Abstract. Viscoelastic properties of amine-cured epoxy-titania composites were investigated. The composites were synthesized by the sol-gel method and analysis of their physico-mechanical properties indicated that higher TiO$_2$ content causes the decrease in glass transition temperature of the composites. Non-linear change of crosslink density with a filler content was observed.

Keywords: sol-gel, titania, epoxy resin, composite, amine curing, viscoelastic properties.
Viscoelastic Properties of Amine-Cured Epoxy-Titania Composites Obtained by the Sol-Gel Method

system (~4 h, 1 kPa, temperature in vacuum chamber gradually increased up to 343 K; the removal of the volatiles was monitored by weighing the mixture until constant weight was achieved; 3) addition of the curing agent and curing of the composite. The composites were cured under conditions like that used to obtain the epoxy polymer. The samples were prepared as films of thickness 0.2 mm and cylindrical blocks 10 mm in diameter and height.

The obtained samples were investigated by X-ray powder diffraction (XRD) using DRON-3M diffractometer (CuKα radiation, Ni-filter). The XRD patterns were received at room temperature in a range of 16–54° (2θ), with a scanning rate of 2°·min⁻¹. The phase composition identification of the samples was performed using the Match software and data bases pdf-2 (ICDD).

Microscopic studies were performed using scanning electron microscope of the JSM-6490LV series (JEOL Ltd., Japan) at an accelerating voltage of 20 kV on chips from the block samples, sputter-coated with carbon.

Sol-fraction yield \( W_{sol} \) (\%) of the polymer and composites was calculated after extraction of low-molecular weight products by methanol (3 days, 323 K) according to the equation:

\[
W_{sol} = \left( m_0 - m \right) \times 100/m_0,
\]

where \( m_0 \) and \( m \) are masses of the sample before and after extraction, respectively.

Viscoelastic characteristics of the epoxy polymer and composites (dynamic modulus \( E' \), storage modulus \( E'' \), loss factor tan \( \delta \)) were determined by a dynamic mechanical analysis (DMA) (TA Instruments DMA Q800, USA). Measurements of film samples (60.0×4.0×0.2 mm) were carried out at 10 Hz frequency in a sinusoidal oscillation mode in the range of 323–443 K with a heating rate of 2 K·min⁻¹. The glass transition temperature (\( T_g \)) was assumed as the maximum of the loss factor curve (tan \( \delta_{max} \)).

Effective network density was characterized by the average molecular weight of an internodal segment. Average molecular weight between two adjacent cross-linking points of the polymeric network \( M_c \) was calculated using the empirical Nielsen formula [10] for highly cross-linked polymers:

\[
\lg G \approx \frac{6 + 293\rho}{M_c},
\]

Shear modulus \( G \) was calculated by the equation:

\[
G = \frac{E_e}{2(1 + n)},
\]

where \( E_e \) – elastic modulus, \( n \) – Poisson’s ratio (\( n \) was taken to be 0.5). The \( E_e \) value was determined from \( E' (T) \) dependence in the rubbery region at \( T_g + 50 \) K. The density of the samples \( \rho \) was determined by the hydrostatic weighing method using Shimadzu AX200 balances, according to the equation:

\[
\rho = \frac{m_1 \cdot \rho_2}{m_1 - m_2},
\]

where \( m_1 \) and \( m_2 \) are the weights of the sample in air and water, respectively; \( \rho_2 \) – the density of water.

3. Results and Discussion

Depending on the composites synthesis conditions amorphous or crystalline phases of TiO₂ could be obtained in the process of titanium alkoxides hydrolytic polycondensation. X-ray diffraction measurements of the synthesized composites were performed to establish the phase structure of the samples (Fig. 2). It was shown that XRD-analysis curves of polymer and composites were almost identical. XRD-pattern of the composite with 3 wt % filler content had no peaks of any crystalline phases of TiO₂, indicating the formation of an amorphous phase of the filler in the composites.

Titania particles size and their distribution in the polymeric matrix of the composites were evaluated by a scanning electron microscopy. Fig. 3 demonstrates TiO₂ particles with the size of less than 0.5 microns randomly distributed in the polymer for the sample with 1 wt % of the filler.
Fig. 2. X-ray diffraction patterns of epoxy polymer (1) and composite with a filler content 3 wt % (2)

Fig. 3. SEM micrograph of epoxy-titania composite with TiO$_2$ content 1 wt %

Fig. 4. Temperature dependence of the loss factor ($\tan \delta$) of the composites with different filler content

Table 1

<table>
<thead>
<tr>
<th>wt(TiO$_2$), wt %</th>
<th>$\tan \delta$</th>
<th>$T_g$, K</th>
<th>$\tan \delta_{max}$</th>
<th>$T_{max}$, K</th>
<th>$E''_{max}$, MPa</th>
<th>$E''$, MPa</th>
<th>$E'$, MPa</th>
<th>$\rho$, g·cm$^{-3}$</th>
<th>$M_r$, g·mol$^{-1}$</th>
<th>$W_{sol}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>343</td>
<td>1.18</td>
<td>330</td>
<td>304</td>
<td>2603</td>
<td>9.2</td>
<td>1.098</td>
<td>1.098</td>
<td>660</td>
<td>0.7</td>
</tr>
<tr>
<td>0.5</td>
<td>341</td>
<td>1.15</td>
<td>327</td>
<td>286</td>
<td>2497</td>
<td>5.8</td>
<td>1.096</td>
<td>1.096</td>
<td>1130</td>
<td>2.3</td>
</tr>
<tr>
<td>1.0</td>
<td>339</td>
<td>1.02</td>
<td>325</td>
<td>313</td>
<td>3037</td>
<td>4.3</td>
<td>1.091</td>
<td>1.091</td>
<td>2000</td>
<td>3.2</td>
</tr>
<tr>
<td>1.5</td>
<td>333</td>
<td>1.05</td>
<td>319</td>
<td>305</td>
<td>2740</td>
<td>8.6</td>
<td>1.090</td>
<td>1.090</td>
<td>690</td>
<td>3.1</td>
</tr>
<tr>
<td>3.0</td>
<td>324</td>
<td>0.85</td>
<td>306</td>
<td>364</td>
<td>2147</td>
<td>8.8</td>
<td>1.119</td>
<td>1.119</td>
<td>700</td>
<td>2.9</td>
</tr>
</tbody>
</table>

As it was demonstrated by small-angle X-ray scattering (SAXS) [11] in contrast to the pure epoxy polymer, the profiles of the synthesized composites with 0.5–1.5 wt % TiO$_2$ content exhibited a wide scattering peak. This might be caused by the short-range periodicity of the titania-rich domains with the distance between the scattering centers of ~5–6 nm. The SAXS profile for the composite with 3 wt % filler content had the linear region with the slope 1.85, with no diffraction maximum. Mass fractal objects with the dimension 1.85 were formed during the synthesis procedure. The size of fractals was more than 250 nm. Thus, with the filler content increase the structure of the composites changed from systems with definite ordering of the titania particles to the formation of submicron-sized branched aggregates. Such changes could significantly influence the characteristics of the received samples.

Inorganic filler incorporation may considerably affect the polymer structure and properties. Polymer/filler interactions lead to the changes of polymeric chains molecular motion in the interfacial layer that may influence the $T_g$ values of the composites and the relaxation processes rate in the $T_g$ region.
The tan \( \delta \) of the unmodified epoxy polymer and composites with 0.5–3 wt % TiO\(_2\) are plotted as a function of the temperature in Fig. 4. For all the curves one maximum is observed corresponding to \( \alpha \)-relaxation transition. The tan \( \delta (T) \) dependence analysis of the received samples revealed that tan \( \delta_{\text{max}} \) was shifted to lower temperatures with the filler content increase, i.e., plasticization of the epoxy matrix occurred. Glass transition temperature and maximum value of tan \( \delta \) are listed in Table 1.

Decrease of glass transition temperature in the sol-gel derived nanocomposites was reported in [12-14]. Lowering of \( T_g \) values in such systems was explained by the shift of epoxy/hardener ratio due to a selective adsorption of one of the matrix forming components [13]. Rubab et al. [15] reported non-linear change of \( T_g \) for amine-cured epoxy-titania composites with the filler content increase. Firstly, growth of glass transition temperature due to immobilization of polymeric chains at the interphase layer was observed. Further reduction of \( T_g \) was explained by the polymeric chains packing disruption in the presence of high filler content. Such effect was also observed by Dorigato et al. [16] for epoxy-zirconia nanocomposites. The occurrence of concomitant reduction of \( T_g \) values and reinforcement of epoxy matrix by the siloxane domains within the rubbery plateau regions was shown by Piscitelli et al. [17]. The authors explained the plasticization effect with chemical interactions between the amine hardener and pre-hydrolyzed alkoxide that led to the appearance of linear flexible epoxy-siloxane sequences in the structure of the hybrid network.

For the synthesized epoxy-titania composites the \( T_g \) values decrease with the filler content increase may be caused by possible non-complete removal of butanol (the TBT hydrolysis product), which may adsorb on the titania surface, and its plasticizing effect, as well as the possibility of the amine hardener selective adsorption on the high-energy filler surface [18]. In the latter case, non-reacted epoxy resin acts as a plasticizer, which leads to the polymeric network topology disruption compared to the pure epoxy polymer. This is confirmed by a sol-fraction yield (\( W_{\text{sol}} \)) increase for the composites with the filler content (see Table 1). Formation of linear flexible Ti–O–Ti sequences in the structure of the composite network may also contribute to the observed decrease of glass transition temperature of the composites, similarly to siloxane chains formation as it was shown in [17].

Fig. 4 also demonstrates the broadening of the tan \( \delta \) peak half-width with the increase of the filler content in the composites. This suggests the growth of the inhomogeneity in the molecular weight of a polymeric network segment which is responsible for the \( \alpha \)-relaxation transition. At the same time, the tan \( \delta_{\text{max}} \) values have a tendency to decrease. It is known that the tan \( \delta \) peak intensity represents the polymeric segment motion extent. Thus, the presence of a titania phase causes the restriction of the polymeric chains motion.

The \( E''(T) \) dependence is similar to that of the loss factor: the peaks are shifted to lower temperatures. The peak intensity demonstrates no change with titania content except for the composite with 3 wt % of the filler (Fig. 5, Table 1).

The analysis of the dynamic modulus temperature dependence indicates that in the glassy region \( E' \) values of the composites are higher than those of the epoxy polymer (Fig. 6, Table 1). Such effect for polymer-titania composites was reported by Xiong et al. [19]. Usually growth of modulus in the temperature range below \( T_g \) is a result of more intensive intermolecular interactions, including the polymer/filler interphase.
It should be noted that a non-linear change of the elastic modulus and the effective network density is observed with the titania content increase. The calculated values of the molecular weight between two cross-linking points \( (M_c) \) are reported in Table 1. The network density of the composites decreases with respect to the pure epoxy polymer. At filler content of 0.5–1 wt% two-fold increase of \( M_c \) is observed. Further titania concentration increase results in the decrease of the network density up to the level of the unfilled polymer. Such effect may be caused by the interphase interactions changes between the system components with the filler content variation. As a result, with the increase of filler concentration not only polymer/filler but also filler/filler interactions could be observed, and relative increase of the effective network density of the composites occurs.

4. Conclusions

Sol-gel method was used to synthesize amine-cured epoxy-titania composites with the filler content 0.5–3 wt%. It was shown that the obtained titanium dioxide was amorphous. SEM results demonstrate that primary titania nanoparticles have formed submicron-sized aggregates, that were randomly distributed in the polymeric matrix. The DMA results indicated that increasing the filler content decreases the glass transition temperature of the epoxy composites, i.e., plasticization effect was observed. The increase of the filler content in the composites resulted in a non-linear change of dynamic modulus and the effective network density.

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References


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В’ЯЗКОПРУЖНІ ВЛАСТИВОСТІ ЕПОКСИДНО-ТИТАНОВИХ КОМПОЗИТІВ АМИННОГО ТВЕРДНЕННЯ, ОТРИМАНИХ ЗОЛЬ-ГЕЛЬ МЕТОДОМ

Анотація. Досліджено в'язкопружні властивості епоксидно-титанових композитів амінного тверднення, отриманих золь-гель методом. Аналіз фізико-механічних властивостей показав, що збільшення вмісту TiO₂ призводить до зниження температури склування композитів, при цьому спостерігається нелінійна зміна густини ванна.

Ключові слова: золь-гель, діоксид титану, епоксидна смола, композити, амінне тверднення, в'язкопружні властивості.