

VISCOELASTIC PROPERTIES OF AMINE-CURED EPOXY-TITANIA
COMPOSITES OBTAINED BY THE SOL-GEL METHODSvitlana Zhil'tsova^{1, *}, Oleksandr Brovko², Natalya Leonova¹<https://doi.org/10.23939/chcht12.02.202>

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 TiO₂ 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.

1. Introduction

Epoxy-inorganic composites are widely used in many branches of industry due to their high strength, thermal stability, chemical resistance, good adhesion to different substrates, *etc.* Variation of epoxy resin and curing method, as well as chemical nature, content and filler size allows to change significantly the resulting material structure and properties. Metal oxides are often used as fillers to improve electrical, optical, photocatalytic properties of the polymers. Recently, researchers concentrated their attention on titanium dioxide as a filler for the obtaining of optically transparent epoxy composites with a controlled refractive index [1], high thermal stability [2], mechanical properties [3], *etc.*

Nano- and submicron particles are often formed *in situ* by the sol-gel method [4, 5]. Epoxy-titania nanocomposite coatings with high refractive index and optical transparency were synthesized using this approach [6]. Optically transparent amine cured epoxy-titania composites with a high scratch resistance were obtained [7]. Yu *et al.* [8] synthesized thin transparent films with low water absorption and high thermal stability.

It is well-known that introduction of a filler significantly affects the relaxation processes in the system. For example, non-linear change of glass transition

temperature and dynamic modulus with TiO₂ content increase was observed for amine-cured epoxy micro- and nanocomposites obtained with the use of commercial fillers [9]. Such changes in the polymer chains molecular mobility often relate to a filler distribution in the polymeric matrix and interfacial interactions of polymer chains with filler particles. It is important to know the influence of sol-gel received TiO₂ particles on the relaxation properties of such composites. Thus, the objective of this work was to obtain amine-cured epoxy-titania composites *via* the sol-gel method, and to study their structure and viscoelastic characteristics.

2. Experimental

The polymer samples were obtained using epoxy resin EPONEXTM Resin 1510 (EEW = 210–220 g·eq⁻¹; $\rho = 1.09 \text{ g}\cdot\text{cm}^{-3}$ (298 K)) and stoichiometric amount of amine hardener Jeffamine@T403 (AHEW = 81 g·eq⁻¹; $\rho = 0.98 \text{ g}\cdot\text{cm}^{-3}$ (298 K)). Structural formulas of epoxide oligomer and hardener are shown in Fig. 1. The samples were cured at 293 K (3 days) and postcured at 393 K (3 h).

The composites were obtained by mixing TiO₂ particles' sol in the epoxy resin with the amine hardener. The titania sol was formed *in situ via* the sol-gel method using a hydrolytic polycondensation of tetrabutyltitanate (TBT) complex with a glacial acetic acid (1:1.5 mole ratio). TBT was hydrolyzed in the presence of the epoxy resin using stoichiometric molar ratio H₂O/C₄H₉O. Water for the hydrolysis was added as a water-ethanol solution (84 wt % C₂H₅OH). Titania content in the system, calculated as titanium dioxide (based on the amount of TBT added), was varied from 0.5 to 3 wt %. After high-temperature thermal oxidative decomposition of the samples, the weight of the dry residue was equal to the theoretical weight of titania particles, calculated as TiO₂.

The composites were synthesized in the next sequence: 1) formation of TBT-acetic acid complex (30 min) and mixing it with the epoxy resin; 2) combining the received mixture with water-ethanol solution to obtain TiO₂ sol (1 h at ambient temperature) and evacuation of the

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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.

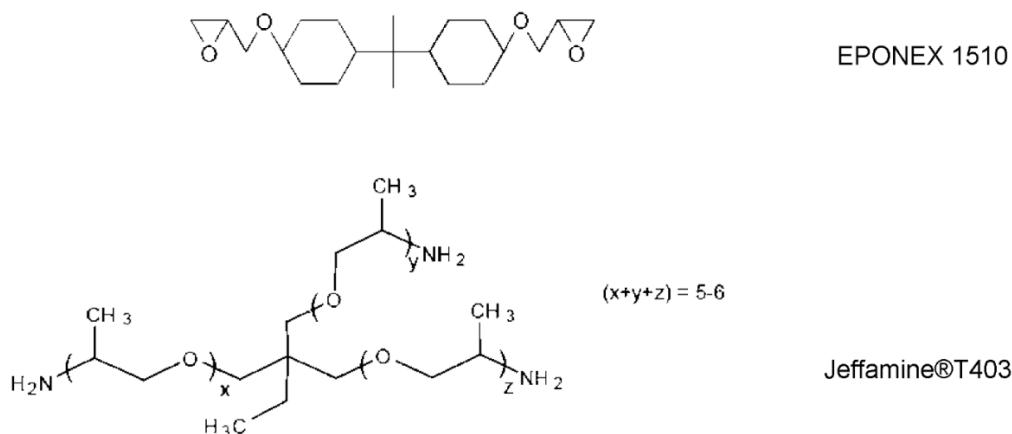


Fig. 1. Chemical structure of epoxy resin and curing agent

The obtained samples were investigated by X-ray powder diffraction (XRD) using DRON-3M diffractometer (CuK α radiation, Ni-filter). The XRD patterns were received at room temperature in a range of 16–54° (2 θ), 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: $W_{sol} = (m_0 - m) \cdot 100 / m_0$, 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: $\lg G \approx 6 + 293\rho/M_c$. Shear modulus G was calculated by the equation: $G = E_e/2(1 + n)$, 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 ρ was determined by the hydrostatic weighing method using Shimadzu AX200 balances, according to the equation: $\rho = m_1 \cdot \rho_2 / (m_1 - m_2)$, where m_1 and m_2 are the weights of the sample in air and water, respectively; ρ_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.

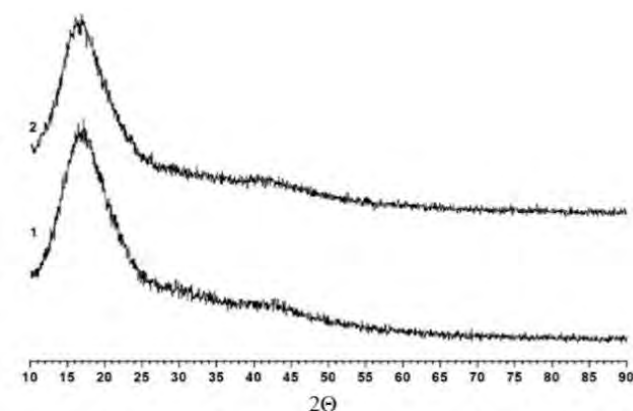


Fig. 2. X-ray diffraction patterns of epoxy polymer (1) and composite with a filler content 3 wt % (2)

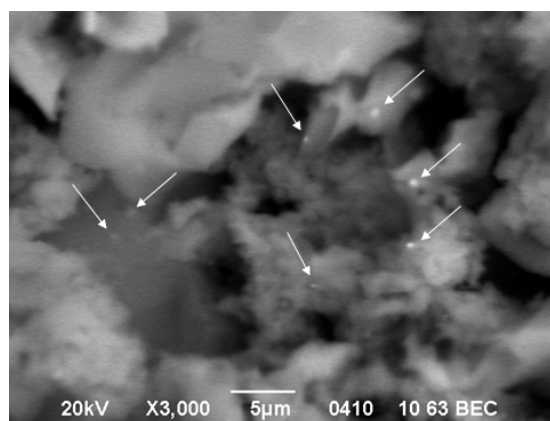


Fig. 3. SEM micrograph of epoxy-titania composite with TiO₂ content 1 wt %

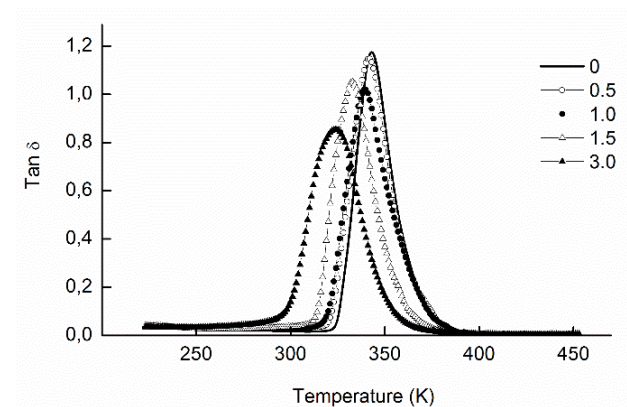


Fig. 4. Temperature dependence of the loss factor ($\tan \delta$) of the composites with different filler content

Table 1

The dynamic mechanical analysis results, density, effective network density and sol-fraction yield of the composites

$w(\text{TiO}_2)$, wt %	$\tan \delta$		E''		E' , MPa		ρ , g·cm ⁻³	M_c , g·mol ⁻¹	W_{sol} , %
	T_g , K	$\tan \delta_{max}$	T_{max} , K	E''_{max} , MPa	E'_{25}	E'_e			
0	343	1.18	330	304	2603	9.2	1.098	660	0.7
0.5	341	1.15	327	286	2497	5.8	1.096	1130	2.3
1.0	339	1.02	325	313	3037	4.3	1.091	2000	3.2
1.5	333	1.05	319	305	2740	8.6	1.090	690	3.1
3.0	324	0.85	306	364	2147	8.8	1.119	700	2.9

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 % TiO₂ 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 α -relaxation transition. The $\tan \delta(T)$ dependence analysis of the received samples revealed that $\tan \delta_{\max}$ 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 possi-

bility 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_{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 α -relaxation transition. At the same time, the $\tan \delta_{\max}$ 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.

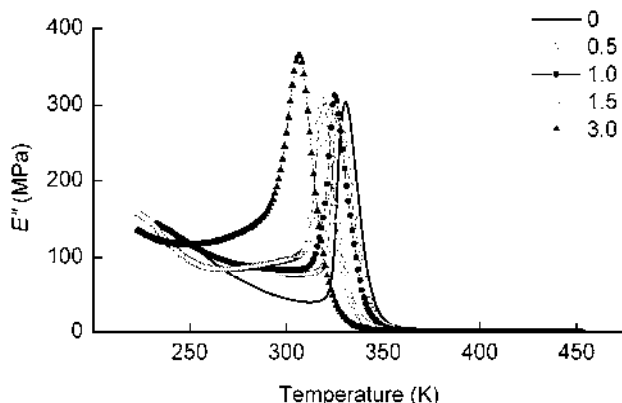


Fig. 5. Temperature dependence of the storage modulus (E') of the composites with different filler content

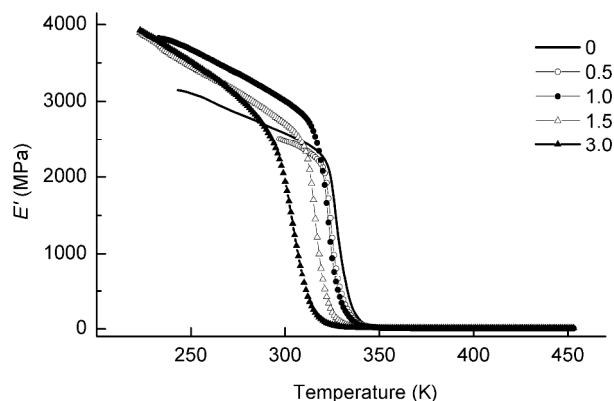


Fig. 6. Temperature dependence of the dynamic modulus (E'') of the composites with different filler content

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

- [1] Liu B-T., Tang Sh-J., Yu Y-Y., Lin S-H.: Colloid. Surface A, 2011, **377**, 138. <https://doi.org/10.1016/j.colsurfa.2010.12.046>
- [2] Ghosh P., Pathak A., Goyat M., Halder S.: J. Reinf. Plast. Compos., 2012, **31**, 1180. <https://doi.org/10.1177/0731684412455955>
- [3] Merad L., Benyoucef B., Abadie M., Charles J.: Exp. Techniques, 2014, **38**, 59. <https://doi.org/10.1111/j.1747-1567.2011.00797.x>
- [4] Pomogailo A.: Colloid J., 2005, **67**, 658. <https://doi.org/10.1007/s10595-005-0148-7>
- [5] Mascia L., Lavorgna M.: Nanostructured Polymer Composites by Sol-Gel Method [in:] Nicolais L., Borzacchiello A. (Eds.), Wiley Encyclopedia of Composites, 2nd edn. John Wiley & Sons, Inc., NJ 2012, 1-20. <https://doi.org/10.1002/9781118097298.weoc158>
- [6] Chau J., Tung Ch-T., Lin Y-M., Li A-K.: Mater. Lett., 2008, **62**, 3416. <https://doi.org/10.1016/j.matlet.2008.02.058>
- [7] Bondioli F., D'Arcchio M., Luyt A., Messori M.: J. Appl. Polym. Sci., 2011, **122**, 1792. <https://doi.org/10.1002/app.34264>
- [8] Yu Y-Y., Rao Y-C., Chang Ch-Ch.: Thin Solid Films, 2013, **546**, 236. <https://doi.org/10.1016/j.tsf.2013.05.038>
- [9] Rajabi L., Mohammadi Z., Derakhshan A.: Iran. J. Chem. Eng., 2013, **10**, 16.
- [10] Nielsen L., Landel R.: Mechanical Properties of Polymers and Composites. Marcel Dekker Inc., New York 1974.
- [11] Glebova I., Zhil'tsova S., Mikhal'chuk V. et al.: Nanostructured Materials – 2014: Belarus – Russia – Ukraine (NANO–2014): VI Int. Sci. Conf., Belarus, Minsk 7–10 Oct., 2014, 94.
- [12] Leonova N., Mikhal'chuk V., Mamunya Ye. et al.: Polym. Sci. D., 2013, **6**, 210. <https://doi.org/10.1134/S1995421213030131>
- [13] Zhil'tsova S., Mikhal'chuk V., Lyga R., Pavlii P.: Theor. Exp. Chem., 2014, **50**, 191. <https://doi.org/10.1007/s11237-014-9365-7>
- [14] Sun Y., Zhang Zh., Wong C.: Polymer, 2005, **46**, 2297. <https://doi.org/10.1016/j.polymer.2005.01.041>
- [15] Rubab Z., Afzal A., Siddiqi H., Saeed Sh.: Sci. World J., 2014, **2014**, 515739. <https://doi.org/10.1155/2014/515739>
- [16] Dorigato A., Pegoretti A., Bondioli F., Messori M.: Compos. Interfaces, 2010, **17**, 873. <https://doi.org/10.1163/092764410X539253>
- [17] Piscitelli F., Lavorgna M., Buonocore G. et al.: Macromol. Mater. Eng., 2013, **298**, 896. <https://doi.org/10.1002/mame.201200222>
- [18] Rosso P., Ye L.: Macromol. Rapid. Commun., 2007, **28**, 121. <https://doi.org/10.1002/marc.200600588>
- [19] Xiong M., Zhou S., You B. et al.: Polym. Sci. B., 2004, **42**, 3682. <https://doi.org/10.1002/polb.20218>

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В'ЯЗКОПРУЖНІ ВЛАСТИВОСТІ ЕПОКСИДНО-ТИТАНОВИХ КОМПОЗИТІВ АМІННОГО 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 TiO_2 приводить до зниження температури склування композитів, при цьому спостерігається нелінійна зміна густини зшивання.

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