

TITANIUM DIOXIDE NANOPARTICLES SURFACE MODIFIED WITH IMINE AS FILLERS FOR EPOXY RESIN

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The surface of anatase TiO₂ nanoparticles was modified with in situ synthesized imine, based on 3,4-dihydroxybenzaldehyde and octadecylamine. The modified TiO₂ nanoparticles were investigated using FTIR and UV-Vis spectroscopy, which confirmed the formation of the charge transfer complex between imine and surface of TiO₂ nanoparticles by the reaction of surface Ti atoms with hydroxyl groups of a modifying agent. TiO₂ nanoparticles modified with imine were further applied as a filler for the preparation of epoxy based nanocomposites. Thermal and mechanical properties of the prepared nanocomposites were examined using the dynamic mechanical analysis, differential scanning calorimetry, thermogravimetric analysis and hardness measurements. The obtained results have shown that modified TiO₂ nanoparticles have no significant influence on the glass transition temperature and that they slow down thermo-oxidative degradation of epoxy resin in the first stage and increase hardness of the crosslinked epoxy resin.

Keywords: epoxy/TiO₂ nanocomposites; surface modification; imine; thermal properties; mechanical properties

Introduction

Epoxy resins are one of the most popular thermosetting polymers usually applied in construction, electronic, automotive and aerospace industries. The benefits of using epoxy resins are related to their good thermal stability, excellent corrosion, chemical and moisture resistance, good electrical and mechanical properties (high compression and tensile strength, good adhesion properties, good impact resistance, high hardness, low creep), etc. [1]. Furthermore, the high brittleness of these thermosetting polymers can be successfully overcome using adequate fillers. Especially, the incorporation of different inorganic nanoparticles as reinforcing agents in epoxy resins is proved to be a powerful tool to achieve remarkable improvement of various properties of epoxy resins, and consequently to accommodate feature requirements for specific applications. It has been shown that the addition of nanoparticles such as TiO₂ [2-16], SiO₂ [17,18], nanodiamonds [19,20], graphene [21-23], carbon nanotube [24-26], clay [27,28], ZnO [29,30], etc. can enhance tensile strength, elongation at break, tensile, storage, and flexural modulus, toughness, impact and compression strength, scratch resistance, hardness, adhesive strength, reduce creep rate, improve rheological properties, enhance thermal stability, thermal and electrical conductivity, flame retardancy, dielectric, barrier, anticorrosion, optical and shielding properties of epoxy resins.

Although various nanoparticles are applied as fillers for epoxy resins, special attention has been given to the epoxy nanocomposites based on TiO₂ nanoparticles [2-16].

This is not surprising since TiO₂ nanoparticles exhibit good optical, catalytic, anticorrosion, dielectric and mechanical properties, high stability, low cost, etc. TiO₂ can be found in anatase, rutile and brookite form, wherein anatase and rutile have a tetragonal and brookite orthorhombic (or rhombohedral) crystalline structure [31,32]. A number of methods have been used to synthesize TiO₂ nanoparticles such as sol-gel, solvothermal, hydrothermal, sonochemical, physical and chemical vapor deposition, electrodeposition, etc. [2,33]. The procedure applied for the synthesis of TiO₂ nanostructures has a strong impact on their size, shape and properties [2,32,33].

Prerequisites for the homogenous distribution of TiO₂ nanoparticles within the epoxy matrix and the improvement of the properties of epoxy resin after incorporation of TiO₂ nanoparticles are good dispersability of nanofiller, as well as enhanced compatibility and interfacial interactions between the polymer matrix and TiO₂ nanoparticles. The high surface area of TiO₂ nanoparticles facilitates the interactions between nanoparticles and polymer matrix, but also between nanoparticles themselves, leading to the formation of aggregates. However, the expected improvement of polymer properties after inclusion of nanofillers will be omitted if aggregates are present. The most common method used to reduce the aggregation is the surface modification of TiO₂ nanoparticles. In addition, by the adequate treatment of the surface of nanoparticles, the compatibility and interfacial in-

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teractions between nanofiller and polymer matrix may be enhanced as well. Wang et al. have shown that aggregation of TiO₂ nanoparticles in epoxy resin can be prevented by their surface modification with a silane coupling agent [9]. Rubab et al. have used TiO₂ nanoparticles surface modified with γ -aminopropyltriethoxysilane to prepare epoxy resin (ER)/TiO₂ nanocomposites with noticeable improved mechanical properties and glass transition temperature (*T_g*), compared to the pure epoxy resin [3]. The reactive amino groups, present on the surface of TiO₂ nanoparticles after the modification with the organosilane coupling agent, provided covalent bonding between TiO₂ nanoparticles and polymer matrix, leading to the effective reinforcement of epoxy resin with TiO₂ nanoparticles. Tao et al. have shown that dispersion of TiO₂ nanoparticles and their compatibility with epoxy resin can be increased by grafting poly(glycidyl methacrylate) onto TiO₂ nanoparticle surfaces [14,34]. Furthermore, Kobayashi et al. prepared transparent and colorless ER/TiO₂ hybrid films using TiO₂ nanoparticles modified with n-octylphosphonic acid [35]. On the other hand, Siddabattuni et al. observed that dielectric properties of ER/TiO₂ nanocomposites depends on the chemical structure of organophosphate ligands applied to modify the surface of TiO₂ nanoparticles [36].

In our previous works, we have investigated the influence of the hydrophobic part length of gallic acid esters used for the surface modification of TiO₂ nanoparticles, on the properties of commercial epoxy resin (CHS-EPOXY 210 × 75) [11,12]. It was found that prepared nanocomposites exhibit higher *T_g*, and better barrier and anticorrosion properties than pure epoxy resin.

Following our previous works, this study is aimed to the investigation of the effect of surface modified TiO₂ nanoparticles and their content on thermal and mechanical properties of ER/TiO₂ nanocomposites prepared using commercial epoxy resin (Araldite GT 7071). For this purpose, TiO₂ nanoparticles were modified with in situ synthesized imine based on 3,4-dihydroxybenzaldehyde (DHBA) and octadecylamine (ODA). The unmodified TiO₂ nanoparticles were examined using transmission electron microscopy (TEM), while modified nanoparticles were investigated by FTIR and UV-Vis spectroscopy. Thermal and mechanical properties of the prepared ER/TiO₂ nanocomposites were tested using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and hardness measurements.

Experimental

Materials

Titanium isopropoxide and 3,4-dihydroxybenzaldehyde were obtained from Acros Organics. Nitric acid (65%) and 2-propanol were purchased from Zorka Pharma, while octadecylamine from Sigma Aldrich. Epoxy resin (Araldite GT 7071) and curing agent (Aradur 115 BD) were obtained from Huntsman Advanced Materials. All chemicals were used as received without further purification.

Synthesis of TiO₂ colloid

The TiO₂ colloid was synthesized by hydrolysis of titanium isopropoxide according to the procedure described by O'Regan et al. [37]. The mixture containing 12.5 mL of titanium isopropoxide and 2.0 mL of 2-propanol was added from the dropping funnel into 75 mL of deionized water and vigorously stirred. As a result of the hydrolysis reaction, a white precipitate was formed. Within 10 min of the addition of alkoxide, 0.57 mL of nitric acid was loaded to the mixture. The obtained mixture was then stirred at 80 °C for 8 h, allowing 2-propanol to evaporate. In this manner, around 70 mL of stable TiO₂ colloidal solution was obtained.

Surface modification of TiO₂ nanoparticles with imine

The surface modification of TiO₂ nanoparticles with imine based on DHBA and ODA (DHBA-ODA) was performed according to the following procedure. The solutions of 0.1067 g of DHBA in 5 mL of methanol and 0.2085 g of ODA in 37.5 mL of chloroform were vigorously mixed with 5 mL of TiO₂ colloid solution, previously diluted with 45 mL of distilled water. The obtained solution was then left overnight. After that, the lower dark-orange phase containing TiO₂ nanoparticles surface modified with DHBA-ODA (TiO₂-ODA) was separated from the upper aqueous phase and then slowly, with simultaneous mixing, using the magnetic stirrer, drop-wise added into 100 times larger quantity of methanol. The surface modified TiO₂-ODA nanoparticles separated as precipitate, which was then redispersed in chloroform.

Preparation of the ER/TiO₂ nanocomposites

The synthesized TiO₂ nanoparticles surface modified with DHBA-ODA were further applied as nanofillers for the preparation of ER/TiO₂ nanocomposites. For that purpose, the commercial epoxy resin Araldite GT 7071 and the curing agent Aradur 115 BD were applied. The weight ratio between the resin and the curing agent were 100:35. The ER/TiO₂-ODA nanocomposites containing 1, 2 and 3 wt.% of TiO₂, calculated with respect to the total mass of the epoxy resin and the curing agent were synthesized by adding the adequate amount of modified nanoparticles, dispersed in chloroform, to the epoxy resin. In order to evaporate chloroform, the mixtures were left at room temperature under the reduced pressure. After that, the adequate amount of xylene (50 wt.% calculated with respect to the total mass of the epoxy resin and the curing agent) and curing agent were added. For the preparation of pure epoxy resin, in the mixture of Araldite GT 7071 and Aradur 115 BD nanoparticles were not added. The films of pure epoxy resin and ER/TiO₂ nanocomposites were formed by drawing prepared mixtures on glass (10 × 10 × 1 cm and 15 × 20 × 0.3 cm) plates using the 100 μ m applicator. Films were cured at room temperature for 21 days. Pure epoxy resin and prepared nanocomposites were also cured in Teflon molds (63 × 12 × 2 mm).

Characterization of unmodified and surface modified TiO₂ nanoparticles

The size and shape of unmodified TiO₂ nanoparticles were determined using TEM (JEOL-1200EX). The size dis-

tribution of TiO₂ nanoparticles was obtained using Image J software. FTIR spectra of dry unmodified and modified TiO₂ nanoparticles in the form of KBr pellets were recorded using a Bomem MB-102 FTIR spectrophotometer. Perkin-Elmer Lambda-5 UV-Vis spectrometer was applied to record the absorption spectra of unmodified and surface modified TiO₂ nanoparticles.

Characterization of the ER/TiO₂ nanocomposites

A dynamic mechanical analysis of the synthesized samples was performed using TA Instruments SDT Q600 operating in the temperature sweep mode. The temperature dependences of the storage (*G'*) and loss (*G''*) modulus and loss factor ($\tan \delta$) of cured pure epoxy resin and prepared nanocomposites were determined in the temperature range 25–150 °C, at the frequency of 1 Hz and deformation of 0.1%. Before DMA measurements, the examined samples were removed from Teflon molds and dried in a vacuum oven until the constant mass was reached. DSC measurements were performed on Perkin-Elmer DSC-2 instrument in a nitrogen atmosphere, at a heating and cooling rate of 20 °C/min. A thermogravimetric analysis (TGA) was performed using the SDT Q600 (TA Instruments) thermogravimetric analyzer. The samples (about 5 mg) were run from 30 to 600 °C at the heating rate of 10 °C/min in an air flow (0.1 dm³ min⁻¹).

The König pendulum hardness of dried films drawn on glass plates was determined using BYK-Gardner tester, as an average value of three measurements. The thickness of the examined dried films was 22 ± 3 μm.

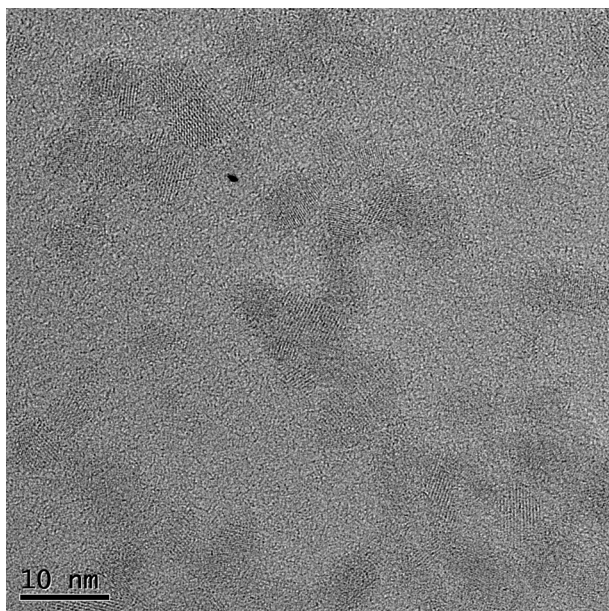


Figure 1. TEM image of prepared TiO₂ nanoparticles

Results and discussion

Properties of unmodified and surface modified TiO₂ nanoparticles

TiO₂ nanoparticles were prepared by acid catalyzed hydrolysis of the titanium isopropoxide precursor. According to

the TEM results, the average diameter of prepared nanoparticles is 3.9 ± 0.9 nm (Figure 1). This is in accordance with the X-ray diffraction (XRD) results presented elsewhere, where it was shown that synthesized TiO₂ nanoparticles are in an anatase crystal form with a coherent domain size of around 3.6 nm [38].

In order to enable the transfer of the synthesized nanofiller from the aqueous to the organic phase, TiO₂ nanoparticles were surface modified with in situ synthesized imine (DHBA-ODA), based on DHBA and ODA (Figure 2). During the modification reactions, the charge transfer (CT) complex was formed between imine and surface of TiO₂ nanoparticles by the reaction of surface Ti atoms with hydroxyl groups of the modifying agent, causing the appearance of the intense dark-orange color of prepared dispersions.

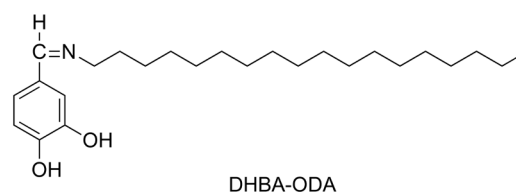


Figure 2. The chemical structure of DHBA-ODA

The chemisorption of DHBA-ODA on the surface of TiO₂ colloid and CT complex formation was confirmed by FTIR and UV-Vis spectroscopy. FTIR spectra of DHBA, ODA, surface modified TiO₂ nanoparticles and dry TiO₂ colloid are given in Figure 3. In the FTIR spectra of ODA, several characteristic bands can be observed: the bands at 3430 and 3332 cm⁻¹ originate from the N-H stretching vibrations, the bands at around 2950 and 2870 cm⁻¹ and at around 2920 and 2850 cm⁻¹ are assigned to the asymmetric and symmetric C-H stretching vibrations of methyl and methylene groups, respectively, the band at around 1615 cm⁻¹ corresponds to the N-H bending vibration of the primary amine, the band at around 1465 cm⁻¹ is ascribed to the C-H bending vibration of the methylene group, while the band at around 723 cm⁻¹ is ascribed to the rocking vibration of more than three methylene groups in the normal hydrocarbon chain. In the FTIR spectra of TiO₂ nanoparticles surface modified with DHBA-ODA (TiO₂-ODA) the bands at around 3331 and 3233 cm⁻¹, related to the stretching vibrations of aldehyde phenolic -OH groups, and the bands at around 1389 and 1192 cm⁻¹, ascribed to the bending vibrations of phenolic -OH groups, are clearly absent. The intensity of the band at around 1296 cm⁻¹, assigned to the stretching vibrations of phenolic -OH groups, is reduced and the band became much broader and probably overlapped with the band corresponding to the stretching vibrations of C-N bond at 1331 cm⁻¹, which shifted to higher frequencies due to the resonant effect of the benzene ring. A band at around 1645 cm⁻¹, assigned to the stretching vibration of C=N bond, and a band at 1576 cm⁻¹, ascribed to the stretching vibration of aromatic ring, can also be observed in the FTIR spectra of TiO₂-ODA nanoparticles.

These results indicate that imine DHBA-ODA was formed during the modification of TiO_2 nanoparticles, and that it was chemisorbed on the surface of TiO_2 through their two adjacent $-\text{OH}$ phenolic groups of the aldehyde residue, leading to the formation of bridging complexes with Ti atoms on the surface [38,39].

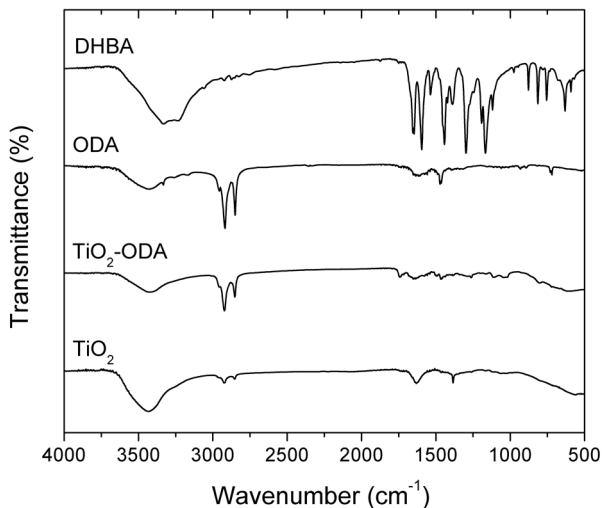


Figure 3. FTIR spectra of DHBA, ODA, surface modified TiO_2 nanoparticles and dry TiO_2 colloid

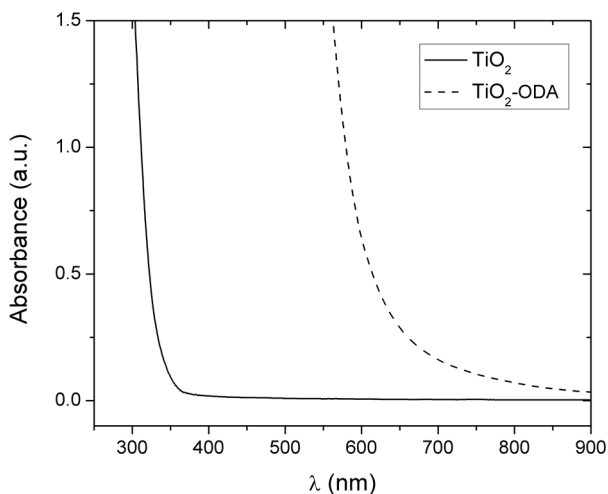


Figure 4. The absorption spectra of aqueous TiO_2 colloid solution and surface modified TiO_2 nanoparticles in chloroform

The formation of the CT complex due to the chemisorption of DHBA-ODA on the surface of TiO_2 nanoparticles was also confirmed by UV-Vis spectroscopy (Figure 4). As it can be observed from the results given in Figure 4, the absorption spectrum of TiO_2 nanoparticles surface modified with DHBA-ODA are red shifted in comparison to the absorption spectrum of TiO_2 colloid. The shift of the absorption spectrum of TiO_2 -ODA for more than 200 nm towards higher wavelengths occurred as a consequence of the CT complex formation between imine and nanocrystalline TiO_2 [38].

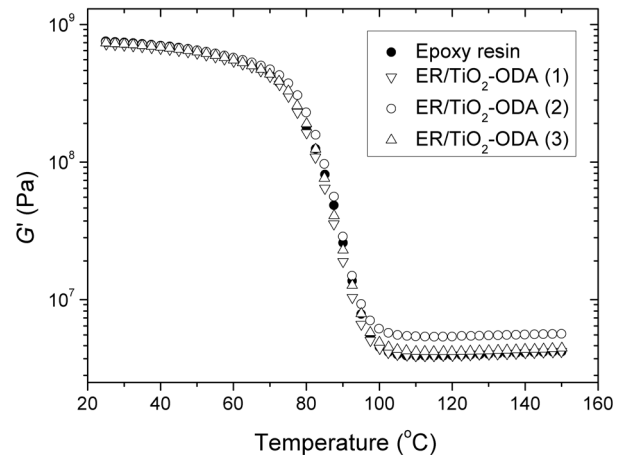


Figure 5. Temperature dependences of the storage modulus (G') of cured pure epoxy resin and prepared nanocomposites

Properties of ER/ TiO_2 nanocomposites

TiO_2 nanoparticles surface modified with DHBA-ODA were used as nanofillers, while commercially available solid epoxy resin (Araldite GT 7071), designed for the application in high performance protective and decorative coatings, was used as polymer matrix for the synthesis of ER/ TiO_2 nanocomposites. In order to investigate the influence of the content of modified TiO_2 nanoparticles on the properties of prepared materials, ER/ TiO_2 -ODA nanocomposites were prepared using 1, 2 and 3 wt.% of nanoparticles.

Using DMA, the influence of the surface modified TiO_2 nanofillers on the dynamic mechanical properties was explored. The temperature dependences of the storage modulus (G'), loss modulus (G'') and loss factor ($\tan \delta$) of cured pure epoxy resin and prepared nanocomposites are presented in Figures 5, 6 and 7, respectively. From the results given in Figure 5, three regions of the viscoelastic behavior characteristic for the crosslinked polymers can be observed: the glassy region, the glass transition region and the rubbery plateau region. In the glassy region, G' of nanocomposites shows no significant difference compared to the G' of pure epoxy resin. Furthermore, G' of all examined samples in the glassy region is for one order of magnitude higher than loss modulus (Figure 6), which indicates that during deformation of the samples at low temperatures more energy is saved than lost. In the glass transition region, G' of pure epoxy resin and prepared nanocomposites sharply decreases due to the increased movement of the polymer chains associated with the glass transition, while in the rubbery plateau region (>100 °C) the flow of the samples is disabled because of the presence of chemical crosslinking. Since G' values in the rubbery plateau region are temperature independent and proportional to the crosslinking density, from DMA curves presented in Figure 5 and values of G' at 120 °C listed in Table 1, it can be concluded that there is no significant difference between the crosslinking density of prepared samples, except in the case of sample ER/ TiO_2 -ODA (2) which has slightly higher G' , i.e. a higher crosslinking density.

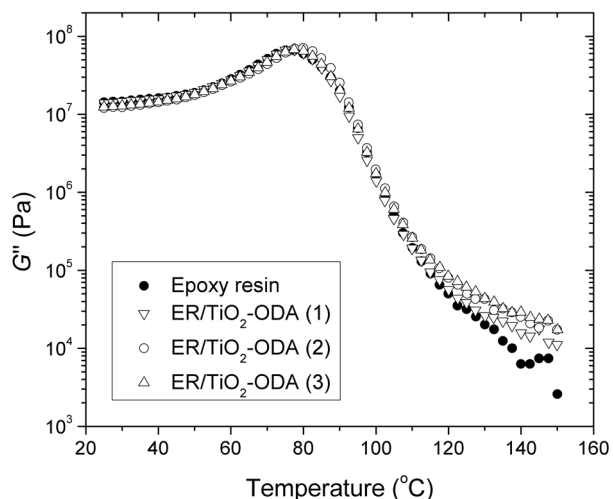


Figure 6. Temperature dependences of the loss modulus (G'') of cured pure epoxy resin and prepared nanocomposites

Table 1. DMA and DSC results for pure epoxy resin and prepared nanocomposites

Sample	$G' \cdot 10^{-6}$, MPa (at 120 °C)	T_g (G''), °C	T_g ($\tan \delta$), °C	T_g (DSC), °C
Epoxy resin	3.9	76	93	81
ER/TiO ₂ -ODA (1)	3.9	77	91	77
ER/TiO ₂ -ODA (2)	5.4	80	92	78
ER/TiO ₂ -ODA (3)	4.2	77	92	77

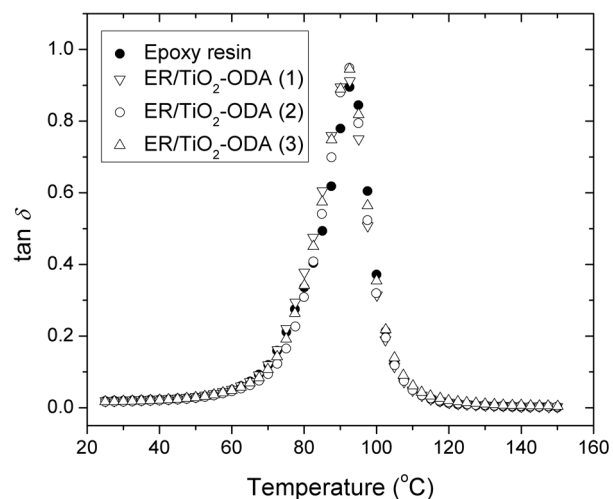


Figure 7. Temperature dependences of the loss factor ($\tan \delta$) of cured pure epoxy resin and prepared nanocomposites

According to the DMA results shown in Figure 6, it can be observed that temperature dependences of loss modulus are similar for all investigated samples in the whole examined temperature region. Glass transition temperatures (T_g) of the prepared samples, determined as the temperature of the G'' peak, are listed in Table 1. From the obtained results, it can be seen that the addition of surface modified TiO_2 nanoparticles into epoxy resin, and the increase of their content from 1 to 3 wt. %

have no significant impact on the T_g of epoxy resin. Similar can be concluded from the $\tan \delta$ temperature dependences presented in Figure 7 and T_g values of the investigated samples, determined as the temperature of the $\tan \delta$ peak, listed in Table 1. Namely, in Figure 7 only one peak can be observed in the $\tan \delta$ temperature dependences, belonging to the main relaxation α -process, corresponding to the glass transition of the epoxy resin. Furthermore, since the widths of the $\tan \delta$ peaks are similar for all samples, it can be concluded that all samples have approximately the same network homogeneity.

The influence of TiO_2 nanoparticles surface modified with DHBA-ODA on the glass transition temperature of nanocomposites was also investigated by DSC. The glass transition temperature of the examined samples was determined as the midpoint of the glass transition event. DSC thermograms of the investigated samples are given in Figure 8, while determined T_g values are listed in Table 1. It can be observed that T_g values slightly decreased after the addition of surface modified TiO_2 nanoparticles into epoxy resin, and show no dependence on the filler content, indicating the existence of weak interactions between TiO_2 nanoparticles and polymer matrix.

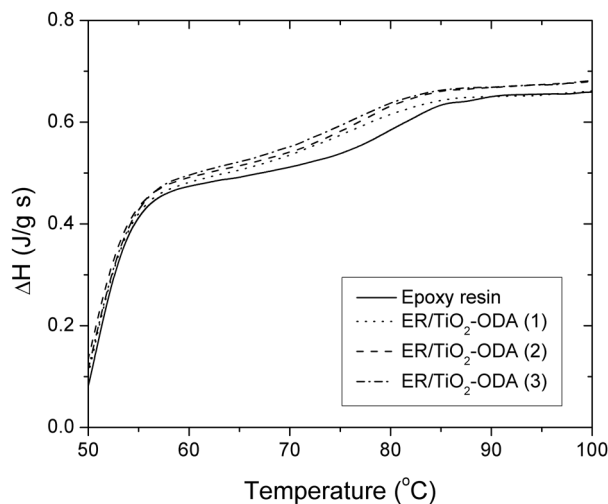


Figure 8. DSC curves of pure epoxy resin and prepared nanocomposites

The influence of the surface modified TiO_2 -ODA nanoparticles on the thermo-oxidative stability of epoxy resin and ER/ TiO_2 -ODA nanocomposites was investigated by non-isothermal thermogravimetry performed in air. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained for all examined samples are shown in Figure 9. The thermo-oxidative degradation of all examined samples starts at about 250 °C, indicating that incorporation of TiO_2 -ODA nanoparticles in epoxy matrix has no influence on the beginning of its thermo-oxidative decomposition. The obtained DTG curves have three peaks. The intensity of the first two peaks is lower for nanocomposites than for the pure ER, implying that

TiO₂-ODA nanoparticles slow down the thermo-oxidative degradation of ER in the examined temperature region. In the last stage (over 500 °C), the weight loss rate of nanocomposites is higher than for the pure ER.

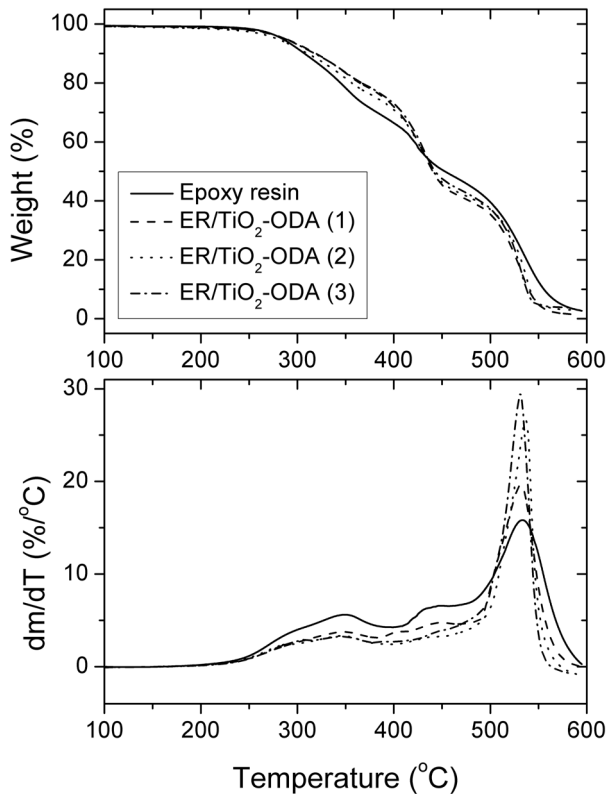


Figure 9. TG and DTG curves of cured pure epoxy resin and prepared nanocomposites obtained in air

The hardness of pure epoxy resin and prepared nanocomposites was determined using König pendulum and the obtained values are listed in Table 2. From the obtained results, it can be concluded that the addition of 1 wt.% of TiO₂ nanoparticles surface modified with DHBA-ODA into epoxy resin induces no changes in the hardness. However, further increase of the TiO₂-ODA content led to the slight improvement of the König hardness, since TiO₂ nanoparticles have higher hardness than pure epoxy resin.

Table 2. Values of the König hardness of pure epoxy resin and prepared nanocomposites

Sample	König hardness, s
Epoxy resin	186
ER/TiO ₂ -ODA (1)	186
ER/TiO ₂ -ODA (2)	192
ER/TiO ₂ -ODA (3)	193

Conclusion

Spherical anatase TiO₂ nanoparticles with the average diameter of 3.9 ± 0.9 nm were prepared using acid catalyzed hydrolysis of the titanium isopropoxide precursor. TiO₂ nanoparticles were then surface modified with imine based on 3,4-dihydroxybenzaldehyde and octadecylamine. The chemisorption of DHBA-ODA on the surface of TiO₂ nanoparticles and charge transfer complex formation through the reaction of surface Ti atoms with hydroxyl groups of the modifying agent were confirmed by FTIR and UV-Vis spectroscopy.

TiO₂ nanoparticles surface modified with imine and commercially available solid epoxy resin were used for the preparation of epoxy based nanocomposites. The influence of the surface modified TiO₂ nanoparticles and their content on thermal and mechanical properties of nanocomposites was investigated. DMA results revealed that all samples had the approximately same network homogeneity and that the sample ER/TiO₂-ODA (2) had a slightly higher crosslinking density than other examined nanocomposites and pure epoxy resin. Furthermore, the obtained DMA and DSC results showed that the addition of TiO₂ nanoparticles surface modified with imines into epoxy resin had no significant impact on the *T_g* of epoxy resin. These results indicate the existence of weak interactions between TiO₂ nanoparticles and polymer matrix.

According to the TGA, the incorporation of TiO₂-ODA nanoparticles in epoxy matrix has no influence on the beginning of its thermo-oxidative decomposition. The intensity of the first two DTG peaks is lower for nanocomposites than for pure ER, implying that TiO₂-ODA nanoparticles slow down the thermo-oxidative degradation of ER in the examined temperature region.

The addition of 1 wt.% of TiO₂ nanoparticles surface modified with DHBA-ODA into epoxy resin showed no influence on the hardness. On the other hand, a further increase of the TiO₂-ODA content led to a slight hardness improvement.

Acknowledgment

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List of symbols and abbreviations

FTIR – Fourier transform infrared
 UV-Vis – Ultraviolet-visible
 TEM - transmission electron microscopy
 DMA - dynamic mechanical analysis
 DSC - differential scanning calorimetry
 XRD - X-ray diffraction
 ER - epoxy resin
 DHBA - dihydroxybenzaldehyde

ODA - octadecylamine
 OA - oleylamine
 DHBA-ODA - imine based on DHBA and ODA
 DHBA-OA - imine based on DHBA and OA
 CT - charge transfer
 T_g - glass transition temperature
 G' - storage modulus
 G'' - loss modulus
 $\tan \delta$ - loss factor
 TGA - thermogravimetric analysis

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Izvod

NANOČESTICE TITAN-DIOKSIDA POVRŠINSKI MODIFIKOVANE IMINOM KAO PUNIOCI ZA EPOKSIDNU SMOLU

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Površina nanočestica TiO₂ modifikovana je "in situ" sintetisanim iminom na bazi 3,4-dihidroksibenzaldehida i oktadecilamina. Modifikovane TiO₂ nanočestice su ispitivane primenom FTIR i UV-Vis spektroskopije, čime je potvrđeno formiranje "charge transfer" kompleksa između imina i površine TiO₂ nanočestica preko reakcije Ti atoma na površini čestica sa hidroksilnim grupama modifikatora. Modifikovane TiO₂ nanočestice su zatim iskorišćene kao punioci za pripremu nanokompozita na bazi epoksidne smole. Termička i mehanička svojstva pripremljenih nanokompozita su ispitana primenom dinamičko mehaničke analize, diferencijalne skenirajuće kalorimetrije, termogravimetrijske analize i ispitivanjem njihove tvrdoće. Dobijeni rezultati su pokazali da TiO₂ nanočestice površinski modifikovane iminom ne utiču značajno na temperaturu ostakljivanja epoksidne smole, da usporavaju termooksidativnu degradaciju u prvom stupnju i da povećavaju tvrdoću umrežene epoksidne smole.

Ključne reči: epoksi/TiO₂ nanokompoziti; površinska modifikacija; imin; termička svojstva; mehanička svojstva