The creation of polymer composites (PCs) of functional designation requires new technological solutions that are technically and economically effective and ecologically safe. Such an advanced technological solution is the polycondensation method for producing PCs (refs. 1 and 2), which ensures a shorter production cycle since the production of an oligomer by a complex layout and its storage, preparation, and transportation to the PC plant are eliminated, and also a reduced energy consumption and smaller ecological impact through the elimination of the organic solvent from the technology.

The polycondensation filling method is extremely promising for the production of fibrous composite materials with ion-exchange properties (refs. 3–5). The present work proposes polypropylene fibres and threads (PPTs) as an effective reinforcing filler in polycondensation filling. They have found fairly limited use in the traditional production of PCs on account of their chemical inertness and smooth glassy surface (ref. 6). At the same time, polypropylene threads are one of the lowest-cost and most promising forms of chemical fibre (ref. 7). They possess a fairly high combination of physicomechanical properties, and their volumes of production and consumption are growing steadily. Polypropylene threads satisfy fully the requirements laid down for reinforcing systems in polycondensation filling: they do not swell or dissolve in the reaction medium during synthesis, do not melt at the process temperature, and retain their physicomechanical characteristics during the production of PCs. Furthermore, the use of modified PPTs characterised by a complex cross-sectional configuration (ref. 8) as a reinforcing system raises the effectiveness of their application still further. Thus, the present investigation was conducted on PCs produced by polycondensation filling, based on profiled polypropylene threads and PPTs of round cross-section.

It was established (ref. 3) that, during polycondensation filling, at the impregnation stage, diffusion of the monomers into the structure of the reinforcing material occurs, with subsequent synthesis of a polymer matrix directly within the fibrous filler, which promotes the production of a solid composite material characterised by a new specific polystructure. Similar structure formation processes are also characteristic of PCs based on PPTs of round cross-section. Using IR spectroscopy, we showed (Fig. 1) that the initial material is identified practically entirely with the classic spectrum of polypropylene. Curve 1 clearly sweeps the intense absorption bands characterising deformation vibrations of the main carbon chain of the polypropylene macromolecule with symmetrically arranged CH₃ groups. Closely positioned maxima of absorption in the region of frequencies of ~1456–1378 cm⁻¹ correspond to the CH₂ and CH groups. The region of frequencies of ~2942–2839 cm⁻¹ is characteristic of stretching vibrations of the CH₃ group.

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In the 1370–1200 cm\(^{-1}\) region there are wagging and torsional vibrations of the CH groups, which strongly interact with each other. The absorption bands in the 1200–800 cm\(^{-1}\) region are due to interaction of pendular vibrations of the CH\(_3\) and CH\(_2\) groups with stretching vibrations of the carbon skeleton.

Curve 2 presents the IR spectrum of PP fibre treated with a dipping composition with subsequent cation exchanger synthesis on the fibre surface. Subsequently the oligomers were eluted with a solvent. The main intense absorption bands characteristic of PPT are retained; here, the presence of certain fragments characteristic of phenol–formaldehyde resins of the resol type was found in the regions of ~3200 cm\(^{-1}\) and ~1700–1600 cm\(^{-1}\). The results obtained indicate that, in the presence of PPTs, a new polystructure is formed, since a shift and change in the main regions of intense absorption are noted; in the overall spectrum there are absorption bands characteristic both of the fibre and of cation-exchange phenol–formaldehyde resin. Thus, during polycondensation filling, PPTs take an active part in forming the composite material, in contrast to the traditional production of PCs, ensuring strong adhesive interaction in the reinforcing filler–polymer matrix system, which is difficult to achieve in the traditional production of PCs.

As noted above, the effectiveness of PPTs as the reinforcing filler can be enhanced by using modified threads with a developed active surface. The use of the new reinforcing system — profiled PPTs — required refinement of the process parameters for the production of PCs by polycondensation filling (ref. 9). The introduction of threads with a complex cross-sectional configuration into the forming composite affects the nature of diffusion of the monomers at the impregnation stage. In view of this, a study was made of the influence of the impregnation parameters on the properties of PPTs and cation-exchange fibrous material based on them.

An assessment of the role of the ratio between the monomers in the polypropylene composition (formalin/phenolsulphonic acid) showed that a change in this ratio within the technologically acceptable range 1.2:1–1.6:1 has no significant effect on the exchange capacity of the material being synthesised (Fig. 2).

The use of profiled threads required an increase in the impregnation time (Table 1). To maintain effectiveness of the process, the impregnation time was varied from 3 to 7 min. The data obtained indicate that the impregnation time of profiled PPTs should amount to 7 min, and that of standard PPTs to 3 min.

This is evidently determined by structural features of the polypropylene threads and, in particular, by the different degree of crystallinity. For profiled PPTs, the degree of crystallinity is 25–27% higher than for threads of round cross-section (ref. 10), which makes diffusion of the monomers difficult and the amorphous regions of the fibres less accessible, and accordingly requires an increase in the contact time with the monomer solution by comparison with polypropylene threads of round cross-section. However, material synthesised on the basis of standard PPTs is characterised by a low exchange capacity.
Physical modification of the threads with change in the cross-section has a positive influence on their capacity for polycondensation filling, i.e. the ion-exchange properties of material produced on the basis of these threads is much higher.

The influence of profiled PPTs on structure formation processes during the polycondensation production of PCs based on them was studied using thermogravimetric analysis (Fig. 3).

An analysis of TG and DTG curves indicates that the introduction of profiled PPT leads to ~20–25 K displacement of the temperature ranges towards higher temperatures.

The synthesis of a resol polymer proceeds in parallel with the removal of water and continues up to 135°C, as indicated by the considerable weight losses. At this stage, a mixture of isomeric phenolic alcohols is preferentially formed, which, as the temperature rises, undergo polycondensation with the formation of more complex products.

In the temperature region 135–230°C, melting of the polymer occurs, which can be seen from the inflection of the TG curve and the peak on the DTG curve. The stable temperature region from 230 to 400°C on the DTG curve is accompanied with the practical absence of weight losses of the material. This seems to be due to the conversion of resitol into resite.

The melting peak of the polymer in the presence of PPT lies in the region 160–250°C and again is accompanied with an inflection of the TG curve. However, it is deeper than the similar peak on the thermogram of the pure polymer, since melting of the PPT occurs in this temperature range. The start of degradation of the material in the presence of PPT is also shifted 20 K towards higher temperatures by comparison with the pure polymer.

Consequently, the introduction of PPT slows down the curing processes of the polymer matrix: the temperature range corresponding to the region of conversion of resol into resite is widened. The presence of PPT with a developed surface possibly leads to an increase in the points of contact of the thread with the oligomer, and consequently to an increase in the crosslink density of the polymer matrix, as indicated by the high heat resistance.

Thus, in polycondensation filling, PPTs take a direct part in the formation of the composite material, ensuring an enhanced combination of properties of the PC.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Impregnation time</th>
<th>Monomer solution/fibre ratio</th>
<th>Yield of volatiles</th>
<th>Matrix/filler ratio</th>
<th>Exchange capacity, mg-equiv./g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>after synthesis</td>
<td>after drying</td>
<td>after curing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>initial thread</td>
<td>IEFM</td>
<td></td>
</tr>
<tr>
<td>Standard PPT</td>
<td>3</td>
<td>6.1:1</td>
<td>15.24</td>
<td>14.24</td>
<td>12.48</td>
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<tr>
<td></td>
<td>5</td>
<td>8.6:1</td>
<td>17.26</td>
<td>17.49</td>
<td>14.81</td>
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<tr>
<td></td>
<td>7</td>
<td>10.1:1</td>
<td>25.36</td>
<td>20.50</td>
<td>29.63</td>
</tr>
<tr>
<td>Profiled PPT</td>
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<td>11.35</td>
<td>4.38</td>
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</tr>
<tr>
<td></td>
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<td>12.22</td>
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<td>6.5:1</td>
<td>16.73</td>
<td>16.57</td>
<td>15.62</td>
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<td>PAN staple fibre</td>
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<td>14.99</td>
</tr>
</tbody>
</table>

Fig. 3 Data of thermogravimetric analysis: 1 — phenol-formaldehyde oligomer; 2 — phenol-formaldehyde oligomer + profiled PPT.
REFERENCES


4. E.I. Titorenko et al., Ion-exchange fibrous materials based on polypropylene threads, Saratov State Technical University, Technological Institute, Engel’s, 1997, VINITI Dep. No. 1043-V97, 2.4.97. Deponirovannye Nauchnye Raboty, No. 6(306), 1997, p. 38 (item 413)


(No date given)