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Epoxy/TiO_2 composite materials and their mechanical properties

The physicomechanical properties and thermal stability of epoxy nanocomposites with TiO_2 (anatase — 75 %, rutile — 25 %) nanoparticles were studied. The TiO_2/epoxy polymer (TiO_2/EP) nanocomposite films were obtained by curing a pre-sonicated mixture of diane-epoxy resin ED-20, 4,4'-diaminodiphenylmethane and TiO_2 nanoparticles using stepwise technique: 90 ºC for 3 hours, then 160 ºC for 3 hours. Tensile tests were carried out according to American Society for Testing and Materials ASTM D882–10. The average size of TiO_2 nanoparticles and microstructure of the obtained nanocomposites were studied by scanning electron microscopy. It was found that addition of the TiO_2 nanoparticles at a concentration above 3 wt.% leads to a decrease in tensile strength at break, apparently due to secondary aggregation processes of nanoparticles. During curing, the average diameter of TiO_2 nanoparticles increases from 40 nm to 60 nm. An increase in the elastic modulus, a slight increase in the glass transition temperature, and a decrease in the elongation at break of epoxy nanocomposites at a concentration of TiO_2 nanoparticles > 1 wt.% indicate an increase in the rigidity of the epoxy matrix. The nanocomposites obtained were shown to be stable at concentrations of TiO_2 nanoparticles up to 5 wt.% and up to 300 ºC in vacuum.

Keywords: epoxy resin, curing, titanium oxide (IV), nanoparticles, tensile strength at break, elastic modulus, elongation at break, thermal stability.

Introduction

The increasing requirements for modern materials lead to intensive search for new composite materials with additional properties (mechanical, magnetic, tribological, radiation protection, etc.). The introduction of inorganic nanoparticles into organic polymers is of considerable interest, because it makes possible to create the hybrid nanocomposite materials with improved properties such as heat resistance, fire resistance, reduced gas permeability, and resistance to chemicals. Titanium oxide (IV) (TiO_2) nanoparticles are often used as inorganic fillers of polymeric materials. Titanium oxide (IV) is one of the most widely used metal oxides for photocatalytic decomposition of organic pollutants in an aqueous or gaseous medium. The photoactivity of TiO_2 is based on the process of a reversible single-electron transition $Ti^{4+} + e^{-} \rightleftarrows Ti^{3+}$. TiO_2 nanoparticles have a stronger photocatalytic effect than TiO_2 microparticles [1], forming reactive oxygen particles, hydroxyl radicals, H_2O_2, etc. under the influence of UV radiation. Due to exceptional characteristics of TiO_2, i.e. chemical and thermal stability, recycling potential, non-toxicity, and low cost, its applications range is quite wide: self-cleaning materials based on titanium oxide (IV), photocatalysts for the decomposition of organic compounds [2–6], anode materials [7,8], anti-bacterial coatings and packaging [9–12], etc. It is important to note that the induction of bactericidal activity due to photocatalysis is achieved by exposure to soft

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ultraviolet (in the range of 360 nm), in contrast to the hard ultraviolet used in medicine, and is more effective than surface sterilization by ultraviolet [13].

Today one of the most pressing problems is the disposal of accumulated polymer waste, for example, based on thermoplastic materials widely used for the manufacture of packaging films, various containers and utensils for food and household purposes. Approaches based on the incineration of such waste have serious environmental consequences. One of the promising solutions to this problem is the use of polymeric materials, which contain titanium oxide nanoparticles and capable to active photodegradation under visible light. TiO_2-containing nanocomposites based on polystyrene [14], polyvinyl chloride [15], polyethylene [16, 17], polybenzyl methacrylate [18] showed significantly increased degradation rates under UV and sunlight irradiation, as compared to the pure polymers.

Containing TiO_2 nanoparticles thermoset nanocomposites have not been studied so extensively, but existing data show that TiO_2 nanoparticles are more effective than microparticles, for example in regard to mechanical properties. The effect of the size of filler particles on the mechanical properties of epoxy composite materials was studied in [19] using the example of TiO_2. Nano- (nanoparticles with a size of ~50 nm) and microcomposites (particles ~50 μm) were compared.

An increase in mechanical properties was observed at the content of nanoparticles up to 4 vol.%. The subsequent recession in properties is associated with enlargement of particles due to their agglomeration. In the case of microparticles the modulus grows while the strength decreases with filler concentration increasing. As it was shown by us earlier [20, 21], elastic and strength properties of epoxy nanocomposites are affected by both the size of nanoparticles as well as the structure of epoxy matrix and the crosslink density as shown by us earlier.

The purpose of this work was to obtain composites based on TiO_2 nanoparticles and an epoxy polymer (EP) prepared by polycondensation, and to study their mechanical properties.

Experimental

Materials

The schematic structure of the diane-epoxy resin ED-20 used in this work is shown in Figure 1a (epoxide group content is 22.6 %).

4,4'-Diaminodiphenylmethane (DDM) was purchased from Aldrich (Fig. 1, *b*). The scheme of polycondensation between epoxy ED-20 and DDM is shown in Figure 1, *c*.

Nanoparticles of TiO_2 have been prepared in the Institute of Problems of Chemical Physics of Russian Academy of Sciences using microwave irradiation [22], anatase 75 %, rutile 25 %, SSA = 33.0 m^2/g, $d_{av.}$ = 46 nm.

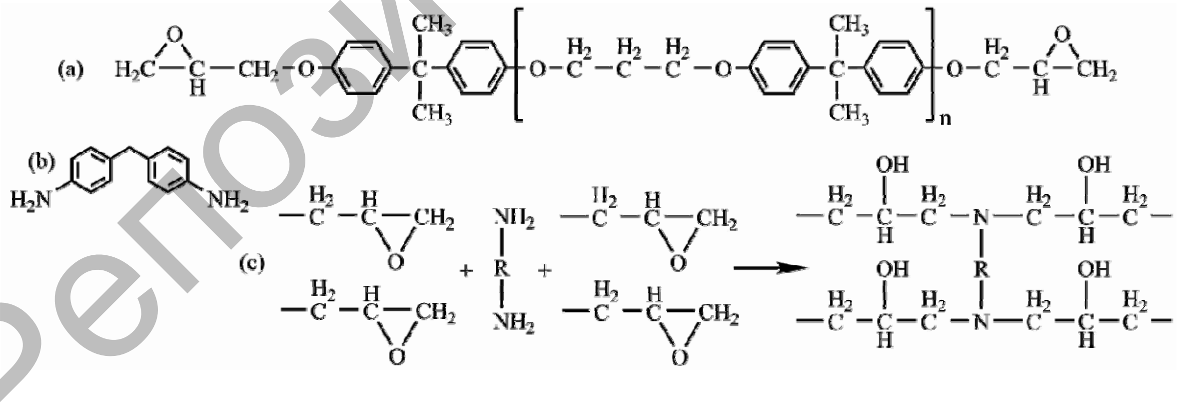


Figure 1. Structure of epoxy resin ED-20 (*a*); structure of DDM (*b*); scheme of polycondensation (*c*)

TiO_2/EP nanocomposite films of 80–100 µm thick were synthesized ex situ, i.e. using earlier prepared nanoparticles. The mixture of ED-20, DDM at equimolar ratio, and TiO_2 was heated slightly to dissolve DDM. Then it was degassed under low vacuum, and subjected to ultrasonic treatment using Sonorex Digital 10p instrument at 35 kHz for 40 min to disperse TiO_2 properly. The suspension obtained was poured between the two glass plates, which were put into a specially designed metal form and placed in an oven for further curing. The glass plates were pretreated with a solution of dimethyldichlorosilane in toluene to prevent adhesion. Mixtures were cured at stepwise increase of temperature, the conditions were determined based on calorimetric data in order to achieve a full cure (90 ºC for 3 hours, 160 ºC for 3 hours). The opaque, gray-blue

TiO_2/EP films were obtained as a result of curing. The film thickness was measured using a micrometer with a 10 microns accuracy.

The glass transition temperature of TiO_2/EP films was determined by differential scanning calorimetry (DSC) on a Mettler Toledo Star System instrument at a 5 deg/min temperature scan. Mechanical tensile tests were carried out according to ASTM D882–10 on a Zwick / Roell Z 010 universal machine at a 1 mm/min loading speed. Thermogravimetric analysis of the samples was carried out using ATV-14 electronic automatic vacuum thermobalance at a 2.4 deg/min constant heating rate in vacuum (residual pressure 1.2 Pa). Size of nanoparticles was determined using FESEM Zeiss Supra 25 on carbon-coated films.

Results and Discussion

Composition and microstructure of nanocomposites

TiO_2/EP nanocomposites were prepared by ex situ ultrasonic dispersion of TiO_2 nanoparticles in epoxy resin followed by curing in the presence of DDM. According to scanning electron microscopy (SEM) data, TiO_2 nanoparticles are fairly uniformly distributed in the volume of the polymer matrix, nevertheless, nanoparticles aggregation is still observed (Fig. 2). Particle size distribution shows that during curing the average size of nanoparticles increases (from 46 nm to 78 nm at 0.5 wt.% TiO_2).

Physicomechanical properties

As can be seen from the data in Figure 3, T_g weakly depends on the TiO_2 concentration, however, it tends to slightly decrease (173 ºC — 167 ºC) at <1 wt.% concentrations and increase (167 ºC — 173 ºC) at up to 5 wt.% concentrations. The concentration dependence of the elasticity modulus shows similar behavior with 27 % increase in modulus at 3 wt.% concentration

Tensile strength at break decreases sharply at TiO_2 more than 3 wt.% concentrations, which is probably due to secondary agglomeration of TiO_2 (Fig. 4). Therefore, the working concentration should not exceed 3 wt.% TiO_2. The average diameter of TiO_2 increases (from 40 to 60 nm at 0.5 wt.% TiO_2 concentration) during curing. The change in strain at break varies by TiO_2 concentration: less than 1 wt.% concentrations cause its increase, while more than 1 wt.% concentrations cause its decrease. A significant decrease in strain at break by almost 80 % indicates a loss of plasticity and an increase in brittleness. This is consistent with an increase in elastic modulus and glass transition temperature at above 1 wt.% TiO_2 concentrations.

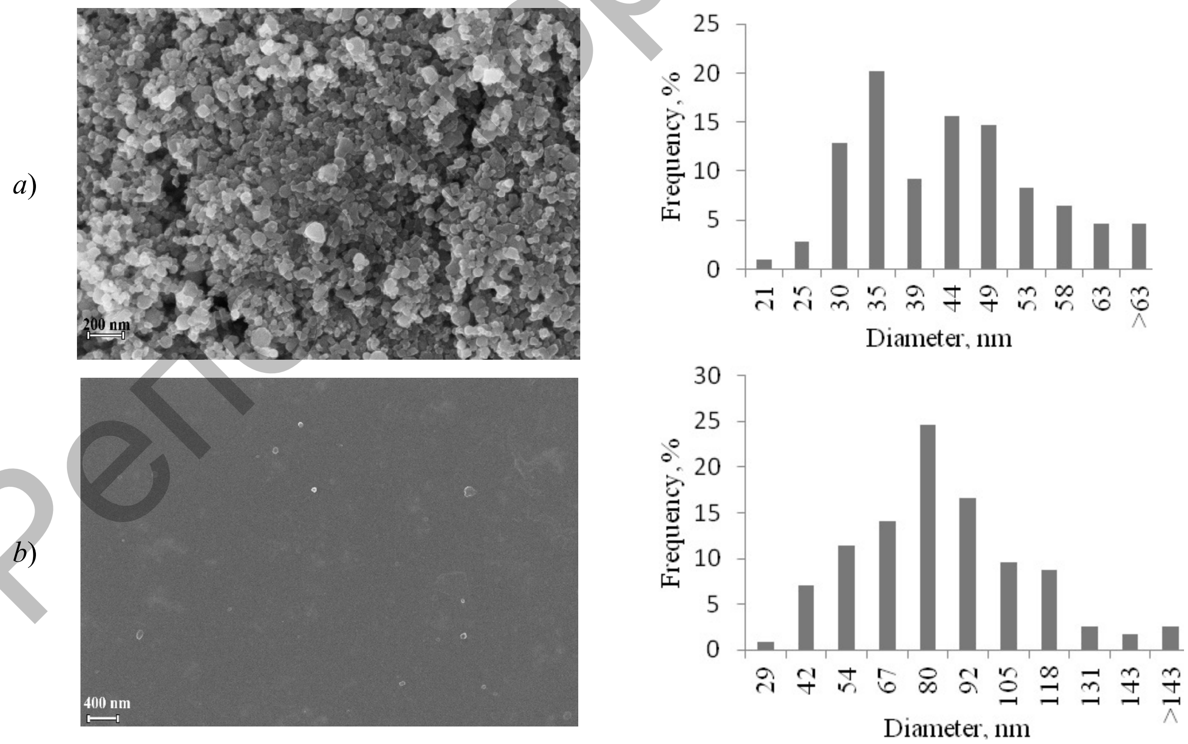


Figure 2. Scanning electron microscope (SEM) image and particle size distribution for TiO_2 nanoparticles (*a*) and TiO_2/EP nanocomposite with 0.5 wt.% of TiO_2 (*b*)

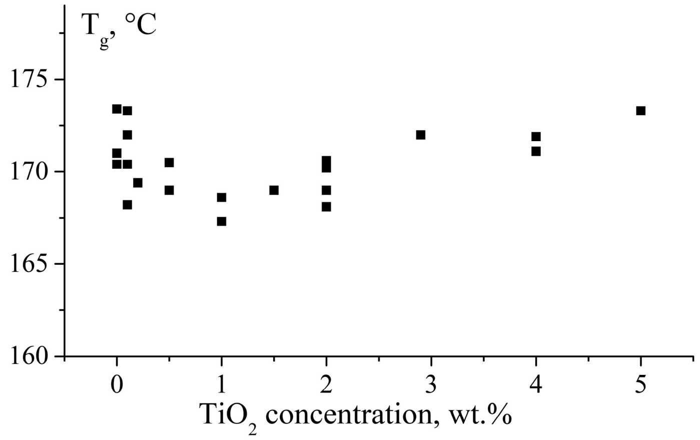
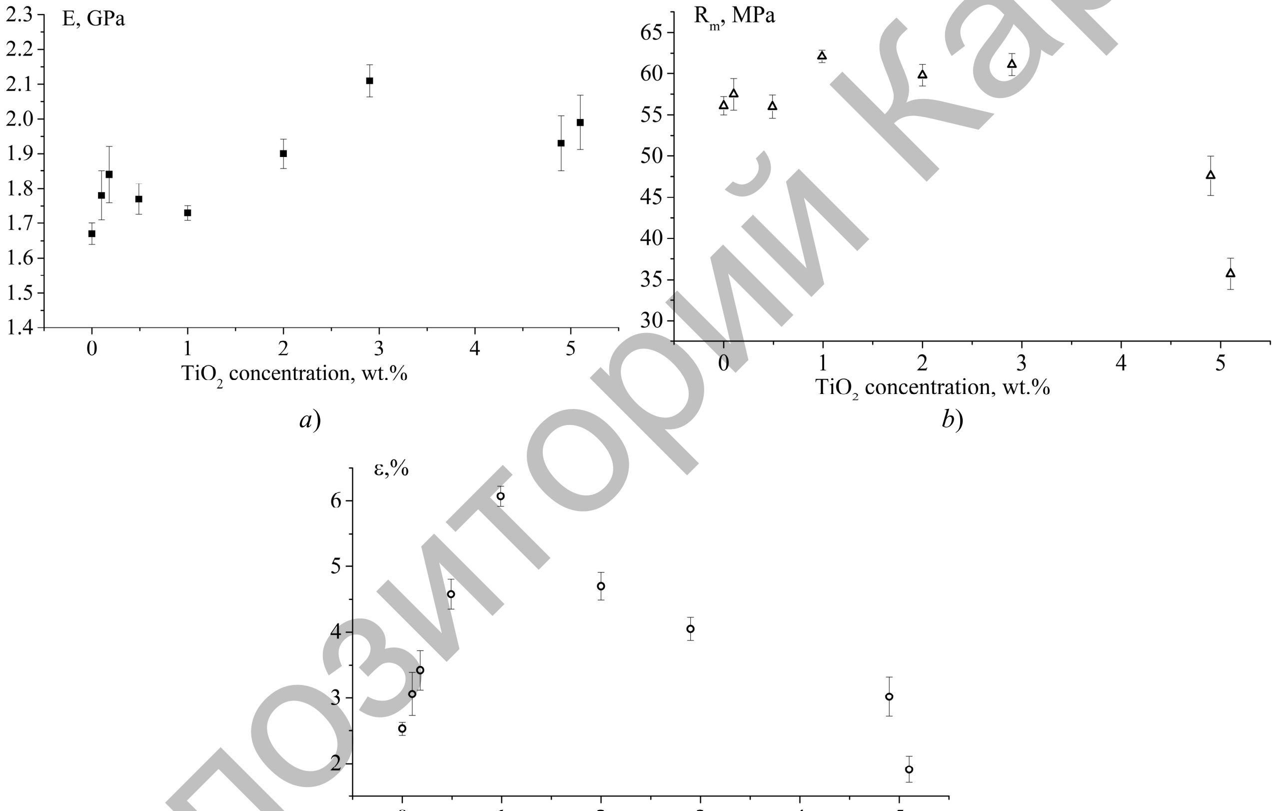


Figure 3. Tg dependence of TiO_2/EP nanocomposites on the concentration of TiO_2 nanoparticles



a)

b)

c)

a — elastic modulus, GPa; *b* — tensile strength at break, MPa; *c* — strain at break, %

Figure 4. The dependence of the mechanical properties of TiO_2/EP nanocomposites on the concentration of TiO_2

Thermal stability of nanocomposites

Stability of nanocomposites is essential for its implementation. Therefore, the thermal stability of TiO_2/EP films with different concentrations of TiO_2 was studied. As can be seen from Figure 5, TiO_2/EP are stable at up to 5 wt.% TiO_2 concentrations and up to 300 °C temperatures in vacuum.

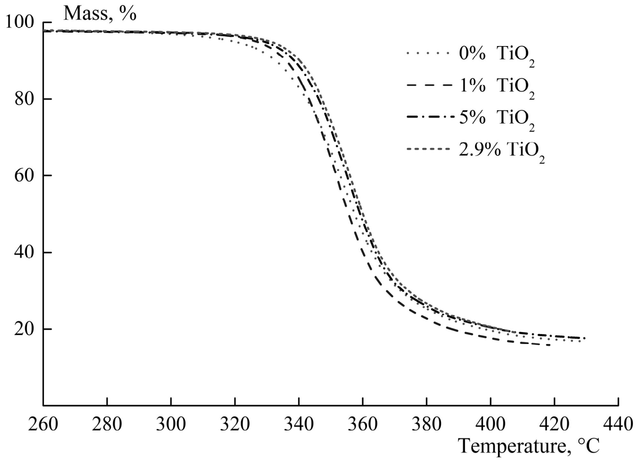


Figure 5. Thermograms of TiO_2/EP nanocomposites with 1–5 wt.% filler concentration (2.4 °C/min heating rate; 1.3 Pa residual pressure)

The results obtained are in good agreement with the literature. It was found that TiO_2/polypropylene nanocomposites have the similar thermal stability in the nitrogen atmosphere [23]. The initial and maximum decomposition temperatures increase from 360 ºC and 455 ºC for the EP to 405 ºC and 479 ºC for the polymer nanocomposites with 2 wt % TiO_2 content.

Conclusions

The TiO_2/EP nanocomposites with 0.5–5 wt.% filler content were obtained by ex situ introduction of TiO_2 nanoparticles into the epoxy resin ED-20 at the stage of curing in the presence of 4,4′-diaminodiphenylmethane. It was found that the addition of TiO_2 nanoparticles at a concentration above 3 wt. % leads to a decrease in tensile strength at break, apparently due to secondary aggregation processes. The average diameter of TiO_2 nanoparticles increases from 46 nm to 80 nm during curing. An increase in the elastic modulus, a slight increase in the glass transition temperature and a drop in the elongation at break of the epoxy nanocomposite at concentrations of TiO_2 nanoparticles above 1 wt. %, indicate an increase in the rigidity of the nanocomposite matrix. The stability of TiO_2/EP in vacuum is shown at temperatures up to 300 ºC and filler concentrations up to 5 wt.%.

This work was performed in accordance with the state task, state registration No. AAAA-A19-119032690060-9 using the equipment of the Multi-User Analytical Center of IPCP RAS.

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TiO_2 эпоксидті нанокомпозиттері және олардың механикалық қасиеттері

TiO_2 (анатаз — 75 %, рутил — 25 %) нанобөлшектері бар поликонденсациялық эпоксидті нанокомпозиттердің физика-механикалық қасиеттері және термотұрақтылығы зерттелген. Эпоксидті полимер (TiO_2/ЭП) негізіндегі қалыңдығы 80–100 мкм нанокомпозитті қабықшалар алдын-ала ультрадыбыспен өңделген эпоксидианды шайыр, 4,4'-диаминдифенилметан және TiO_2 нанобөлшектерінің қоспасын сатылы температуралық режим бойынша (90 ºC — 3 сағ) + (160 ºC — 3 сағ) қатайту арқылы алынды. Созылуға механикалық сынақтар ASTM D882–10 стандарты бойынша жүргізілді. TiO_2 нанобөлшектерінің өлшемдері мен алынған нанокомпозиттердің микроқұрылымдары сканерлеуші электрондық микроскопия әдісімен зерттелді. TiO_2 нанобөлшектерін 3 масс. % жоғары қосу нанобөлшектер агрегациясының екіншілік процестері салдарынан беріктіктің төмендеуіне әкеледі. Қатаю процесінде TiO_2 нанобөлшектерінің орташа диаметрі 40 нм-ден 60 нм-ге дейін артады. TiO_2 нанобөлшектерінің концентрациясы >1 масс. % кезінде серпімділік модулінің ұлғаюы, шынылану температурасының жоғарылау тенденциясы және эпоксидті нанокомпозиттердің деформациясының төмендеуі эпоксидті матрицаның қаттылығының артқанын көрсетеді. TiO_2 нанобөлшектерінің концентрациясы 5 масс. % дейін болғанда және вакуумда 300 ºC-қа дейінгі температураларда зерттелген нанокомпозиттердің тұрақтылығы көрсетілген.

Кілт сөздер: эпоксидті шайыр, қатаю, титан диоксиді, нанобөлшектер, механикалық қасиеттер, термиялық тұрақтылық.

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TiO_2 эпоксидные нанокомпозиты и их механические свойства

Исследованы физико-механические свойства и термостабильность поликонденсационных эпоксидных нанокомпозитов с наночастицами TiO_2 (анатаз — 75 %, рутил — 25 %). Нанокомпозитные плёнки на основе эпоксидного полимера (TiO_2/ЭП) толщиной 80–100 мкм получали отверждением предварительно обработанной ультразвуком смеси эпоксидиановой смолы ЭД-20, 4,4'-диаминодифенилметана и наночастиц TiO_2 по ступенчатому температурному режиму (90 ºС — 3 ч) + (160 ºС — 3 ч). Механические испытания на растяжение проводили по стандарту ASTM D882–10. Размеры наночастиц TiO_2 и микроструктуру полученных нанокомпозитов изучали методом сканирующей электронной микроскопии. Найдено, что добавление наночастиц TiO_2 выше концентрации 3 масс.% приводит к падению прочности, по-видимому, вследствие вторичных процессов агрегации наночастиц. В процессе отверждения средний диаметр наночастиц TiO_2 возрастает от 40 до 60 нм. Увеличение модуля упругости, тенденция к повышению температуры стеклования и падение деформации эпоксидных нанокомпозитов при концентрациях наночастиц TiO_2 >1 масс.% свидетельствуют о повышении жёсткости эпоксидной матрицы. Показана стабильность изученных нанокомпозитов при концентрациях наночастиц TiO_2 до 5 масс.% и температурах до 300 ºС в вакууме.

Ключевые слова: эпоксидная смола, отверждение, диоксид титана, наночастицы, механические свойства, термическая стабильность.

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