RHEOLOGICAL BEHAVIOUR OF STARCH ADHESIVES IN DEPENDENCE OF THEIR COMPOSITION

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ABSTRACT

Study of the adhesive compositions for labels is an important for the practice field. The labels are necessary and unavoidable part of all the goods with informative and publicity function. The adhesives for labels must cover a number of specific requirements. This study is focused on the partial or whole substitution of expensive casein adhesives by starch ones and investigation of the rheological properties of these compositions.

Keywords: starch adhesive, labels, rheological properties.

INTRODUCTION

Recently the environmental protection is of crucial importance for our life and the scientists are looking for new bio-based materials to replace the synthetic polymers. One of the branches where the use of polymers (synthetic latex-based adhesives) is wide-spread is the labeling of different products: bottles, jars for beer and beverages, pharmaceutical, cosmetic and food products [1]. Most adhesives currently used in the beer bottle industry include polyvinyl formal (PVF), acrylic ester, modified corn and potato starch, and casein [2]. Proteins and polysaccharides are used in a variety of non-food applications [3]: to modify the product’s flow behaviour, or to improve adhesion performance. For example, biopolymers are used in paper coating formulations to improve flow and consistency. Casein and starches are used in adhesive applications because of excellent flow behaviour as well as superb adhesion performance. Every adhesive has its shortcomings and limitations as health harm (PVF), high price (casein), poor water resistance (modified starch), etc.

There are many specific requirements regarding the properties of adhesives for labels. In the literature [1, 4] is underlined that high quality label adhesives should have the following characteristics: high reliability of the adhesive joint in the initial stage of drying, short setting time, and pseudoplastic flow behavior. The adhesives usually are complex multi component systems. The use of traditional casein in these compositions is economically unfavorable. So its application is limited by its high price and viscosity. Recently different investigations showed the possibility of its substitution by natural products based on soy been proteins [1] or modified starch [5, 6]. The starch is wide spread, cheap and it can be used as a thickener bonding water or as emulsions stabilizer or gelatinizing agent. Its use in adhesive compositions increases. During the labeling the adhesive creates a water-resistant bond paper-glass or paper-metal. It allows immersing the bottles in cold water without label separation (unstuck). These adhesives are suitable to high speed manufacturing. They possess fast stick qualities for the paper and the folio.

The aim of the present paper is to study the rheological properties of adhesives based on modified starches “Solvitose” produced by “Avebe” and of those partially substituted by enzyme destructed starch, produced in the Institute for cellulose and paper (ICP) – Sofia, Bulgaria.
EXPERIMENTAL

Materials and methods

Six adhesive compositions were formulated in laboratory conditions. The following materials were used: *Solvitose HNP* – oxidized hydroxypropyl ether of potato starch. The product is white granulated or powdered material, without smell, soluble in hot water.

*Solvitose P5* – netlike carboxymethyl ether of maize starch. The product is pale yellow granulated or powdered material, soluble in hot water.

*Enzyme destructed potato starch* - type of the starch “EQU” destructed by α-amylase by original receipt of ICP-Sofia with 50 % mass concentration.

*Carbocel MM35* – carboxymethylcellulose by “Lamberty”.

*Urea*

The technology consists in a thin boiling of enzyme destructed starch, cooling, dissolution of Solvitose and the carboxymethylcellulose and finally, urea addition. In Table 1 the compositions of the laboratory-made adhesives are summarized. As No 1 the original receipt of “Avebe” is presented for comparison. Compositions 2 to 6 are laboratory-made compositions; No 7 is an industrially manufactured one using the results of the present study.

As a standard for the results estimation a casein adhesive “SPC-2280-Super” of “Schauer Produkte GMBH”-Germany was used. Two types of this product were tested: light and dark. Their characteristics are given below:

- viscosity determined by Brookfield viscometer at 20°C – about 80 000 mPa s
- apparent viscosity determined by Rheotest RV2 at shear rate 9 s⁻¹ – 96 Pa s for the light and 75.2 Pa s – for the dark adhesive. For shear rate of 27 s⁻¹ both samples exhibited apparent viscosity of 52 Pa s.
- concentration - 12.7 % mass.
- pH - 7.5-8.
- quality in exploitation – high speed of initial hold, stable fixing of the paper labels, good sticking on the bottles at all the speeds, good sticking on dry and wet, hot and cold packing, high stability to condensed water and moisture. The adhesive can be applied by all types of machines: with or without pump and with or without heating.

As a standard the adhesive „SPC-2240” was also tested. It is manufactured by the same company and its field of use is similar. The flow characteristics of this type of adhesive almost coincide with the dark “SPC-2280-Super” ones.

It is well established that the adhesives are usually non-Newtonian fluids, and it is important to have an information concerning their rheological behaviour. In our experiments their flow curves were determined by the use of viscometer Rheotest RV2 (Germany) with H cylinder at 20°C. Unique experiments with S2 cylinder showed no slip effect on the wall.

<table>
<thead>
<tr>
<th>№</th>
<th>Material, %</th>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solvitose HNP and Solvitose C5</td>
<td>85.7</td>
<td>64.5</td>
<td>61</td>
<td>57.2</td>
<td>54.9</td>
<td>52.3</td>
<td>57.3</td>
<td></td>
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<tr>
<td>2</td>
<td>Enzyme destructed potato starch</td>
<td>23.3</td>
<td>27.4</td>
<td>32</td>
<td>34.6</td>
<td>37.8</td>
<td>31.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CMC</td>
<td>1.4</td>
<td>1.4</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Urea</td>
<td>14.3</td>
<td>10.8</td>
<td>10.2</td>
<td>9.6</td>
<td>9.3</td>
<td>8.7</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Total, %</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Analysis for dry matter content, %</td>
<td>42.1</td>
<td>42.2</td>
<td>42.2</td>
<td>42.1</td>
<td>42.1</td>
<td>42</td>
<td>42.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degree of substitution of Solvitose by starch, %</td>
<td>0</td>
<td>24.7</td>
<td>28.8</td>
<td>33.3</td>
<td>35.9</td>
<td>39</td>
<td>33.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

In Fig. 1 typical flow curves of the samples studied are presented. It can be seen that they are non-linear without intercept. So, their rheological behaviour could be described easily by power-law rheological model of Ostwald de Waele:

\[ \tau = K \gamma^n \]  \hspace{1cm} (1)

here \( \tau \) is the shear stress, Pa, 
\( \gamma \) is the shear rate, \( s^{-1} \),
\( K \) is the consistency index, \( Pa.s^n \)
\( n \) is the flow index

The flow index \( n \) is a measure for the degree of the non-Newtonian behaviour (more it differs unity, more non-Newtonian is the fluid). The consistency index \( K \) is a measure for the consistency of the fluid.

The rheological parameters of the power-law model were found by Excell standard statistics. Their values are given in Table 2, where \( C \) is the degree of substitution for the compositions studied (% of Solvitose substituted by starch).

The relationship between the substitution degree and the rheological parameters of the power-law model is presented in Fig. 2.

It can be seen from Fig. 2 that the increase of the degree of substitution leads to the decrease of the consistency index and to the increase of the flow index thus making the compositions more Newtonian and less consistent. This evidently worsens the quality of the samples. In the same time the price of the adhesives is strongly dependent on their composition. So, the purpose of this study was to find out an adhesive composition optimal at quality and price.

The consistency index seems to be more dependent on the substitution degree. This dependence was determined statistically. Its form is depicted in Fig.3. Evidently this relationship exhibits a maximum. A polynomial dependence of second order was tried to describe this phenomenon. The comparison between the experimental data and the calculated by this second order polynomial function is presented in Fig.3. The following form of equation was found:

\[ K = -0.2503C^2 + 3.7443C + 343.65 \]

To calculate the value of \( C \) assuring maximal consistency, the first derivative of this equation was found.

To exhibit an optimum it must be equal to zero. A value of \( C_{opt} = 7.48\% \) was determined.

During the rheological measurements up and down flow curves were found. A hysteresis was observed between the two curves, i.e. the compositions exhibited thixotropic behaviour – Fig.4. In Fig.1 and Table 2 the results concerning the upward flow curves are presented.

It was found that the apparent viscosity at a given shear rate and the degree of thixotropy decreased with

![Fig. 1. Typical flow curves for the samples studied (numbers of the samples are as in Table 1).](image)

![Fig. 2. Dependence of rheological parameters of adhesives on the degree of substitution.](image)

Table 2. Rheological parameters of the power-law rheological model for different substitution degrees.

<table>
<thead>
<tr>
<th>No</th>
<th>C, %</th>
<th>K, Pa.s^n</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>342.76</td>
<td>0.4702</td>
</tr>
<tr>
<td>2</td>
<td>24.7</td>
<td>293.81</td>
<td>0.3582</td>
</tr>
<tr>
<td>3</td>
<td>28.8</td>
<td>223.72</td>
<td>0.4483</td>
</tr>
<tr>
<td>4</td>
<td>33.0</td>
<td>199.27</td>
<td>0.4478</td>
</tr>
<tr>
<td>5</td>
<td>35.9</td>
<td>148.24</td>
<td>0.5226</td>
</tr>
<tr>
<td>6</td>
<td>39</td>
<td>116.09</td>
<td>0.5415</td>
</tr>
</tbody>
</table>
the increase of substitution degree of adhesive compositions. Taking into account the viscosity values required by the clients (about 100 – 140 Pa s) almost coinciding with standard apparent viscosities of industrial casein glues SPC 2280 and SPC 2240, sample 4 was chosen as a basis for industrial experiments. In Fig. 5 the comparison between the flow curves of adhesive compositions in dependence on their substitution degree studied is presented. It can be seen that for low shear rates typical for the practice, samples 4 and 5 exhibit apparent viscosity values required. Sample 7 is the one, manufactured on the basis of sample 4 and tested industrially. In Fig. 6 the comparison between the flow curves of standard glues, the chosen laboratory sample 4 and the industrially tested one 7 is presented. Quite a satisfactory coincidence in their flow behaviour is observed. It can be also said that in samples 4 and 7 the thixotropy is low, almost negligible.

**CONCLUSIONS**

From the experiments on the flow behaviour of casein glues and substituted with starch glues the following conclusions can be derived:

All the compositions studied are pseudoplastic with different degree of thixotropy decreasing with the starch substitution degree.

It was determined an optimal laboratory receipt for producing of adhesive compositions based on modified starch “Solvitose” and enzyme destructed starch. This composition can successfully be used instead of the expensive casein glues for labeling of glass packing.

According to this optimal receipt was produced an industrial batch of the glue substitute of the casein one with rheological parameters close to those of standard casein glues SPC 2280-Super.

The cost price of the created compositions is lower than that of the casein standard glues and than the made
by receipt of “Avebe” company adhesive with about 0.15 Euro/kg. The cost price of the casein glue was lowered with about 0.60 Euro/kg.

The rheological parameters and their dependencies on the substitution degree found can be used to produce industrial glues in according to clients’ requirements.

REFERENCES