Physical, Mechanical and Surface Properties of Calendered PVC Films Filled with Bentonite and Pectin

Eugene Sivtsov, Maya Uspenskaya, Kseniia Volkova and Evgeny Belukhichev

ABSTRACT

The influence of bentonite and pectin as PVC fillers taken in the amount up to 10% is considered on thermal stability, processability, strength, elasticity and surface properties of PVC films obtained by rolling used as a simplified model of calendering. The effect of heat treatment on the films colour was estimated when colour was used as a parameter indicating the degree of degradation by mechanism of formation of sequences of polyconjugated double bonds. To solve the problem of suitability of bentonite and pectin as fillers optical methods of investigation, thermomechanical analysis, thermogravimetry, DSC were used. Recommendations on application of bentonite and pectin in PVC formulations were given.

INTRODUCTION

PVC films market is difficult to overestimate [1]. PVC is mostly used in packaging: blisters for medicines, batteries, electronic parts and accessories, tools, toys, for disposable syringes and medical devices, cling film for meat, fish, cheese, vegetables, toiletries, adhesive tapes. Their wide application creates a significant environmental problem. This is partly solved by recycling of PVC materials. But the packaging is often difficult to collect for recycling. This requires a responsible attitude of the people. Most packaging is simply thrown in the recreation areas, along roads, in nature. Then the problem of PVC degradation under the influence of natural factors should be addressed. PVC is one of the most poorly biodegradable plastics. It is obvious that giving PVC the properties of biodegradability is a very important task of modern plastics technology. Typically this is achieved by adding into the polymer composition an appropriate filler. Fillers have to meet a wide range of requirements: they must be cheap, non-toxic, compatible with polymer matrix, not degrade the polymer processability in the film, not to lower the thermal stability of the polymer. Thermal stability is a very important problem for PVC,

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since the polymer begins to degrade intensively already during its processing into the product. Bentonite and pectin can be such fillers. Therefore, the aim of this study is to investigate the effect of bentonite and pectin in the physical, mechanical and surface properties of calendered PVC films.

EXPERIMENTAL PART

Samples Preparation

PVC composition was prepared in a high-speed mixer at a speed of 6000 rotations per minute and barrel heating of 40°C. All components of the mixture were added simultaneously and mixed for 5 minutes. Samples of PVC rigid films for food packaging were produced on a laboratory mill at a temperature of 170-175°C and a shaft rotation rate of 26 rotations per minute. Hinge dosed into the working gap of rolling mill and stirred for 3 minutes. After removal from the rolls, PVC-film sample smoothed on the heated polished stand. The film thickness is 350 microns.

A typical formulation consists of:
- Suspension PVC, Fikentscher constant value is 57-58, the mass fraction of volatile compounds is 0.04%,
- Organotin thermo stabilizer (mercapto dioctyl tin) 0.2-1.5%,
- Flow modifier of polymer mixture 2.0-4.0%,
- External lubricant (paraffin wax) 0.1-0.5%
- Filler (bentonite, pectin) 1-10%:
  - Sample 1 - 10% bentonite,
  - Sample 2 - 10% pectin,
  - Sample 3 - 5% bentonite,
  - Sample 4 - 5% pectin,
  - Sample 5 - 1% bentonite,
  - Sample 6 - 1% pectin.

Methods of Investigation

Yellowness index of the samples $b$ was measured with a spectrophotometer DataColor SF600 Plus using CIELab colour coordinates system. In these coordinates $L$ – black-and-white channel of the colour measurement, $a$ – a red-green one, $b$ – blue and yellow one. Index $b$ was measured along the length of the sample subjected to heating according to the procedure described below. Estimate of degradation was carried out at a depth of yellowing. The deeper degradation, the higher the value $b$. Specific degradation effects should be considered in isolation without reference to the index $b$.

The degree of degradation was investigated using a special device. A strip sample passed through an oven heated to 210°C at a certain speed. The initial portion of the strip was in the oven during the longest time (40 minutes), the last portion of the strip is not subjected to degradation at all. Thus, the gradient of the depth of degradation is observed along the length of the strip. You can compare the samples with each other by comparing the variation of colour in the length.

The photos were taken with an optical microscope OlympusSTM6, under a tenfold increase.

The strength and elasticity of the films were measured on the texture analyzer TA.Xtplus with nozzle holder for film XTP/FSP and spherical probe P/SS Ø5mm. Speed of the probe lowering was 1 mm/sec. Software «Exponent» was used.

Thermomechanical tests were conducted using a TMA analyzer 402 F1 Hyperion under the following conditions: sample length – 30 mm; sample width – 30 mm; heating rate – 1°/sec; static force – 0.1 N.

Thermogravimetric analysis was performed using the device TGA 209 F1 libra. Conditions: initial temperature – 25°C; final temperature – 500°C; linear heating speed – 10K/min. Differential Scanning Calorimetry (DSC) was conducted using a DSC 204 F1 Phoenix. Conditions: initial temperature – 25°C; final temperature – 500°C; speed linear heating – 10 K/min; an inert gas (nitrogen) feed rate – 20 mL / min.

RESULTS AND DISCUSSION

The very complicate problem must be solved. On the one hand, it is necessary to provide PVC of thermostability, on the other hand, PVC should be easy biodegradable. Moreover, additives which give biodegradability to PVC can negatively and positively influence on its thermal stability. Therefore, these two questions should be examined together.

Accordingly, the first test was one for thermal stability of PVC samples containing various amounts of bentonite and pectin. It was carried out using a specially designed apparatus and by the procedure described above. Figure 1 shows the test strips along the length of which temperature exposure varies smoothly from the right side (the lowest exposure) to the left – the maximum of exposure. Pectin begins to degrade upon heating even at 70-80° C [2]. It is obvious that the effect of pectin on PVC thermal stability is very deep. Moreover, the date of figure 1 clearly shows that process of thermal-oxidative degradation is non-stationary at the pectin content of 5 and 10%. It is avalanche-like and develops very fast capturing the entire volume of the sample, even those parts which have not been exposed to heat (Fig. 1, samples 2 and 4). Perhaps the reason for this are the organic acids released during the degradation of pectin [3]. Apparently the use of only 1% pectin allowed to stay within suitable thermal stability.

On the contrary, bentonite increases the thermal stability of PVC composition. Figure 2 shows the dependence of yellowness index \( b \) on the distance from the left edge of the strip (the beginning of heat treatment).

![Figure 1](image)

**Figure 1.** The test strips in the thermal stability of samples experiment. Temperature exposure increases from the right side to the left (above duration of stay in the oven is indicated).
Adding of bentonite and pectin to the films composition changes the surface morphology of PVC. Bentonite (sample 1 and 5, Figure 3) makes the surface more heterogeneous. When filling is up to 10% there is considerable unevenness of the surface and opaque white agglomerates of 30-360 microns size are observed. This film scatters light strongly. At the same degree of filling bentonite sample (sample 2) has a uniform surface. Agglomerates have the size of 80-100 microns. When the degree of filling is 1% (samples 5 and 6) the surface has homogeneous structure with the inclusion of a small amount of agglomerates.

Figure 2. The dependence of yellowness index b on the distance from the left edge of the strip.

Surface properties and optical characteristics of the films (Table 1) is a consequence of the morphology described above.
Table 1. Surface properties and optical characteristics of the films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Turbidity</th>
<th>Light transmission coefficient</th>
<th>Brightness</th>
<th>Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>49.9</td>
<td>61.5</td>
<td>32.9</td>
<td>5.88</td>
</tr>
<tr>
<td>Sample 2</td>
<td>47.8</td>
<td>67.0</td>
<td>35.7</td>
<td>5.09</td>
</tr>
<tr>
<td>Sample 3</td>
<td>31.9</td>
<td>69.1</td>
<td>53.2</td>
<td>6.10</td>
</tr>
<tr>
<td>Sample 4</td>
<td>31.8</td>
<td>40.2</td>
<td>55.5</td>
<td>11.05</td>
</tr>
<tr>
<td>Sample 5</td>
<td>14.1</td>
<td>72.4</td>
<td>84.2</td>
<td>3.34</td>
</tr>
<tr>
<td>Sample 6</td>
<td>14.1</td>
<td>73.4</td>
<td>89.5</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Sample 1

Sample 2

Sample 6


Figure 3. Optical microscopy of the samples under various observation modes.
Adding of bentonite and pectin also affects the strength of the compositions. Data of Table 2 show the strength and elasticity of the samples compared to the unfilled PVC film. It is clearly seen that both the fillers reduce the strength of the polymer. Elasticity is sharply reduced. However, these properties poorly depend on the amount of added filler.

Table 2. The strength and elasticity dependence on fillers content.

<table>
<thead>
<tr>
<th></th>
<th>Strength, MPa</th>
<th>Elasticity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC without filler</td>
<td>13.2</td>
<td>110</td>
</tr>
<tr>
<td>Sample 1</td>
<td>6.5</td>
<td>19</td>
</tr>
<tr>
<td>Sample 2</td>
<td>7.4</td>
<td>22</td>
</tr>
<tr>
<td>Sample 3</td>
<td>6.4</td>
<td>23</td>
</tr>
<tr>
<td>Sample 4</td>
<td>6.0</td>
<td>22</td>
</tr>
<tr>
<td>Sample 5</td>
<td>7.8</td>
<td>27</td>
</tr>
<tr>
<td>Sample 6</td>
<td>9.1</td>
<td>38</td>
</tr>
</tbody>
</table>

Thermomechanical test showed that fillers affect the shape of thermomechanical curve, glass transition temperature $T_g$, flow temperature $T_f$, as well as their ratio. Typical curves are shown in Figure 4. Devitrification of unfilled PVC sample begins at about 50°C, and it flows at 84°C. Such low value of $T_f$ is due to the presence of flow modifier in the formulation. It also affects the $T_g$. Adding 5% of pectin shifts $T_g$ to about 70°C and $T_f$ to 86°C. Adding 1% of bentonite reduces the difference between $T_g$ and $T_f$.

![Figure 4. Thermomechanical curves: 1 – unfilled PVC, 2 – sample 4, 3 – sample 5.](image)

The transition from *elastic* behavior to *plastic* behavior is also displayed on the DSC data. Figure 5 shows the thermogram of sample 4. Temperature of the beginning of endothermal peak is in a good accordance with $T_f$.

Thermogravimetric analysis showed a weak effect of bentonite and pectin and their content on the thermal stability of the films. Temperatures at which weight loss reached 10 and 50% are presented in Table 3. Taking into account the error and the statistical nature of the data presented it is difficult to assert the existence of a certain relationship between these characteristics and filler content.
Table 3. Characteristic temperatures in thermogravimetric analysis of PVC samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperatures of 10% weight loss</th>
<th>Temperatures of 50% weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled PVC</td>
<td>288</td>
<td>337</td>
</tr>
<tr>
<td>Sample 1</td>
<td>290</td>
<td>332</td>
</tr>
<tr>
<td>Sample 2</td>
<td>284</td>
<td>335</td>
</tr>
<tr>
<td>Sample 3</td>
<td>290</td>
<td>327</td>
</tr>
<tr>
<td>Sample 4</td>
<td>278</td>
<td>329</td>
</tr>
<tr>
<td>Sample 5</td>
<td>278</td>
<td>318</td>
</tr>
<tr>
<td>Sample 6</td>
<td>282</td>
<td>325</td>
</tr>
</tbody>
</table>

CONCLUSION

Bentonite and pectin are fillers interesting from point of view of probable biodegradability of PVC films and they can be added up to 10% in the polymer without seriously compromising with physical and mechanical characteristics of the films. These fillers have no significant effect on the thermal stability of the materials expressed as weight loss rate. However, they strongly influence on colour of the films due to the presence of sequences of polyconjugated double bonds. Processability of the compositions depends on the content of bentonite and pectin because they alter T_g and T_r. The results of this study should be taken into account when such formulations are developed for certain products from PVC.

REFERENCES