While the CH concentration 5 wt-% has practically no influence on thermal stability, the rate of degradation strongly decreases at higher concentrations.

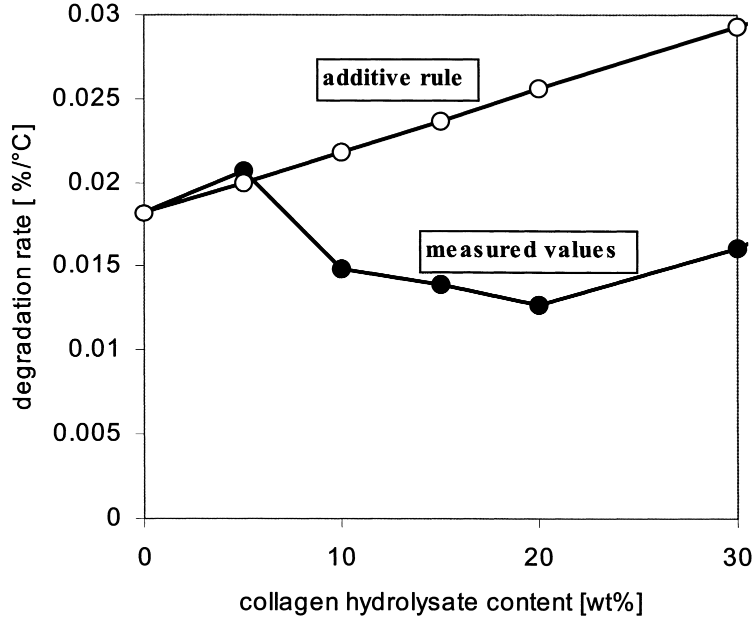
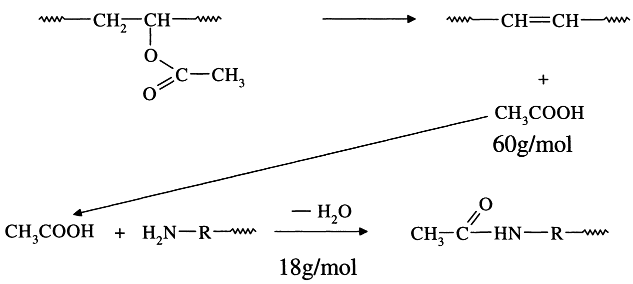


Fig. 3. Effect of collagen hydrolysate content on the rate of degradation of PVA/CH blends. Full circles are measured values, open circles are calculated values bases on the additive rule.

This effect can be explained by reactions scheme **3** :



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Deliberated acetic acid can react with free NH_2 group of collagen hydrolysate, releasing water. This reaction reduces the total mass of low molecular weight products approximately by a factor of three due to the differences in the molecular weight of acetic acid and water. In addition, this reaction substitutes the acidic substance (acetic acid) with neutral substance (water), which reduces the probability of acidic catalysis on PVA degradation.

The above mentioned hypothesis was verified by pH measurements at 20 °C (pH meter HI 9017, Hanna Instruments). Water solutions of 2 wt-% concentration were prepared from all blends given in Table 1. The solutions consisted of mechanical mixtures made of the same components but without thermal treatment were prepared and analyzed as well. The results are presented in Figure 4.

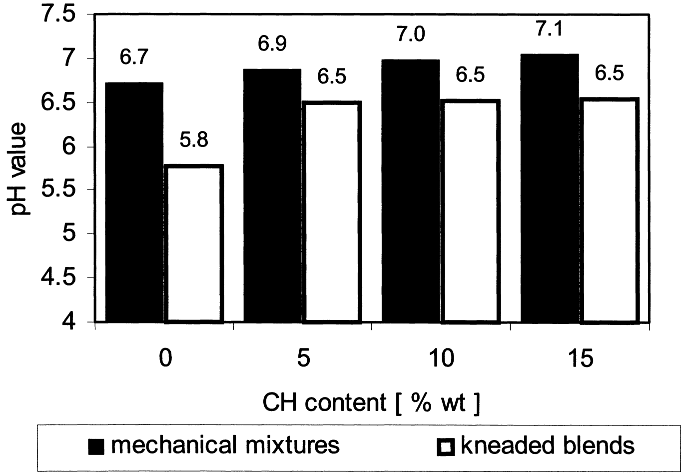

Fig. 4. Dependency of pH values on CH content for the Brabender-kneaded blends (250 °C, 5 min.) and for the corresponding mechanical mixtures PVA-CH, respectively.

Comparison of the pH values for solution of pure PVA before blending and after thermal treatment during blending in the Brabender kneader reveals a significant decrease in pH after blending. This confirms the concept of acetic acid deliberation during thermal processing of PVA. After adding of 5 wt.% of CH, the difference in pH between solutions of the mixture before processing and the blend after processing is significantly reduced. The pH value of solution of processed blend containing 5 wt-% of CH is significantly increased compared to PVA processed without CH. pH measurements indirectly confirm the proposed reaction scheme **3**. From this point of view, CH can be considered as a stabilizer for PVA in a thermal processing.

Influence of collagen hydrolysate on blend processing

During testing the PVA blends containing a higher quantity of CH from the processing point of view, a gel formation in the melt was observed. In the unmodified PVA blends, this effect is connected with crosslinking that follows the process of degradation. The previous part showed that CH prevents the degradation of PVA. The evaluation of the torque of the Brabender kneader during blending PVA with CH was used to examine the effect of CH on melt viscosity. PVA and CH at different CH concentration were blended without additives during 10 minutes at the conditions as described in the previous part. The torque records are shown in Figure 5.

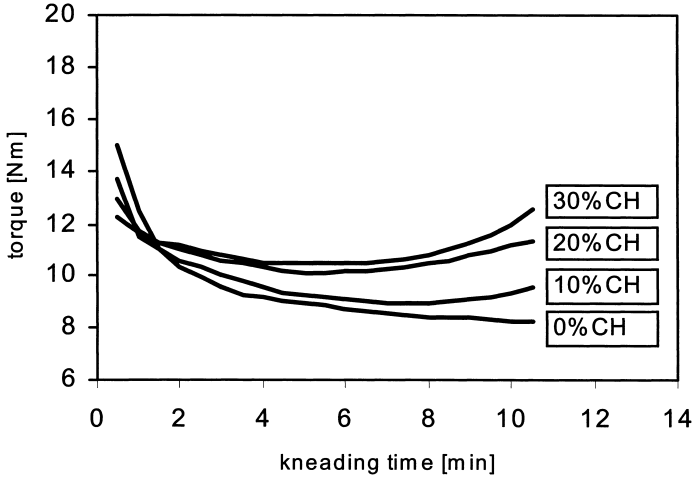

Fig. 5. Torque records for PVA and PVA/CH blends at different CH content (wt.%).

Torque slightly increases with increasing the CH concentration. This indicates the viscosity increase due to crosslinking reactions in the blend. Based on the previous results obtained from TG analysis, this crosslinking has no origin in the PVA degradation, but more likely this is the crosslinking of PVA by CH. However, the increase in the melt viscosity is relatively small and should not lead to the intractable blend. The commercial PVA blends for blow extrusion usually contain silica (SiO_2) as the antiblock agent. Because of its acidic character, silica can potentially cause also the PVA degradation. Therefore, a few experiments with silica and CH were done. The torque records were obtained as it is shown in Figure 6.

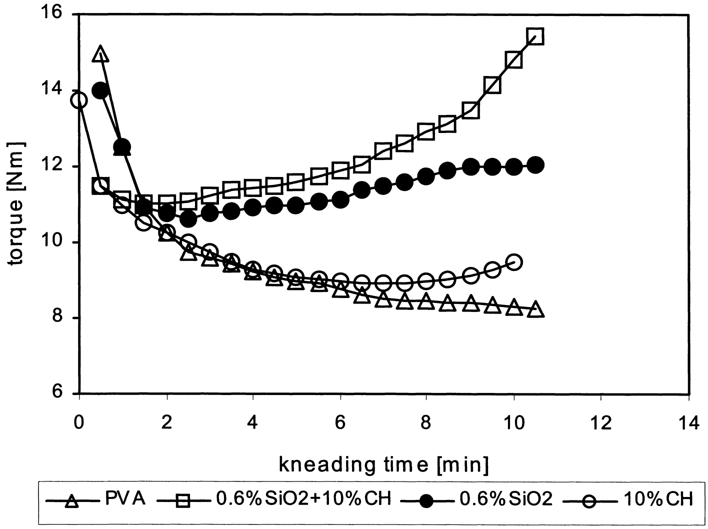

Fig. 6. The torque records for PVA and its blends with CH, silica and CH+silica.

A torque increase caused by silica (black circles) is much higher than that caused by CH addition (empty circles). The highest increase is caused by a mutual effect of CH and silica in PVA, which is higher than the additive effect and the blends become intractable when CH contents is 15 wt-% or higher. If this assumption is true, the processability of PVA/CH blend must be improved by replacing silica with another antiblock agent which is having a non-acidic character. For this purpose, talc ($Mg_3[(OH)_2(Si_4O_{10})]$) was used for further testing. The torque for these blends is shown in Figure 7.

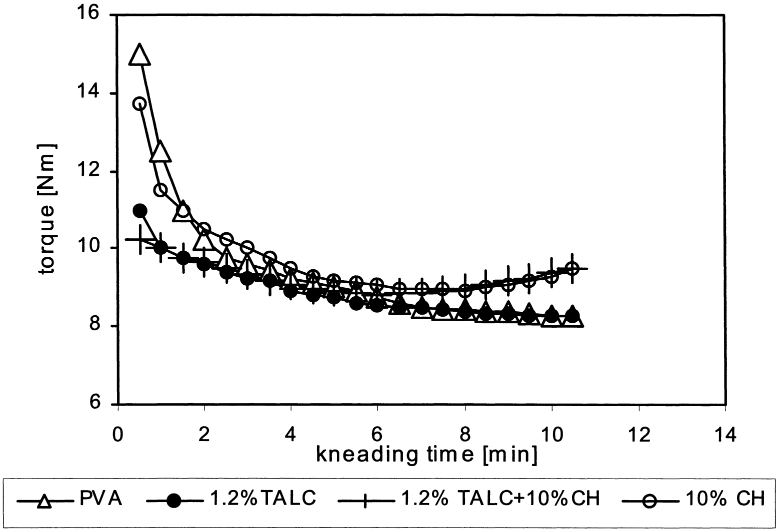

Fig. 7. The torque records for PVA and its blends with CH, talc and CH+talc.

In spite of a higher concentration of talc in comparison with silica (Figure 6), no synergism between talc and CH on torque was observed on the recorded curves. Torque was much lower if talc was used instead of silica and also the blown films of very good quality were prepared from such blends.

Conclusion

Based on the obtained results, we can conclude that collagen hydrolysate reduces the amount of low molecular weight products in the first stage of PVA degradation by elimination of acetic acid in reaction with NH_2 during the blend processing. As a consequence, the elimination of acetic acid prevents the PVA degradation processes via acidic catalysis. The torque records imply that collagen hydrolysate causes partially crosslinking of PVA. Crosslinking reactions are catalyzed by silica as a result of the synergistic effect between silica and collagen hydrolysate. The negative mutual effect of collagen hydrolysate at higher concentration (above 5 wt-%) and silica can be eliminated using talc as the antiblock agent. The basic talc did not result in the torque increase neither in pure PVA nor in PVA/CH blends. The results obtained in this work make possible to use collagen hydrolysate as PVA modifier for producing the high quality biodegradable blown films with a higher collagen hydrolysate content.

Acknowledgements

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