Heat-resistant films of silanol-crosslinked polyethylene

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This article looks at the process of silanol crosslinking of high-pressure polyethylene using the PENTA®-1002 modifier. Demonstrates that silanol-crosslinked PE films with a gel fraction content of over 50% may be used at high temperatures, as when this is done, a sparse but continuous network of chemical intermolecular bonds is formed in the polyethylene.

Silanol crosslinking is an effective way of increasing the heat resistance of polyethylene [PE]. Crosslinked polyethylene is mainly used to produce pressure pipes, cable insulation and shells [1,2]. There is industrial experience of production of films made from crosslinked PE [3-6]. Generally, however, the process that is used is that of manufacture of radiation-modified heat-shrinking PE materials. The manufacture of radiation-crosslinked and peroxide-crosslinked products requires specialised process equipment. Silanol-crosslinked products may be manufactured on ordinary extrusion equipment [1]. But the special brands of silanol-crosslinked graft copolymers currently produced by industry (“Sioplas” method) are intended solely for tube manufacture. There is wider potential in the use of granular concentrates of silanol-crosslinked agents and ordinary polyethylene (dry “Monosil”), which is used in the manufacture of metal-containing polymer pipes and cable products. In the latter case, a concentrate containing vinyl trialkoxysilanes, peroxide initiators ensuring grafting of silanes to PE, stabilisers and organo-tin catalysts of hydrolysis and condensation of silanes is mixed with ordinary PE granules and processed into products on ordinary extrusion equipment. During the extrusion process, the concentrate disperses in the PE melt, and the reagents it contains diffuse into the polymer. The extrusion conditions ensure grafting of silane to PE without any substantial change to the process characteristics of the latter. Crosslinking of PE takes place after product formation when it is treated with steam or in boiling water, or when they are stored for a certain time under normal conditions. The present work looks at the potential to manufacture crosslinked PE films with a high operating temperature using the latter method. Use of such heat-resistant films in the manufacture of bags and bag inserts enables hot materials to be packed without wasting time on their cooling.

The objects of the study were composites based on 10803-020 brand PE with a density ($\rho_{PE}$) of 925 kg/m$^3$ and a mean molecular weight ($M_{PE}$) of around 50000. The composites contained the modifier Penta®-1002 (TU [tech. spec.] 2240-079-40245042-2005 OOO “Penta-91”, Moscow), which is a concentrate of trialkoxyvinyl silane (vinylsilane) with the addition of a peroxide initiator, stabilisers and a tin-containing catalyst in an optimum ratio [7]. The content of the Penta®-1002 modifier was between 0 and 5% by wt.

Extrusion of mixtures of polyethylene granules and granules of Penta®-1002 concentrate took place on a single-screw extruder with screw diameter 20 mm and a length-to-diameter ratio of 25, equipped with an annular head with annular clearance diameter 50 mm and 0.5 mm slit. Extrusion conditions: temperature of final zones of extruder cylinder and extrusion head 200°C. Hose inflation factor 1.5, thickness of extrusion films 0.30-0.35 mm. Final silanol crosslinking took place with treatment of the films in boiling water for a period of 8 hours.

The gel fraction content ($\omega_g$) in the polyethylene specimens was determined from the difference in weight between the initial specimen and the residue in the gauze mesh following extraction of the sol fraction using o-xylene.
at 140°C for 8 hours and drying, relating the weight of the residue to the weight of the initial specimen.

In the films studied, the value of $\omega_g$ varied from 0 to 67%. As may be seen from Table 1, the value of $\omega_g$ for the films under study varied widely.

With a low crosslinking agent content (up to 2% Penta®-1002), the molecular weight of the polymer rises virtually without a gel fraction being formed. In the range of crosslinking agent contents of 2.4%, a linear rise in gel content $\omega_g$ is seen. Subsequently this rise smoothly decreases. We should observe that for cable materials, including shrink-fit tubes and couplings, a 50-60% gel fraction content is considered adequate, while for pressure pipes it should be over 65% (International standard DIN 16892-2000).

For evaluation of the heat resistance of the films, use was made of the “Hot set” methodology, which is for cable insulation made from crosslinked PE (GOST R IEC 60811-2-1-2006. Thermal deformation testing). This methodology envisages holding specimens in blade form at high temperature, fastened in a vertical position, with a weight attached to the bottom end to provide an initial tension of 0.2 MPa. After 15 minutes of warming up, the rupture elongation of the stretched specimen is measured, then, without taking the specimen out of the chamber, the load is removed and after 5 min of repeat warming and cooling the residual deformation that is irreversible at the test temperature is established. Materials that have a rupture deformation of less than 150% at 200°C and a residual deformation of less than 15% are considered to be heat-resistant. In this work tests were performed on films over a wide range of temperatures from 60 to 220°C. The summarised results of these tests at 0.1 MPa are shown in Figure 1.

In terms of their behaviour in the test in question, the specimens tested may be divided into two groups. Specimens with $\omega_g$ of up to 40%, like the initial PE, melted and stretched to elongations which were only limited by the height of the chamber and (or) destruction of the specimen (over 200%). In most cases, plastic rupture was observed with no perceptible subsequent contraction. This made it impossible to fix the exact points of rupture and residual elongation. The nature of the deformation/temperature graphs for these specimens was similar to that of the thermomechanical curves for crystalline polymers, of which the LDPE under study is one. In the area of temperatures above the melting point of LDPE, the gradient of these curves declines as the extent of crosslinking and the melt viscosity increase.

Specimens with $\omega_g$ of over 50% behave like crosslinked elastomers at high temperatures. On the relevant curves (Figure 1), after complete disappearance of the crystalline phase, a plateau appears. Such specimens with a high level of crosslinking stretch under test to ultimate rupture deformations.

Specimens with large $\omega_g$ values withstood this test even at temperatures of over 200°C. The rise in the concentration of intermolecular crosslinks brings about an increase in the modulus of rigidity of the material, which leads to a fall in the rupture deformation values for specimens of crosslinked PE with a rise in the values of $\omega_g$.

These differences in the behaviour of the two types of specimen may be linked to a difference in their structure [6]. The gel fraction may be pictured as areas of microgel, the number of which increases as the crosslinking agent content rises. In our view, the reason for this is that in the initial stage of component blending (dispersion of silanol crosslinking agents in PE melt), micro-zones are formed with a higher content of these agents. Subsequent balancing of the concentration takes place through diffusion of the crosslinking agents from these micro-zones into the surrounding melt. The vinylsilane diffusion process is, however, accompanied by binding of it as a result of grafting to the PE. This limits diffusion and leads to an uneven diffusion of vinylsilane grafts. As a result, after processing in boiling water, numerous micro-gel zones are formed in the material, in which the crosslinking density falls from centre to periphery (as in pattern II, Figure 1). These features of the structure are also typical of peroxide-crosslinked PE, in a melt of which

![Figure 1](image-url)

**Figure 1.** Impact of temperature on magnitude of rupture deformation of PE films. The numbers next to the curves correspond to the mean value of $\omega_g$ (%) in the films

<table>
<thead>
<tr>
<th>Penta®-1002 content, %</th>
<th>0</th>
<th>1.0</th>
<th>1.6</th>
<th>2.2</th>
<th>2.8</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
<th>5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean gel fraction content ($\omega_g$), %</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>15</td>
<td>29</td>
<td>44</td>
<td>55</td>
<td>63</td>
<td>67</td>
<td>71</td>
</tr>
</tbody>
</table>
peroxide diffusion during extrusion is accompanied by crosslinking and a rise in viscosity of the PE melt generally. Separate areas of the gel fraction may be found visually as “little gels” in such extrusion films.

At low crosslinking agent concentrations (ωg less than 50%), a steady rise in ωg leads to the formation of structures analogous to that illustrated as pattern I in Figure 1. The deformation properties of such films at elevated temperatures are governed by the properties of the matrix in the form of the non-crosslinked sol fraction, which makes the transition into a plastic state in the area of LDPE melting points.

When the gel fraction content rises to 50% or more, the specimens begin to behave as “crosslinked”. It is at these particular ωg values that effective contact is achieved and the micro-gel zones overlap, to form what is in effect a continuous gel fraction phase (pattern II in Figure 1). This leads to the appearance of a plateau on the corresponding curves in Figure 1 (stable rupture deformation values). It is no fluke that for silanol-crosslinked and peroxide-crosslinked PE intended for the manufacture of pressure pipes operating at elevated temperatures, according to the international standard DIN 16892-2000, ωg should be at least 65-70%. This content is close in value to φm – the limiting content of spherical particles at the packing density limit.

Such films retain lower rupture deformation values at higher temperatures than “non-crosslinked” films (up to 130°C in Figure 1). The reason for this is that, right up to the moment of fusion of the most “high-melting” crystallites, which are connected by chemical bonds in such films, the amorphous phase is not capable of flowing.

Rupture deformations in such films are stable in magnitude even at temperatures of over 200°C, and do not exceed 70%. Residual deformations tend towards values not in excess of a few percent, i.e. deformation of crosslinked specimens is almost entirely reversible.

The yield strength, tensile strength and breaking elongation determined in the longitudinal direction in accordance with GOST 14236-81 are given in Figure 2.

Their level is determined not only by the extent of crosslinking of the polymer, but also by its crystalline structure. The breaking stress of crystalline PE has little relation to its degree of crosslinking. Since the degree of crystallinity of LDPE is quite low (less than 50%), however, the tensile yield strength rises steadily as the gel fraction content increases. At the same time the rupture elongation falls sharply at a gel fraction content of over 50%, i.e. when a continuous gel fraction is formed.

Table 2 gives calculated values for the number of crosslinks (Ncl) related to the number of PE molecules (NPE) per unit of volume, or the number of crosslinks attributable to each PE molecule (Ncl/NPE).

If intermolecular crosslinks were made with all vinylsilane molecules involved, on condition that two of its molecules were lost in forming one crosslink, and with an even distribution of crosslinks (ideal network) in the body of the specimen, the magnitude of Ncl/NPE could be:

\[
\frac{N_{cl}}{N_{PE}} = \frac{\Phi_{vs} M_{PE}}{2M_{vs}}
\]

where MPE and Mvinylsilane are the molecular weights of PE and vinylsilane (ratio of proportions by wt. of PE and vinylsilane), \(\Phi_{vs}\) is the proportion by wt. of vinylsilane in the composite. It follows from this that for the formation of a continuous network of siloxane bonds (Ncl/NPE > 1), the quantity of vinylsilane contained in 2% Penta®-1002 modifier is sufficient (Table 2). The gel fraction content in such specimens, however, is 15%. At elevated temperatures these films behave like non-crosslinked films (Figure 1). Films with Penta®-1002 modifier contents of 4% or over may be considered as “crosslinked”.

Figure 2. Properties of crosslinked PE films. 1 – rupture deformations (\(\epsilon_{rupt}\)) at 200°C and 0.1 MPa; 2 – tensile yield strength (\(\sigma_Y\)); 3 – tensile strength (\(\sigma_P\)); 4 – breaking elongation (\(\epsilon_P\)).

### Table 2. Impact of the gel fraction content on the deformation and strength characteristics of PE films

<table>
<thead>
<tr>
<th>Gel fraction content, %</th>
<th>0</th>
<th>15</th>
<th>29</th>
<th>44</th>
<th>55</th>
<th>63</th>
<th>67</th>
<th>71</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ncl/NPE calculated from (\Phi_{vs}) (eq. 1)</td>
<td>0</td>
<td>1.1</td>
<td>1.4</td>
<td>1.8</td>
<td>2.0</td>
<td>2.25</td>
<td>2.5</td>
<td>2.75</td>
</tr>
<tr>
<td>Ncl/NPE calculated from (E_\infty) (eq. 3)</td>
<td>failed to withstand test</td>
<td>0.8</td>
<td>1.0</td>
<td>1.15</td>
<td>1.25</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proportion of effective crosslinks, %</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>44</td>
<td>50</td>
<td>51</td>
<td>50</td>
<td>51</td>
</tr>
</tbody>
</table>
The number of effective ("load-bearing") crosslinks was assessed from the values of the equilibrium tensile moduli \( E_\infty \) of specimens previously heat-treated at temperature \( T \) equal to 200°C. The elastic deformation value was taken as the difference between the rupture and residual deformations. Using the rupture tensile deformation obtained for various loads, we may determine the coefficients of the Mooney-Rivlin equation [8] for the crosslinked polyethylene specimens under study:

\[
\frac{1}{2(\lambda - \lambda^{-2})} = C_1 + C_2\lambda^{-2}
\]

(2)

where \( \lambda \) is the stress level, \( C_1 \) and \( C_2 \) are constants. We should observe that for \( \lambda < 1.5 \), the coefficient \( C_2 \) was close to 0, rising at greater degrees of stretching. Knowing the value of the equilibrium shear modulus \( G_\infty = 2C_1 \), we may evaluate the number of sections of molecular chains between crosslinks per unit of volume \( N_{cl} \):

\[
N_{cl} = \frac{G_\infty}{kT}
\]

(3)

where \( k \) is the universal gas constant. Since the number of polyethylene molecules per unit of volume \( N_{PE} \) is:

\[
N_{PE} = \rho_{PE} \frac{N_A}{M_{PE}}
\]

(4)

where \( N_A \) is the Avogadro number, \( M_{PE}/N_A \) is the mean mass of a PE molecule (g) and \( \rho_{PE} \) is the density of the PE. We may calculate the ratio of the mean number of effective sections per polyethylene molecule \( N_{cl}/N_{PE} \). Table 2 gives the effective magnitudes of the mean numbers of the effective nodes of the chemical crosslinks \( N_{cl}/N_{PE} \) per polyethylene molecule, calculated on the basis of equations (3) and (4), taking into account that, because of geometrical considerations:

\[
2N_{cl}/N_{PE} = 1 + N_{cl}/N_{PE}
\]

(5)

As may be seen from the table, the number of effective siloxane crosslinks is less than the total number of possible crosslinks. The vinylsilane losses during composite processing are not so large as to explain this discrepancy. Some of the crosslinks are probably concentrated inside the micro-gel zones that have already formed. This would account for the difference between the real (incomplete) network and the ideal, in which each macromolecule is linked to the neighboring one by an identical number of crosslinks. This tallies well with the assumptions made above concerning the structure of the PE subject to crosslinking. Thus at the moment of formation of a continuous gel fraction (at \( \omega_g \) around 50%), in zones where micro-gel particles overlap, a sparse network of inter-molecular links is formed. It is this network that is responsible for the deformation properties of polyethylene films at elevated temperatures. With an increase in the gel fraction content, the density of this intermediate network rises at an accelerated rate. This is shown by the increase in the proportion of effective crosslinks, calculated as the ratio of values of \( N_{cl} \) calculated from equations (3) and (1). It may be seen from Table 2 that the method of introduction of crosslinking agents into PE using Penta®-1002 concentrate provides quite a high level of effectiveness of use of vinylsilane, especially in view of the likelihood of formation of intermolecular siloxane crosslinks from more than 2 vinylsilane molecules.

The data obtained indicate that silanol-crosslinked PE films with a gel fraction content of over 50% may be used at elevated temperatures, since in this case a sparse but continuous network of chemical intermolecular links is formed in the polyethylene. Experience of work with such films has shown that there is real potential for their crosslinking without a special operation involving hot water or steam treatment. High levels of crosslinking are achieved with their storage for 6-7 days under normal conditions. In this case steam or hot water treatment of films is not mandatory.

REFERENCES


