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Cellulose acetate butyrate nanocomposites synthesized *via* sol-gel method

Summary — Novel hybrid nanocomposites were synthesized from modified cellulose acetate butyrate (MCAB) *via* sol-gel reaction at ambient temperature. The inorganic phase was introduced *in situ* by hydrolysis-condensation of tetraethoxysilane (TEOS) in different concentrations, using an acid catalyst, in the presence of organic polymer dissolved in acetone. Infrared spectroscopy (IR) was used to monitor modification of CAB and nanocomposites characterization. The silica network of obtained nanocomposites was characterized by solid state ^{29}Si NMR. Morphology of the samples and degree of dispersion of inorganic phase in the polymer matrix were investigated using atomic force microscopy (AFM). The organic-inorganic nanocomposites exhibit better mechanical properties than unmodified cellulose acetate butyrate.
Keywords: nanocomposites, cellulose acetate butyrate, sol-gel.

NANOKOMPOZYTY NA BAZIE OCTANOMAŚLANU CELULOZY OTRZYMANE METODĄ ZOL-ŻEL

Streszczenie — Metodą zol-żel otrzymano nowe nanokompozyty na bazie modyfikowanego octanomaślanu celulozy (MCAB). Fazę nieorganiczną wprowadzano do matrycy polimeru na drodze reakcji hydrolizy i kondensacji, jako prekursor stosując tetraetoksysilan (TEOS), w środowisku kwaśnym. Przebieg reakcji modyfikacji CAB kontrolowano wykorzystując spektroskopię w podczerwieni (IR). Do charakterystyki otrzymanych materiałów stosowano analizę IR oraz magnetyczny rezonans jądrowy ciał stałych ^{29}Si NMR. Morfologię próbek określono przy użyciu mikroskopu sił atomowych (AFM). Uzyskane nanokompozyty wykazują lepsze parametry mechaniczne niż niemodyfikowany polimer.
Słowa kluczowe: nanokompozyty, octanomaślan celulozy, zol-żel.

In recent years polymer nanocomposites have been attracting extensive research interest due to their unique chemical and physical properties. These materials have become a new class of composites which are reinforced with different nanofillers: layered silicates, carbon nanotubes, nanoparticles or inorganic phase formed by sol-gel technique [1, 2]. Depending on the nanocomposite nature and structure the following properties like hardness, stiffness, tensile, fire resistance, thermal stability, optical, and gas barrier properties of a variety of polymers can be significant improved. Wide ranges of application of these materials have been reported including such fields as packaging and automotive industry, construction materials, electrochemistry, optics, nanophotonics or advanced bionanomaterials for medical application [1].

Sol-gel technique involve hydrolysis of the precursor (metal alkoxide) followed by condensation reactions. The most commonly used silica precursor is tetraethoxysilane (TEOS) which yields a silica network. The structure of obtained metal oxide network depends on the reaction conditions: the H_2O/alkoxy groups ratio, the kind of the solvent, temperature, pH value. The advantages of sol-gel route are the ability to obtain organic-inorganic nanostructured materials at ambient conditions and the possibility to control morphology of the growing inorganic phase by the subtle control of various reaction conditions. Such hybrids offer the opportunity to combine desirable properties of organic polymers (toughness, elasticity) with those of inorganic solids (hardness, chemical resistance) [2, 3]. Two methods have generally been employed for the synthesis of polymer/silica nanocomposites: *in situ* polymerization of one or two components and direct blending of polymeric chains and nanoparticles (both separately synthesized in a preliminary stage). Silica particles display a range of specific properties, which contribute to their wide use and potential novel applications in the following areas: nanocomposites, biomaterials, sensor materials, and coatings. In order to improve compatibility of nanosilica with organic matrix modification of the particles surface can be applied. Organo-modifica-

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tion may be carried out either by grafting or by co-condensation [4]. Another approach of nanosilica modification is incorporation of silver ions allowing to obtain nanofiller showing antimicrobial activity [5, 6].

Considering the nature of the interface between the organic and inorganic phases, hybrid materials can be categorized into two different classes. The first class corresponds to not covalently-bound networks of inorganic and organic phases. These hybrids show weak interactions between the polymer matrix and inorganic phase (van der Waals, hydrogen bonding or weak electrostatic interactions) and can be prepared by physical mixing of an organic polymer with a metal alkoxide. In the second class, organic and inorganic phases are linked through strong chemical bonds (covalent or ionic). The use of a suitable coupling agent reduces the phase separation at the interface between organic and inorganic phases and permits an interconnected network to be obtained [7].

There are numerous reports in the literature associated with polymer nanocomposites based on cellulose derivatives [8—12]. Yoshioka *et al.* [8] developed biodegradable cellulose acetate/layered silicate grafted poly(ε-caprolactone) [(CA/layered silicate)-*g*-PCL] nanocomposites prepared by *in situ* polymerization of ε-caprolactone in the presence of cellulose acetate (CA) and organically modified layered silicate (OMLS). Grunert and Winter [9] obtained nanocomposites based on cellulose acetate butyrate (CAB) reinforced by dispersing either native or silylated crystals into polymer matrix. Park *et al.* [10] reported fabrication of injection molded nanocomposites from cellulose acetate (CA), triethyl citrate (TEC) plasticizer, and organically modified clay with and without maleic anhydride grafted cellulose acetate butyrate (CAB-*g*-MA) as a compatibilizer. Zoppi and Goncalves [11] prepared hybrids based on CA and SiO_2 generated by hydrolysis of tetraethoxysilane (TEOS), *via* sol-gel process. They obtained more rigid materials, which showed a decrease of water permeability with the incorporation of the inorganic phase and thermal stability similar to pure CA. In a further study Silva *et al.* [12], applied the sol-gel process for preparation of organic-inorganic nanocomposites from CA and a highly branched alkoxysilane (HB) precursor. Multifunctional alkoxysilane crosslinker (HB) was obtained *in situ via* a Michael-type reaction from the PETA (pentaerythrithol triacrylate) and APTS (γ-aminopropyltrietoxysilane) mixture. CA/HB films containing polysiloxane nanodomains dispersed in the polymer matrix showed increased rigidity caused by increased inorganic phase content, thermal stability similar to that shown by pure CA and improved dimensional stability.

This paper describes synthesis and properties of novel organic-inorganic hybrid nanocomposites based on cellulose acetate butyrate functionalized with silane-coupling agent. CAB has good mechanical properties and can be processed by injection molding or extrusion what makes this polymer a promising material for packaging applications. Moreover, considering the growing problem of plastic waste disposal, renewability and susceptibility to biodegradation of CAB is an important advantage [13]. Several approaches have been reported in the literature to perform functionalization of polymers [14—18]. The polystyrene-silica hybrid materials from styrene and tetraethoxysilane in the presence of 3-(trimethoxysilyl)-propyl-methacrylate (MPS) and allytrimethoxysilane (ALS) as coupling agents were prepared by Jang and Park [14]. Nadeem *et al.* [15] reported preparation and properties of the two types of co-poly(vinyl chloride-vinyl acetate-vinyl alcohol)-silica hybrids *via* sol-gel process. In the first type, hydroxyl groups of copolymer chains were directly connected with silica network derived from TEOS, while in the second type the chemical bonding between the two phases was established through ICPTES (3-isocyanatopropyltriethoxysilane). As reported by Nadeem *et al.* [15] and other research groups [16—18], among silane-coupling agents, ICPTES is known as an efficient molecule allowing to introduce alkoxysilyl functionalities to the polymer chain. Flesch *et al.* [16] described the coating of maghemite nanoparticles with poly(ε-caprolactone) functionalized in the reaction with ICPTES. Jo and Park [17] obtained silanated poly(ethylene glycol) (PEG) by direct coupling of 3-isocyanatopropyltriethoxysilane to monomethoxy-PEG (m-PEG). Messori *et al.* [18] reported preparation and characterization of hybrid materials based on α- and α,ω-triethoxysilane terminated PCL, and their application as protective coatings on poly(methyl methacrylate) (PMMA) substrates. To the best to our knowledge this is the first report on functionalized CAB-silica nanocomposites obtained *via* sol-gel process. The silica nanophase was introduced into CAB matrix using as a coupling agent ICPTES with three pendant epoxy groups providing chemical bonding to the silica network. Thus, we expected for MCAB-silica nanocomposites more pronounced changes of properties, different from the applied polymer matrix.

Previously, we reported the preparation and characterization of organic-inorganic hybrids based on unmodified CAB *via* sol-gel process [19, 20]. SEM images showed that obtained materials comprised silica particles uniformly distributed within polymer matrix with dimensions: width *ca.* 460—800 nm, length *ca.* 5—8.5 μm. Inorganic particles were situated parallel to the surface and in this type of hybrids (first class) debonded from the surrounding CAB matrix. Obtained samples exhibited good transparency in comparison with neat polymer [19] and showed increased susceptibility to biodegradation in sea water environment than pure CAB [20]. This paper deals with the synthesis of novel MCAB/silica nanocomposites with covalently bounded inorganic phase (second class hybrids) obtained by reacting functionalized CAB with TEOS that could be useful as a new, susceptible to degradation, packaging material. In this work spectro-

scopic, morphological and mechanical properties of MCAB nanocomposites are discussed.

EXPERIMENTAL

Materials

Cellulose acetate butyrate (CAB, $\overline{M}_n \approx 70\ 000$), 3-isocyanatopropyltriethoxysilane (ICPTES, 95 %), dibutyltin dilaurate (95 %) and tetraethoxysilane (TEOS, 98 %) were purchased from Sigma Aldrich. Tributyl citrate (TBC, 97 %) was purchased from Fluka. Acetone, tetrahydrofuran (THF), diethyl ether, hydrochloric acid (HCl, 35—38 %) were purchased from POCH S.A. and used as received.

Samples preparation

Modification of cellulose acetate butyrate

CAB was chemically modified through the reaction of ICPTES with the free hydroxyl on the CAB backbone. The procedure was modeled on the ones reported by Jo, Park [17] and Messori *et al.* [18]. Functionalization of CAB was performed at a three-necked round-bottom flask equipped with a magnetic stir bar, thermometer and an argon inlet. In this flask 13.7 g of CAB was dissolved in 300 cm^3 of THF and stirred until homogenous solution was obtained. To this mixture 1.24 g of ICPTES in a 10:1 polymer/silane molar ratio and 0.085 g of dibutyltin dilaurate in a 35:1 polymer/catalyst molar ratio were added. For this study one substituent was grafted per ten CAB repeat units (assuming CAB monomeric molecular weight of 274). The solution was kept under argon atmosphere with stirring for several hours at 60 °C until the reaction was complete. When the reaction was complete modified polymer (MCAB) was purified by precipitation in diethyl ether (in which the catalyst and ICPTES are soluble) and afterwards dried for 24 hours and kept under argon for the preparation of cellulose acetate butyrate nanocomposites.

Preparation of organic-inorganic hybrid nanocomposites

A detailed procedure of organic-inorganic hybrids preparation we described in patent [21]. Sample compositions and characteristics are listed in Table 1. Due to the high brittleness of neat CAB, in order to avoid cracking of the samples, all MCAB nanocomposites were prepared with 30 % of plasticizer (tributyl citrate). A typical preparation of organic-inorganic hybrid was as follows: polymer was placed in a polyethylene beaker and dissolved in acetone. Plasticizer and TEOS was then added and mixed vigorously. To this solution catalytic amount of HCl (0.1 M) was added to initiate the sol-gel process and mixed until it appeared clear and homogenous. The solution was cast in an evaporating PTFE dish and after solvent removal dried in a vacuum drier at 40 °C for 12 hours to ensure complete solvent evaporation. A reference sample of neat CAB and 30 % of TBC was also prepared for comparison.

Methods of testing

— IR analysis was performed with a double-beam spectrophotometer Specord M80 (Carl Zeiss Jena) over a range of 400—4000 cm^{-1}.

— The ^{29}Si solid-state NMR was performed using a Bruker DSX 300 Avance spectrometer. The spectra were obtained using cross polarization and magic-angle spinning (CP/MAS). The spinning rate was 8 kHz. Standard Bruker 4 mm CPMAS probe was used.

— Thermogravimetric analysis was carried using a Shimadzu TGA-50 thermal analyzer. The sample was heated from room temperature to 900 °C at 10 °C/min under the air atmosphere.

— AFM imaging was conducted using easyScan2 atomic force microscope (AFM) from NanoSurf. Images were recorded in tapping mode using PPP-NCLR silicon probes (NanoAndMore GmbH). Height, amplitude and phase images were collected at various scan sizes, maximum X and Y axis range was 10 micrometers.

— Mechanical properties were investigated using a universal tensile machine (Instron 5565) with sample films 150 mm in length and 10 mm in width and at a crosshead speed of 100 mm/min at room temperature (according to International Standards PN-EN ISO 527-1: 1998, PN-EN ISO-3:1998). At least five tests were performed for each type of the sample, to ensure the reliability of the test results, and the average was used. The films thickness were measured using a Sylvac s229 digital indicator equipped with a 10 mm diameter flat point, with a resolution of 0.001 mm.

T a b l e 1. Sample compositions and characteristics

Sample	Polymer/TEOS wt. ratio	TGA SiO_2, wt. %	Nature of the sample	Tensile strength MPa	Elongation at break, %
CAB	—	—	transparent	21.8 ± 2.3	30.2 ± 6.9
MCAB	—	0.5*)	translucent	19.1 ± 0.1	47.0 ± 0.4
MCAB 6.25	93.75/6.25	2.5	translucent	22.5 ± 0.9	37.4 ± 0.6
MCAB 12.5	87.5/12.5	4.7	translucent	24.0 ± 1.3	37.8 ± 0.7

*) SiO_2 from ICPTES.

RESULTS AND DISCUSSION

The CAB modification reaction progress was monitored using IR spectroscopy by observing decreasing of the absorption band related to isocyanate groups at 2272 cm^{-1} [18]. On the IR spectrum of modified CAB new characteristic peaks at 1650 and 1550 cm^{-1} representing urethane group and bending vibration of -NH- respectively, appeared (Fig. 1). Under experimental conditions used in this study the modification of CAB was complete within 6 hours.

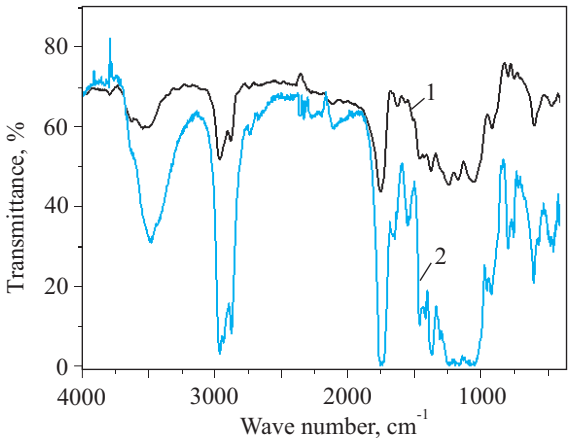


Fig. 1. IR spectra of pure CAB — 1 and modified CAB — 2

Organic-inorganic nanocomposites obtained as thin, flexible films with thickness in the range of 170—190 μm exhibited translucent appearance. Photographs of unmodified CAB and nanocomposites are presented on Fig. 2.

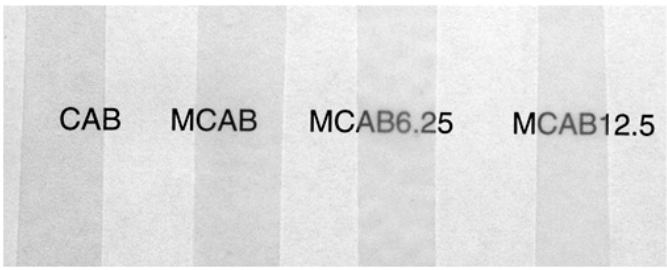


Fig. 2. Photographs of the samples: CAB, MCAB, MCAB6.25, MCAB12.5

The IR spectra of organic-inorganic hybrids showed peaks around 1000—1100 cm^{-1}, 800 cm^{-1} and 460 cm^{-1} indicating that silica is formed *via* the sol-gel reaction. The peak at 1000—1100 cm^{-1} can be attributed to asymmetric stretching vibration of the Si-O-Si bonds. The band at 800 cm^{-1} is due to symmetric stretching vibration of the Si-O-Si atoms. The presence of the band at 460 cm^{-1} reveals the existence of Si-O-Si bending mode. The band at ~930 cm^{-1} can be assigned to the Si-OH (silanol) stretching vibrations indicating that an incomplete condensation occurred during the sol-gel process.

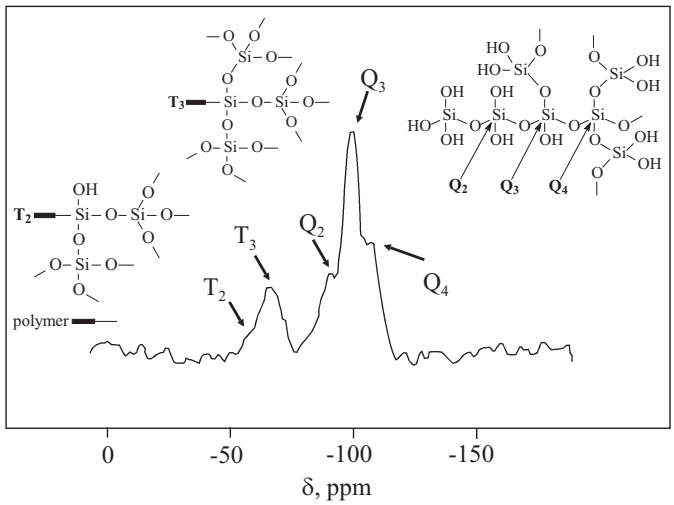
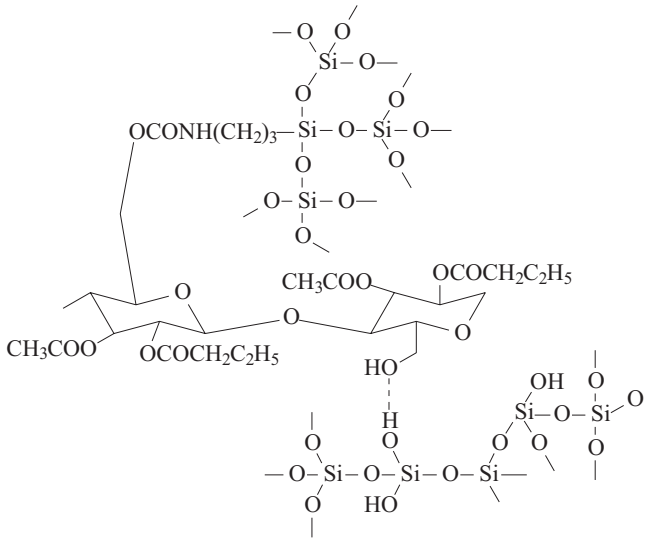


Fig. 3. MAS ^{29}Si NMR spectrum of MCAB12.5

The ^{29}Si solid state NMR spectrum of the nanocomposite obtained using modified polymer and 12.5 wt. % of TEOS (MCAB12.5) is shown in Figure 3.

The ICPTES grafted polymer (modified CAB) evolves in the presence of water and TEOS into T_3 structure (trisubstituted siloxane bonds) but also a weak T_2 peak of disubstituted siloxane bonds is observed (Fig. 3). The chemical shifts are -67 and -59 ppm, respectively, and agree closely to the literature values [22]. In the spectrum there is no peak related to T_1 structure. The Q-type structures in the spectrum are related to the *in situ* formed silica network. The band at -108 ppm (Q_4 structure) is characteristic of the silica network formation and indicates fully condensed SiO_2. The peak observed at -101 ppm is assigned to a Q_3 structure with a silicon atom connected to the three silicon and one hydrogen atom or an alkyl group in the second coordination sphere. The high intensity of the Q_3 band suggesting the existence of -OH or -OR groups and Q_2 structures observed in the spectra (at -92 ppm) indicate that the condensation reaction was incomplete which is coherent with the IR study. In the spectrum there is no peak related to the Q_1 structure. According to the literature data [22] very high Q_4 and Q_3 structures content but low population of Q_2 states suggest a highly intraconnected, or crosslinked silicate nanophase. ^{29}Si NMR spectrum of modified CAB (MCAB) revealed peaks T_2 and T_3 observed at -58 and -66 ppm, respectively. Chemical structure of MCAB/silica nanocomposite is depicted in Scheme A.

Tapping-mode atomic force microscopy (TM-AFM) is a common used nanoscale imaging technique for topographical and compositional mapping due to high spatial and the minimal lateral interaction. In tapping mode, material composition mapping is performed by recording



Scheme A. Chemical structure of MCAB/silica nanocomposite

the shift between the cantilever excitation signal and photodetector signal. This shift is known as a „phase signal" and depends on the energy dissipation during the tip-sample interactions [23]. Very common use of phase imaging is to show material contrast in polymer blends and composites. Varied colors displayed on material contrast images allow to distinguish two mechanically different phases that show distinct local mechanical properties (adhesion, Young's modulus, hardness). Phase images of MCAB6.25 and MCAB12.5 nanocomposites (Figure 4b left and 4b right) revealed that samples consists of two regions with different chemical and thus mechanical properties. Inorganic phase-rich regions (siloxane network formed during sol-gel process) within soft CAB matrix generated a significant contrast which is visible on phase images as white areas dispersed in dark polymer matrix. In topography of the MCAB6.25 nanocomposite (Fig. 4a, left) dominate small regions (diameter in the range of 20—100 nm) with modified mechanical properties by inorganic phase, dispersed homogenously within polymer matrix. RMS roughness for this sample is about 1.5 nm. Fig. 4a (right) shows surface morphology of MCAB12.5 sample. Surface of this nanocomposite is much rougher (RMS about 21.2 nm). In topography dominate also regions with modified mechanical properties but with bigger size (diameter in the range of 30—300 nm) and with tendency to aggregation. The structure of MCAB12.5 sample is a little bit more inhomogenous. From the phase images analysis we can estimate that the surface of MCAB6.25 and MCAB12.5 samples contains about 53 % and 38 % of neat polymer regions, respectively. AFM images revealed that inorganic phase-rich region size formed in the sol-gel process depends on the amount of TEOS used in the reaction and increases with the higher tetraalkoxysilane content.

Thermograms of CAB, MCAB and MCAB-silica nanocomposites are shown in Figure 5. In the case of organic-inorganic hybrids the decomposition of the samples occured over a range of ~180 °C to 600 °C. Two main reaction stages took place during degradation of MCAB hybrids. The first stage for the range between 180 °C and 350 °C is divided into two steps which is connected with decomposition of the plasticizer. An initial mass loss before 180 °C is related with the volatilization of residual water. In the second stage the onset of decomposition temperature was around 350 °C (representing the main thermal degradation of cellulose chains) and became

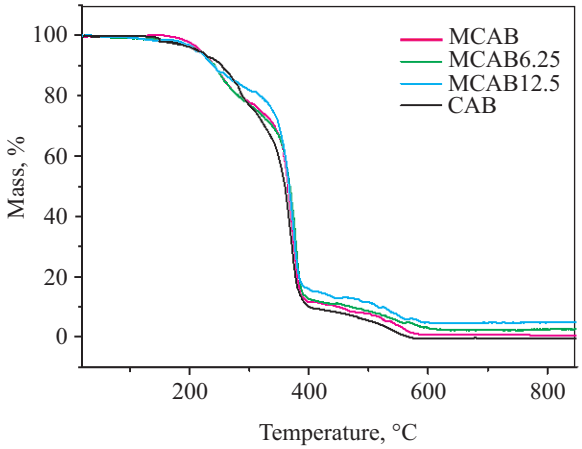


Fig. 5. Thermogravimetric curves of CAB, MCAB, MCAB6.26 and MCAB12.5

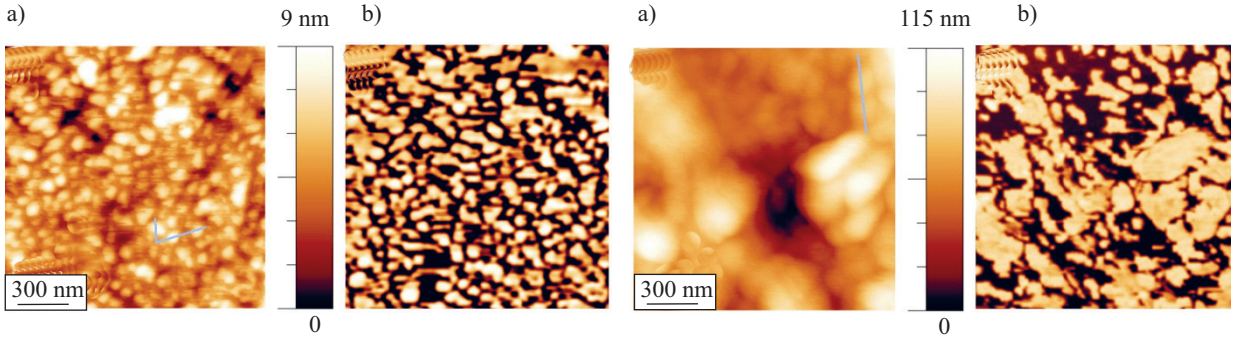


Fig. 4. AFM images of MCAB6.25 (left) and MCAB12.5 (right) samples, scan size 1500 × 1500 (nm²): a) topography, b) phase (material contrast)

relatively stable at about 600 °C. All the MCAB samples showed residual mass after heating up to 900 °C, due to the presence of inorganic phase, therefore, the actual incorporation of the silica into the organic-inorganic hybrids can be determined by TGA (values are listed in Table 1). The weight loss for the MCAB12.5 is slower over the range 250 to 350 °C in comparison with MCAB and MCAB6.25. Similar TGA curve was obtained for unmodified CAB. However, at around 280 °C CAB showed faster decomposition rate than MCAB samples. CAB was entirely burned at 900 °C presenting no residue. TGA results suggest that the introduction of silica into the polymer matrix slightly influence the thermal stability of the nanocomposite, which may be attributed to the high thermal stability of silica and the nature of interaction between the inorganic and organic phase.

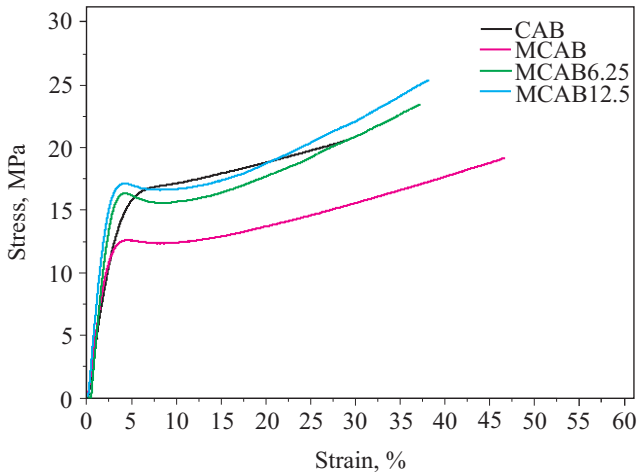


Fig. 6. Stress-strain curves of CAB, MCAB, MCAB6.25 and MCAB12.5

Mechanical properties of the investigated materials regarding tensile strength and elongation at break are presented in Table 1. Representative tensile stress-strain curves for the MCAB nanocomposites prepared with 30 % of TBC are showed in Fig. 6. Mechanical properties of neat CAB with 30 % of TBC were measured as reference data. MCAB and MCAB-silica nanocomposites stress-strain curves indicated hard, tough behavior of the samples, exhibiting good plasticizing efficiency. All the curves showed a plateau region representing cold drawing and strain hardening in the final section of the curve. A similar behavior is observed for CAB sample. For the MCAB-silica nanocomposites, however, curves show better defined yielding point and exhibit elastic deformation in smaller strain ranges depending on silica content. The results showed that tensile strength of MCAB-silica nanocomposites increased with the increase of silica content, taking the mechanical properties of modified CAB as a reference. The tensile strength of MCAB6.25 and MCAB12.5 nanocomposites increased by 22 % and 32 %, respectively. It is known that in polymeric composites the external stress is transferred from the continuous polymer matrix to the discontinuous reinforcing phase. Thus, the ultimate properties of composite materials are dependent on the extent of bonding between the two phases, the surface area of the dispersed phase and the geometry of the reinforcing phase. For MCAB nanocomposites, with covalently bounded inorganic phase, the increased tensile strength may be the result of a better interfacial adhesion and the formation of continuous morphologies, which improve the efficiency of stress transfer mechanisms between the two components. Also a proper dispersion of inorganic phase may be responsible for enhanced physical properties as compared to modified CAB. It is interesting that in comparison with neat CAB the highest value of elongation at break showed MCAB sample (an increase by 28 %), while for MCAB-silica nanocomposites plastic flow was hindered by inorganic phase.

CONCLUSIONS

Hybrid nanocomposites comprising modified CAB and silica were successfully prepared by the sol-gel method. IR studies indicated formation of Si-O-Si links within these materials. ^{29}Si solid state NMR confirmed that nanocomposites with covalently bounded inorganic phase were obtained. The varying amount of TEOS gave rise to different silica content of the hybrids. AFM studies showed that modification of CAB allowed to obtain hybrid materials with inorganic phase-rich regions with dimensions in the nanometer scale. AFM images demonstrated more uniform distribution of the inorganic phase within polymer matrix for the MCAB6.25 nanocomposite than for the MCAB12.5 hybrid. In terms of mechanical properties it was found that MCAB-silica nanocomposites exhibited improved tensile strength in comparison with modified CAB. The higher reinforcement effect is mainly due to a strong interaction between the polymer matrix and the inorganic component as well as the nanoscale dispersion of the silica in the MCAB matrix.

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