The effect of ethylene copolymers on the properties of crosslinking polyolefin composites modified with trimethylolpropane trimethacrylate

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SUMMARY

An investigation was made of the effect of copolymers of ethylene with vinyl acetate (CEVA) on the thermodynamic stability and structural and mechanical properties of cured composites based on low-density polyethylene (LDPE) and dicumyl peroxide with crosslinking coagent trimethylolpropane trimethyleneacrylate (TMPTMA). It was shown that, in the presence of CEVA, thermodynamic compatibility of LDPE with TMPTMA is ensured, and the chemical network density is increased significantly.

INTRODUCTION

Crosslinked polyethylene (CPE) is widely used in cable engineering, for the manufacture of cable insulation with increased heat resistance, heat-shrink couplings, polymer water piping, and in other sectors of the national economy [1]. With the peroxide method of crosslinking, the necessary network density values are ensured by a fairly high content of dicumyl peroxide (DCP), 3–4%, with which some deterioration in the electrophysical properties and heat stability of CPE cable insulation is possible [2]. The main shortcoming of the peroxide method of crosslinking is the high energy requirement and the inadequate speed of the process, requiring the use of bulky crosslinking units of 80–120 m length [1]. Furthermore, the necessary degree of crosslinking of the insulation is not always ensured at cable industry enterprises [3].

In this context, the task of speeding up the curing process and lowering the energy consumption, for example by introducing so-called stabilisers into the composition of the accelerating agents/crosslinking coagents [4], becomes very urgent.

The application of crosslinking coagents promotes the formation of a three-dimensional chemical network owing to the presence of highly reactive functional groups. The crosslinking coagents generally comprise polyfunctional monomers (PFMs) with active terminal groups (acrylate, methacrylate, allyl, etc.) [5] capable of polymerisation among themselves and of grafting to the polyolefin macromolecule. One of the most effective crosslinking coagents is trimethylolpropane trimethacrylate (TMPTMA) [6]. When TMPTMA is used, the crosslink yield by comparison with the treatment of pure PE increases more than fivefold [7].

The main shortcoming of using PFMs as crosslinking coagents is that, owing to their high polarity, they possess low thermodynamic compatibility with non-polar polyolefins such as PE [8].

The limited compatibility of PFMs leads to their exudation (blooming) from the polyolefin matrix, which makes prolonged storage and transportation of the crosslinking composite to the manufacturing works impossible, and also breaks the ecofriendliness standards.

Besides exudation, with limited compatibility between PFM and polymer, the sensitiser blends very poorly in the polymer matrix [Figure 1].
Most PFM molecules form agglomerates (A), which, instead of forming a three-dimensional chemical network with fragments of polymer macromolecules, are capable only of polymerisation with each other. Only a small proportion of the PFM molecules are capable of forming a three-dimensional network (B) or of forming new, free terminations of chains (C) [9]. This may lead to an insufficiently effective curing process and consequently to a deterioration in the service properties of articles. Therefore, when using polyfunctional monomers as crosslinking coagents, solving the problem of their thermodynamic compatibility with the polyolefin matrix becomes very urgent.

**EXPERIMENTAL**

The investigation was conducted on composites based on low-density polyethylene (LDPE 10803-020) with 2 wt% curing agent dicumyl peroxide (DCP) (Laporte Catalysts & Initiators) with crosslinking coagent trimethylolpropane trimethacrylate (TMPTMA) (Bisomer). The modifiers used were copolymers of ethylene with vinyl acetate (VA): CEVA 11104-030 (6% VA), CEVA 11306-075 (12% VA), CEVA 11507-070 (22% VA), CEVA 11607-040 (19% VA), CEVA 11708-210 and CEVA 11807-340 (28% VA), and also a ternary copolymer of ethylene, vinyl acetate (28%), and maleic anhydride (0.8%) – TSEV 2113 GB (2113) (Germany).

The composites were manufactured in a Banbury-type paddle mixer at \( T = 135–140°C \) for 25 min. DCP was introduced 5–7 min before the end of mixing. The composites were cured under conditions of pressing at \( T = 150 \) and 180°C.

The thermodynamic compatibility of the polymers with TMPTMA was assessed using the interference method [10]. The thermodynamic stability constant \( (K_{tds}) \) was determined on the basis of the GOST 14926-81 standard “Plastics. Method for assessing the migration of plasticisers – the ‘spot method’”, according to which the size of a spot of plasticiser on a substrate of tracing paper, squeezed from a pellet of 2 mm height under a stress of 1 kgf/cm² over a period of 14 days, was measured. Here, the \( K_{tds} \) constant was assessed, comprising the ratio of the diameters of the spot and the initial pellet [11].

The network density of the cured specimens under equilibrium conditions at \( T = 130°C \) in a stepped increase in load regime was assessed using the high-elasticity equation [3].

**RESULTS AND DISCUSSION**

During curing of the composite immediately after mixing of the components, the introduction of 3% TMPTMA accelerates appreciably the process of crosslinking of PE in the presence of 2% DCP and promotes an increase in the density of the three-dimensional network (Figure 2).

However, an uncured system of PE with TMPTMA is unstable during storage. If curing is carried out a certain time after mixing, the network density decreases, and after 20 days approaches the value for a composite without TMPTMA. At the same time, the formation of drops of liquid on the surface of specimens – exudation – is recorded at the same time. The \( K_{tds} \) constant assessed by the ‘spot method’ increases to a value of 1.4.

This indicates thermodynamic incompatibility associated with exudation of TMPTMA from the system.

To prevent this undesirable effect, and to increase the thermodynamic stability, it was proposed to introduce into the system an additional polymer, a compatibiliser possessing on the one hand a fairly good affinity for TMPTMA and on the other hand a moderate compatibility with the polyethylene matrix.

The compatibilisers used were copolymers of ethylene with vinyl acetate (CEVA) with a vinyl acetate content of 7–28%, and also a ternary copolymer of ethylene, vinyl acetate, and maleic anhydride (grade TSEV 2113 GB).
2113). For preliminary assessment of the compatibility of polymers with TMPTMA, the solubility parameters calculated by the Askadskii method [12, 13] were compared (Table 1).

The difference between the solubility parameters of the TMPTMA and the polymers PE and CEVA 113 is greater than the threshold value of 4.0, which indicates clear incompatibility of the components [13]. For the more polar copolymers CEVA 118 and TSEV 2113 (28% VA), any conclusion about the level of compatibility requires special investigations.

From an analysis of interferograms for PE, CEVA 118, and TSEV 2113 it follows that a certain distortion of bands in the region of mutual diffusion with TMPTMA is observed, which indicates their limited compatibility. However, the small difference in the refractive indices of copolymers and TMPTMA makes a precise quantitative assessment of the degree of compatibility impossible. In view of this, for a semi-quantitative assessment of compatibility, use was made of a technical method for assessing $K_{ts}$. With increase in the content of polar units of vinyl acetate in CEVA, its compatibility with TMPTMA consistently increases (Figure 3).

For CEVA-118 and TSEV 2113, satisfactory compatibility is observed with a TMPTMA content of no more than 20% (Table 2).

CEVA-118 and TMPTMA were introduced into PE by two methods: 1 – by simultaneous blending of all components during mixing in a melt; 2 – in two stages, initially by preparing a 20% concentrate of TMPTMA in CEVA-118 and TSEV 2113, and then introducing this concentrate into the polyethylene melt.

With the simultaneous introduction of components (10% CEVA-118 and 3% TMPTMA) into the polyethylene melt, considerable precipitation of the crosslinking coagent is observed ($K_{ts} = 1.16$). When TMPTMA and TSEV 2113 are introduced in the form of an already prepared 20% concentrate in the copolymers, the system is thermodynamically stable. Therefore, the second method of introduction is more attractive.

Figure 4 gives the dependences of the network density of cured composites (2% DCP) on the content of copolymers CEVA-118 and TSEV 2113, and also composites with 3% TMPTMA introduced during the simultaneous mixing of all components and in the form of a concentrate in the copolymers.

### Table 1. The values of the solubility parameters of the components

<table>
<thead>
<tr>
<th>Component</th>
<th>$\delta$ (MJ/m$^3$)$^{-1/2}$</th>
<th>$\delta_{TMPTMA} - \delta_{polym}$ (MJ/m$^3$)$^{-1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>16.1</td>
<td>4.7</td>
</tr>
<tr>
<td>CEVA 11306-075</td>
<td>16.5</td>
<td>4.3</td>
</tr>
<tr>
<td>CEVA 11808-340</td>
<td>17.0</td>
<td>3.8</td>
</tr>
<tr>
<td>TSEV 2113</td>
<td>17.1</td>
<td>3.7</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>20.8</td>
<td>—</td>
</tr>
</tbody>
</table>

### Table 2. The compatibility of copolymers with TMPTMA

<table>
<thead>
<tr>
<th>Grade</th>
<th>Thermodynamic stability constant $K_{ts}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMPTMA, %</td>
<td>10</td>
</tr>
<tr>
<td>CEVA-118 (28% VA)</td>
<td>0.8</td>
</tr>
<tr>
<td>TSEV 2113 GB (28% VA, 0.8% MA)</td>
<td>No spot</td>
</tr>
</tbody>
</table>
The introduction of copolymers in a quantity of up to 10% leads to a more than twofold increase in the network density in comparison with the initial PE, evidently on account of their higher reactivity with peroxide radicals [14]. In the case of the simultaneous introduction of copolymers and TMPTMA into PE, the network density increases markedly. Here, with the introduction of TMPTMA in the form of a concentrate in the copolymers, the network density is appreciably higher than with the simultaneous mixing of all the components in the melt, evidently on account of its more homogeneous distribution [9].

The extremal nature of the dependence of the network density on the content of modifiers seems to be due to the lower molecular weight of the copolymers (high melt flow index values) and to a reduction in the efficiency of mixing with a copolymer content of over 10–12%. For the individual copolymers CEVA-118 and TSEV 2113 with 2% DCP, the network density amounts to $4.45 \times 10^{-5}$ mol/cm$^3$ respectively.

The dependences of strength and strain causing failure at 130°C on the crosslink density for different polyolefin composites practically coincide (Figure 5), which indicates a similar nature of the structure of their three-dimensional network.

![Figure 5. The dependences of strength (a) and strain causing failure (b) at 130°C on the network density for the composites in Figure 4](image)

The use, as polymers, of compatibilisers of polar copolymers of ethylene ensures thermodynamic compatibility of the polyethylene matrix with crosslinking coagent TMPTMA, which is extremely important during the storage and transportation of composites to the manufacturing works. The high curing rate enables the productivity of the crosslinking process to be increased considerably. Furthermore, higher network density values make it possible with a 50% degree of crosslinking to reduce the curing time still further or to reduce the content of curing agent dicumyl peroxide to 1–1.5%.

REFERENCES