Modification of polypropylene for manufacture by thermoforming

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Polypropylene is one of the most widely used materials for the production of containers. However, it has certain shortcomings that lower the quality of products or make the production process difficult, both at the stage of extrusion of sheet materials and at the stage of thermoforming (a narrow forming temperature range of about 10 K).

Furthermore, the great variety of polymeric containers requires the creation of special composites for colouring, the production of transparent articles, and so on. In recent years, an increasing number of materials based on polymer blends have been created. This is due to the simplicity and accessibility of their manufacture, and also to the fact that new properties are obtained that are not inherent in any of the components of the blend.

The use of different copolymers – ethylene with propylene, vinyl acetate, and other monomers – as modifying additives is also known.

As modifying additives, we used a block copolymer of ethylene with propylene (SEP), atactic fraction of a copolymer of ethylene with propylene (ASEP) in the form of a ternary copolymer of ethylene with propylene of the formula \((PE)_m(PP)_n(PE)_m\), and also a copolymer of ethylene with vinyl acetate (SEVA), since it has a high elasticity and low melting temperature and can be distributed well in the polymer matrix.

An investigation was made of the effect of the above compounds on the melt flow index (MFI) and deformation and strength characteristics. The results of the investigations are presented in Figures 1 and 2 and in Tables 1–4.

When SEP and SEVA are introduced there is a certain increase in the MFI of polypropylene (in a 10% range) with an increase in the modifier content to 5 wt.% (Figure 1).

A sharp increase in the flow of PP is observed when ASEP is introduced into it. A feature of ASEP is the fact that, in fairly long polypropylene blocks, the methyl groups are distributed irregularly, forming an atactic structure. With an ASEP content in the polymer of 2%, the MFI values increase by a factor of 2, and with increase in the amount of ASEP to 4% they increase by a factor of more than 4 (Figure 1).

Thus, to intensify the processing of polypropylene, ASEP is a promising modifier making it possible not only to increase the extrusion rate in the production of sheet materials but also to lower the processing temperature.

The physicomechanical properties for the examined composites of PP with different modifiers were determined on pressed specimens produced on a press with a nominal force of 10 t at a temperature of 200°C.

The dependence of the yield point in elongation of PP on the SEVA and ASEP content is presented in Figure 2.

From the data presented in Figure 2 it can be seen that the yield point in elongation increases little with a SEVA content of 1 wt.%.

Table 1 presents data of deformation and strength tests of PP modified with different additives.

From the data in Table 1 it follows that, when PP is modified with ASEP, the yield point in elongation increases roughly by 20% with retention of the elongation at yield point. To a lesser extent the yield point in elongation is increased by the introduction of 1 wt.% SEVA, but the given
composition has the highest indices of elongation at yield point. Such a nature of change in the deformation and strength properties is connected with change in the degree of crystallinity of PP under the action of modifiers.

As is known, PP is a highly crystalline polymer, which narrows the region of its melting temperature and makes it difficult to process it by thermo- and vacuum forming.

The degree of crystallinity of polypropylene has a considerable influence on the strength and deformability of the material during the production of PP articles by thermoforming.

In this connection, the effect of modifiers on change in the degree of crystallinity was determined from data of differential scanning calorimetry (DSC) and IR spectroscopy.

DSC data were taken on a Dupont Instruments differential scanning calorimeter with a rate of rise in temperature of −5 K/min, while IR spectra were taken on a Specord instrument in the wavelength range 500–4000 cm⁻¹.

Table 2 is based on an analysis of DSC curves and presents the melting start temperature, \( T_s \), the temperature of the maximum heat effect of melting, \( T_{\text{max}} \), the difference in these quantities, \( \Delta T \), and also the degree of crystallinity, \( X \).

The degree of crystallinity was calculated as the ratio of the heat of melting of the polymer under investigation to the heat of melting of paraffinic hydrocarbon dotriacontane, adopted as the heat of melting of entirely crystallised polypropylene, equal to 116 J/g. The melting temperature was also determined from data of thermomechanical analysis.

From the data in Table 2 it can be seen that modifiers have practically no effect on the melting temperature but change the degree of crystallinity.
The introduction of modifiers leads to an increase in the free volume, to an increase in the kinetic flexibility of the chain, and to an increase in the rate and degree of crystallinity. Furthermore, during cooling, the high molecular weight additives introduced, which have lower melting temperatures, are converted more rapidly into the glassy state and may act as crystallisation nuclei. Thus, the introduction of ASEP and SEVA into polypropylene increases the degree of crystallinity by a factor of 1.5.

Reduction in the diffuseness of melting processes is due to change in the size and defectiveness of the spherulites.

Data on increase in the degree of crystallinity of PP in the presence of additives are confirmed by IR spectroscopic studies.

This is judged from the change in optical density of the absorption bands in the IR spectra of PP that are characteristic of regular spirals:
- at 998 cm\(^{-1}\) (isotactic spirals containing more than 12 monomer units);
- at 840 cm\(^{-1}\) (short spirals).

The 1440 cm\(^{-1}\) band characteristic of vibrations \(\delta_s\) of CH\(_2\) bonds was chosen as the internal standard.

Table 3 presents data on the relative optical densities of the crystallinity bands indicated above for PP and for PP with modifiers.

From the data in Table 3 it can be seen that the number of regular conformers, both long and short, is higher for the modified grades of PP than for the initial PP, and this difference (as indicated also by DSC data) is considerable.

The influence of the obtained characteristics on the quality of thermoforming products was investigated.

Articles (beakers) were produced by vacuum forming from pressed sheets of about 1 mm thickness, and the elongation factors, thickness variation, and proportion of high-elastic strain were determined.

The proportion of high-elastic strain was determined at a temperature of 150°C and during holding for 1 h from the shrinkage of specimens cut out from the bottom of the formed beakers.

The thickness variation of the specimens was calculated as the ratio of the maximum thickness to the minimum thickness at a near-angular point on transition to the vertical wall of the beaker. The results are presented in Table 4.

From the experimental data it can be seen that a lower proportion of high-elastic strain is possessed by unmodified PP. The introduction of modifiers into the given grade of PP increases this characteristic by a factor of 4–5. The high value of high-elastic strain in formed articles indicates that, on the basis of modified polymers, considerably higher elongation factors can be achieved, i.e. deeper-drawn articles can be produced, and the forming process can be carried out in a greater temperature range.

### Table 2. Data of DSC analysis of modified PP of grade 01007

<table>
<thead>
<tr>
<th>Modifier</th>
<th>(T_m,^\circ C)</th>
<th>(T_s,^\circ C)</th>
<th>(DT,^\circ C)</th>
<th>(X,%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without modifier</td>
<td>171/176</td>
<td>143</td>
<td>28</td>
<td>31</td>
</tr>
<tr>
<td>+ 3 parts ASEP</td>
<td>170/177</td>
<td>144</td>
<td>26</td>
<td>45</td>
</tr>
<tr>
<td>+ 1 part SEVA</td>
<td>170/178</td>
<td>145</td>
<td>29</td>
<td>48</td>
</tr>
</tbody>
</table>

* Numerators – melting temperature determined from data of DSC analysis; denominators – melting temperature determined from TMA data.

### Table 3. Values of relative optical density of crystallinity bands for PP of grade 01007 as function of type of modifier

<table>
<thead>
<tr>
<th>Composite</th>
<th>(D_{998}/D_{1440})</th>
<th>(D_{840}/D_{1440})</th>
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<tbody>
<tr>
<td>PP of grade 01007</td>
<td>0.813</td>
<td>0.670</td>
</tr>
<tr>
<td>PP of grade 01007 + SEVA 113</td>
<td>0.867</td>
<td>0.698</td>
</tr>
<tr>
<td>PP of grade 01007 + ASEP</td>
<td>1.643</td>
<td>1.323</td>
</tr>
</tbody>
</table>

### Table 4. Assessment of quality of articles produced by vacuum forming from PP-based materials

<table>
<thead>
<tr>
<th>Composition of composite</th>
<th>Proportion of high-elastic strain, %</th>
<th>Thickness variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP of grade 01007</td>
<td>3.3</td>
<td>1.1</td>
</tr>
<tr>
<td>PP of grade 01007 + 2% ASEP</td>
<td>5.0</td>
<td>1.1</td>
</tr>
<tr>
<td>PP of grade 01030 + 3% ASEP</td>
<td>10.0</td>
<td>1.2</td>
</tr>
<tr>
<td>PP of grade 01007 + 4% ASEP</td>
<td>14.2</td>
<td>1.2</td>
</tr>
<tr>
<td>PP of grade 01007 + 1% SEVA</td>
<td>13.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Therefore, from modified composites of PP it is expedient to produce articles with high degrees of elongation or at higher heating temperatures of the semiproduct.

On the basis of the data obtained, the following conclusions can be drawn:

• the modification of PP makes it possible to control the main characteristics of the material having an effect both at the stage of sheet material production and at the stage of forming of articles from sheets;
• all of the modifiers investigated can be used for controlling the deformation characteristics of polypropylene.

With an ASEP content in the PP of 3–4 parts, the values of the MFI of polypropylene increase by a factor of 4, which will make it possible to lower the processing temperatures by 20–30 K and to increase the throughput of the extrusion equipment at the stage of sheet semiproduct production. Composites of PP with ASEP possess a considerably greater proportion of high-elastic strain, which makes it possible to form deep-drawn articles from them, and are characterised by higher strength properties.

REFERENCES