Processing of the waste materials of a cured solid urethane elastomer

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A considerable problem in the production of urethane elastomers is the utilisation of the waste materials formed: pressings of sprues, low-quality products, flash, strips of up to 10 m length, sheets, and cylindrical blocks. The solution of this problem is of great importance both from the economic viewpoint (initial feedstock — isocyanates and polyols) and from the ecological viewpoint, since polyurethane waste materials cause environmental pollution through their release of toxic substances.

Methods for the processing of polyurethane waste materials by hydrolysis, thermo-oxidative and oxidative degradation, pyrolysis, and photodegradation are known. However, these methods involve the provision of many specific processing conditions and present certain difficulties in application, especially under conditions of milling-calender technology for the production of materials from the melt.

For brittle solid crosslinked solid elastomers there is the method of processing by mechanical comminution into crumbs of the required fineness with subsequent granulation of the latter. The granules are used as a filler of polymer composites for moulding powders.

The authors proposed to carry out the processing of polyurethane waste materials by heat treatment of the polyurethane mass in a mixture with butadiene-styrene rubber at a temperature of 140–180°C in a closed RSVD or internal mixer. Here, a homogeneous plasticised material suitable for reuse is produced.

The given method is based on the condition that, in similar thermomechanical treatment, it is primarily biuret and allophanate groups that are broken down. Depending on the process parameters and the component composition of the modifying additives, the process may be reversible or accompanied with the complete rupture of bonds, which leads to the release of gaseous products: amines, carbon dioxide, aldehyde, and carbon monoxide. As a result of the proposed method of processing, a crosslinked solid polyurethane thermosetting plastic is converted into a viscous-flow thermoplastic state, and then bond rupture ceases.

By pyrolysis gas chromatography it was initially established that, during such treatment of polyurethane waste materials, toxic gases, in particular, hydrogen cyanide, are not formed. It is this fact that made it possible to test the process under production conditions. The plasticised polyurethane obtained is added to rubber mixes based on butadiene—styrene rubber for the production of the bottom part of footwear.

When polyurethane waste materials are added to a rubber mix, the process of its vulcanisation is accelerated. When waste materials are added, the Shore A hardness increases only by 1–2 units. There is a certain improvement in the adhesion properties — the bonding strength increases from 2.7 to 3.3 kN/m. In the case of flexing, the vulcanisate withstands over 50 000 loading cycles. The strength properties are illustrated by the examples given in Table 1.

The given change in properties is most likely due to corresponding structural changes in the polyurethane waste materials as a result of processing by the thermomechanical method. The mixing of waste materials with butadiene rubber and their subsequent thermomechanical interaction may influence changes both in the chemical and in the physical structure of the polymer. To determine such characteristics it is possible to use physical methods: IR spectroscopy, X-ray diffraction analysis, electron microscopy.
**Table 1** Tensile strength and breaking elongation of vulcanisates with and without addition of polyurethane waste materials

<table>
<thead>
<tr>
<th>Vulcanisates</th>
<th>Physicomechanical properties of specimens produced by vulcanisation for different times</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 min</td>
</tr>
<tr>
<td>Tensile strength, MPa</td>
<td></td>
</tr>
<tr>
<td>Without polyurethane waste materials</td>
<td>8.7–11.3</td>
</tr>
<tr>
<td>With polyurethane waste materials</td>
<td>9.8–10.2</td>
</tr>
<tr>
<td>Breaking elongation, %</td>
<td></td>
</tr>
<tr>
<td>With polyurethane waste materials</td>
<td>400–420</td>
</tr>
</tbody>
</table>

The processing of a porous polyurethane elastomer consists in it being subjected to natural plasticisation at room temperature by adding compounds of the aprotic type, taken in a ratio of 1:(0.2–0.4), and subsequent forced plasticisation by milling at room temperature. The compression moulding of articles of the polymeric material obtained is carried out at a temperature of 125–130°C and a pressure of 50–80 MPa for 12–15 min.

Dimethylformamide, methylacetamide, and dimethylsulphoxide are used as the aprotic organic compounds.

The moulded polyurethane elastomer has a tensile strength of 26–30 MPa, a tear strength of 0.8 kN/m, and a melt index at 190°C of 35 g/10 min.

One recent study has involved the processing of waste materials of cured solid urethane elastomers by ecologically safe technology and the production of a thermoplastic material with high physicomechanical and service properties.

The waste materials of cured solid polyurethane elastomer, precomminuted to a size of 3–8 mm, are mixed in a turbomixer with an ester plasticiser and a passive filler at a temperature no higher than the boiling temperature of the plasticiser for 25–35 min. Milling is then carried out at a temperature of 150–170°C for 4–6 min, and polymeric material is produced. Shaping and sizing of film of certain width and thickness from the material obtained is carried out on a calender. The film can be plied up with a base of natural, artificial, and synthetic strands.

In the work, the following waste materials of crosslinked solid polyurethanes were used:

- based on polyoxytetramethylene glycol, 2,4-toluylene disocyanate, and 3,3′-dichloro-4,4′-diaminodiphenylmethane, taken in a ratio of 1.0:2.0:0.95;
- based on polyethylene glycol adipinate, 2,4-toluylene disocyanate, and 3,3′-dichloro-4,4′-diaminodiphenylmethane, taken in a ratio of 1.0:1.9:0.7.

The thermoplastic material has the following physicomechanical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature</td>
<td>-34 to -36°C</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>33–36 MPa</td>
</tr>
</tbody>
</table>

Breaking elongation 330–400%

Tear strength 0.95–1.2 kN/m

Melt index at temperature of 190°C 28–30 g/10 min

By introducing diester plasticisers of different grades it is possible to vary the swelling time and to produce a material with the prescribed properties.

The use of fireproofing agents with a high degree of dispersion, and also active fillers, makes it possible to produce a non-flammable material possessing a high coefficient of static friction. The introduction of mechanical stabilisers makes it possible to lower the coefficient of near-wall friction and to increase linear compression during the processing of polyurethane waste materials.

**CONCLUSIONS**

1. A method has been developed for the processing of a cured solid urethane elastomer into a thermoplastic material on equipment of the S. M. Kirov Works.

2. Use of the thermoplastic material obtained in polymer composites will make it possible to reduce the consumption of composite feedstock.

**REFERENCES**

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