PATRYCJA WOJCIECHOWSKA[1)*], ZENON FOLTYNOWICZ[2)]

Synthesis of organic-inorganic hybrids based on cellulose acetate butyrate

RAPID COMMUNICATION

Summary — Novel organic-inorganic hybrids based on cellulose acetate butyrate (CAB) were synthesized applying sol-gel process. The inorganic phase was introduced into polymer matrix by hydrolysis and condensation using tetraethoxysilane (TEOS) as the precursor, under acidic conditions. The obtained organic-inorganic hybrids were characterized by different techniques such as IR spectroscopy, thermogravimetric analysis (TGA), solid state ^{29}Si NMR and scanning electron microscopy (SEM). Organic-inorganic hybrids obtained with 20 % of diethyl phthalate (DEP) as plasticizer exhibit good transparency in comparison with unmodified CAB.
Key words: cellulose acetate butyrate, sol-gel process, organic-inorganic hybrids, thermogravimetric analysis, IR spectroscopy, ^{29}Si NMR, scanning electron microscopy.

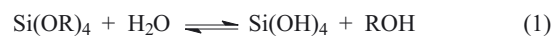SYNTEZA ORGANICZNO-NIEORGANICZNYCH MATERIAŁÓW HYBRYDOWYCH NA BAZIE OCTANOMAŚLANU CELULOZY
Streszczenie — Nowe organiczno-nieorganiczne materiały hybrydowe na bazie octanomaślanu celulozy (CAB) otrzymano techniką zol-żel. Fazę nieorganiczną wprowadzano do matrycy polimeru w wyniku reakcji hydrolizy w środowisku kwaśnym i kondensacji stosując jako prekursor tetraetoksysilan (TEOS). Otrzymane materiały charakteryzowano za pomocą spektroskopii w podczerwieni (IR), analizy termograwimetrycznej (TGA), magnetycznego rezonansu jądrowego ciał stałych ^{29}Si NMR oraz skaningowej mikroskopii elektronowej (SEM). Organiczno-nieorganiczne hybrydy otrzymane z udziałem 20 % ftalanu dietylu jako plastyfikatora cechują się dobrą przejrzystością w porównaniu z polimerem niemodyfikowanym.
Słowa kluczowe: octanomaślan celulozy, metoda zol-żel, organiczno-nieorganiczne materiały hybrydowe, analiza termograwimetryczna, spektroskopia IR, ^{29}Si NMR, skaningowa mikroskopia elektronowa.
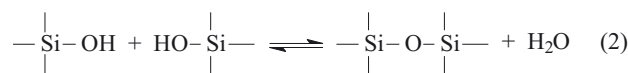
Organic-inorganic hybrids have been studied intensively in past decades due to their unique properties. The combinations of the two components on a molecular level (organic polymer and inorganic solid) open possibilities of tailoring of the materials with improved mechanical and chemical properties, required toughness as well as elasticity comparing to pure organic polymers. One of the most efficient methods of preparation of hybrid materials is sol-gel process. The advantages of the sol-gel process are mild conditions, *i.e.* low reaction temperature, and ease of control. Sol-gel technique comprises initial hydrolysis of metal alkoxides (silicon, titanium or zirconium) and subsequent condensation reactions, resulting in metal oxides. The most commonly used precursor is tetraethoxysilane (TEOS) which yields a silica network. Chemical reactions involved in the sol-gel process of alkoxysilanes are depicted in following equations [1, 2]:
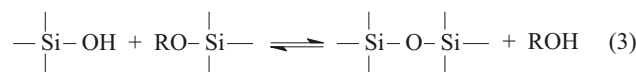
— hydrolysis

$$Si(OR)_4 + H_2O \rightleftharpoons Si(OH)_4 + ROH \qquad (1)$$

— water condensation

$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \rightleftharpoons -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O \qquad (2)$$

— alcohol condensation

$$-\overset{|}{\underset{|}{Si}}-OH + RO-\overset{|}{\underset{|}{Si}}- \rightleftharpoons -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + ROH \qquad (3)$$

The structure and properties of the resulting hybrid are strongly dependent on reaction conditions (pH value, water and alkoxy groups ratio, type of the catalyst, solvent and precursor used) [1, 2]. In the acid-catalyzed reaction (pH 2—5) a hydrolysis step is faster than the condensation one. This results in a more extended,

[1)] Poznan University of Economics, Department of Industrial Commodity Science, al. Niepodległości 10, 61-875 Poznań, Poland.
[2)] Poznan University of Economics, Department of Product Ecology, al. Niepodległości 10, 61-875 Poznań, Poland.
[*)] Corresponding author; e-mail: p.wojciechowska@ue.poznan.pl

polymer-like network. Under basic conditions, the condensation step is faster, resulting in a highly condensed species that may agglomerate. It has been shown that a base-catalyzed sol-gel process yielded often opaque hybrids, whereas transparent materials were usually formed under acidic conditions [3—5].

In the literature organic-inorganic hybrid materials were categorized into two different classes, depending on the nature of the interface between the organic and inorganic phases [6]. Class I corresponds to materials where there are physical interactions between the two phases (no covalent bonding). Non-covalent hybrids show weak interactions between polymer matrix and inorganic phase, due to the van der Waals, hydrogen bonding and electrostatic forces. In the latter type of hybrids—class II, organic and inorganic phases are linked by stable chemical bonds (covalent or ionic ones). Class I hybrids can be obtained by direct mixing of an organic polymer with metal alkoxide. Chemical bonding can be achieved by the incorporation of silane coupling groups into organic polymers [2, 6].

Hybrid materials, due to their unique properties, are promising systems with potential applications in coatings, membranes, biomaterials, sensors and catalysts [7—12]. In recent years the numbers of organic-inorganic polymer hybrids with a large variety of functionality have been synthesized by the sol-gel process [4, 9, 13—16].

In this paper the preparation procedure and characterization of novel organic-inorganic hybrids based on cellulose acetate butyrate obtained *via* sol-gel process is described.

EXPERIMENTAL

Materials

Cellulose acetate butyrate (CAB, $\overline{M}_n$ = 70 000, containing 12—15 wt. % of acetyl, 1,2—2,2 wt. % of hydroxyl, 35—39 wt. % of butyryl groups) and tetraethoxysilane (TEOS) (98 % purity) were supplied from Sigma Aldrich. Diethyl phthalate (DEP) used as a plasticizer, HCl (35—38 % aqueous solution) and acetone were purchased from POCh and used as received.

Samples preparation

Organic-inorganic hybrids were synthesized according to the procedure we described in detail in [17]. Due to the high brittleness of neat CAB, organic-inorganic hybrids were prepared with 20 parts of DEP per 100 parts of CAB. Samples compositions and transparency characteristics are presented in Table 1. In the typical preparation cellulose acetate butyrate was dissolved in acetone at room temperature, followed by DEP and TEOS addition and mixed vigorously using a magnetic stirrer. Afterwards, catalytic amount of HCl (0.1 M solu-

tion) was added to initiate the sol-gel process. The mixture was continuously stirred until it appeared clear and homogeneous. The solution was cast on a poly(tetrafluoroethylene) (PTFE) dish and left exposed to atmospheric conditions at room temperature (for approximately 8 hours) followed by drying in a vacuum drier at 40 °C for 12 hours to reach complete evaporation of acetone. Sample of neat CAB with 20 % of plasticizer was prepared as a reference material.

T a b l e 1. **Samples compositions and transparency characteristics**

Symbol of sample	CAB/TEOS weight ratio	TEOS/HCl molar ratio	SiO$_2$ content[a] wt. %	Transparency of the sample
CAB	—	—	—	transparent
CAB 6.25	93.75/6.25	30/1	1.9	translucent
CAB 12.5	87.5/12.5	30/1	5.8	translucent
CAB 25	75/25	30/1	10.9	translucent
CAB 50	50/50	30/1	21.9	translucent

[a] Determined by TGA.

Methods of testing

IR spectra were recorded over a range of 400—4000 cm^{-1} using double-beam Specord M-80 spectrophotometer (Carl Zeiss Jena).

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

Thermogravimetric analysis (TGA) was carried out using Shimadzu TGA-50 thermal analyzer. The sample was heated from room temperature to 900 °C with rate 10 °C/min under the air atmosphere. Samples weight were approximately 5—7 mg.

Scanning electron microscopy (SEM) images were recorded using Zeiss Evo 40 instrument. The samples were gold-coated prior to the examination.

RESULTS AND DISCUSSION

Chemical structures of obtained organic-inorganic hybrids were determined using IR spectroscopy and ^{29}Si NMR. Figure 1 demonstrates IR spectra of neat CAB and the organic-inorganic hybrids prepared with various amounts of TEOS.

The IR spectra of organic-inorganic hybrids showed absorption at around 800 and 460 cm^{-1} indicating the formation of silica network during sol-gel process. The presence of the band at 800 cm^{-1} can be assigned to the symmetric stretching vibration of the Si-O-Si bonds. The band at 460 cm^{-1} can be attributed to Si-O-Si bending mode. The absorption band at 1000—1100 cm^{-1} showed increased intensity due to the asymmetric stretching vibration of the Si-O-Si bonds formed *via* sol-gel process.
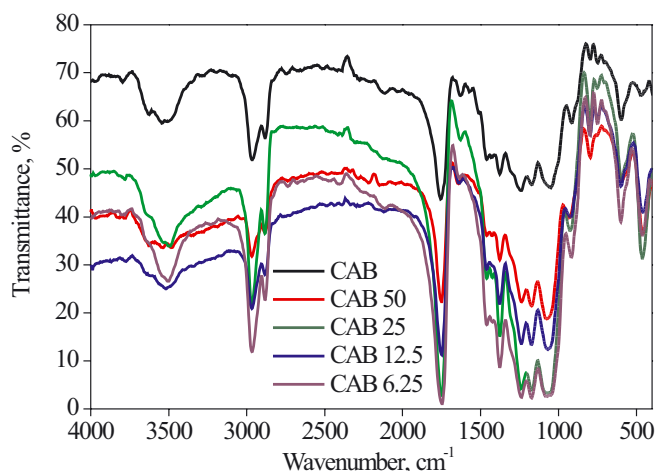
Fig. 1. IR spectra of CAB and organic-inorganic hybrids: CAB 50, CAB 25, CAB 12.5 and CAB 6.25; descriptions of samples as in Table 1

Fig. 2. ^{29}Si NMR spectrum of organic-inorganic hybrid CAB 12.5

Figure 2 shows the ^{29}Si NMR spectrum of the organic-inorganic hybrid CAB 12.5 revealing the presence of Q-type structures. Observed Q^2, Q^3, Q^4 species are related to the *in situ* formed inorganic network. The peak at -109 ppm (Q^4) indicates fully condensed SiO_2. The high intensity of Q^3 band (-101 ppm) indicates that major structures forming silica network are structures with a silicon atom connected to the three silicon atoms and one hydrogen atom or an alkyl group in the second coordination sphere. The existence of Q^3 and Q^2 structures (-90 ppm) observed in the ^{29}Si NMR spectrum revealed that the condensation of silanol was not complete.

TGA showed the differences in degradation of neat CAB and organic-inorganic hybrids during heating from room temperature to 900 °C. CAB started to decompose at around 280 °C (due to the degradation of organic constituents) and became relatively stable at about 580 °C.
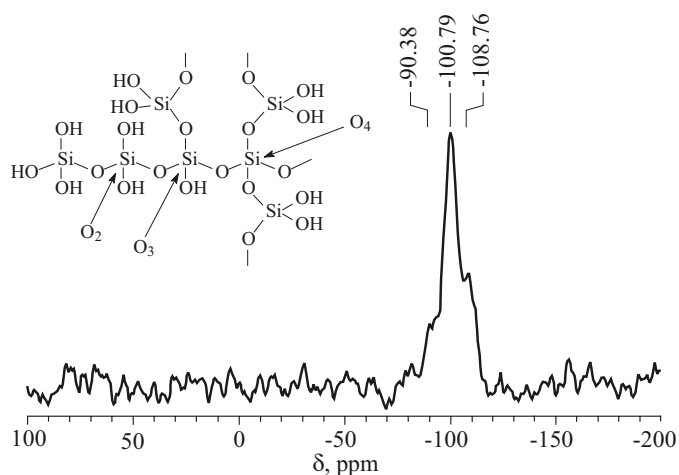
The neat polymer was entirely burned at 900 °C. The weight loss curve of organic-inorganic material was similar to neat CAB, however all hybrids showed residual mass after heating up to 900 °C, due to the presence of an inorganic phase. The amounts of silica incorporated into organic-inorganic hybrids determined by TGA are listed in Table 1.

Figure 3 presents SEM micrographs of the organic-inorganic hybrids obtained with various amounts of TEOS. SEM images revealed the uniform distribution of inorganic phase within the polymer matrix. Silica particles with dimensions: width *ca*. 460—800 nm, length ca. 5—8.5 μm are situated parallel to the film surface. The number of silica particles depends on the amount of TEOS used for the preparation of hybrids and increases with the higher alkoxysilane content. The SEM images showed also that silica particles are debonded from the surrounding polymer matrix, indicating poor inter-
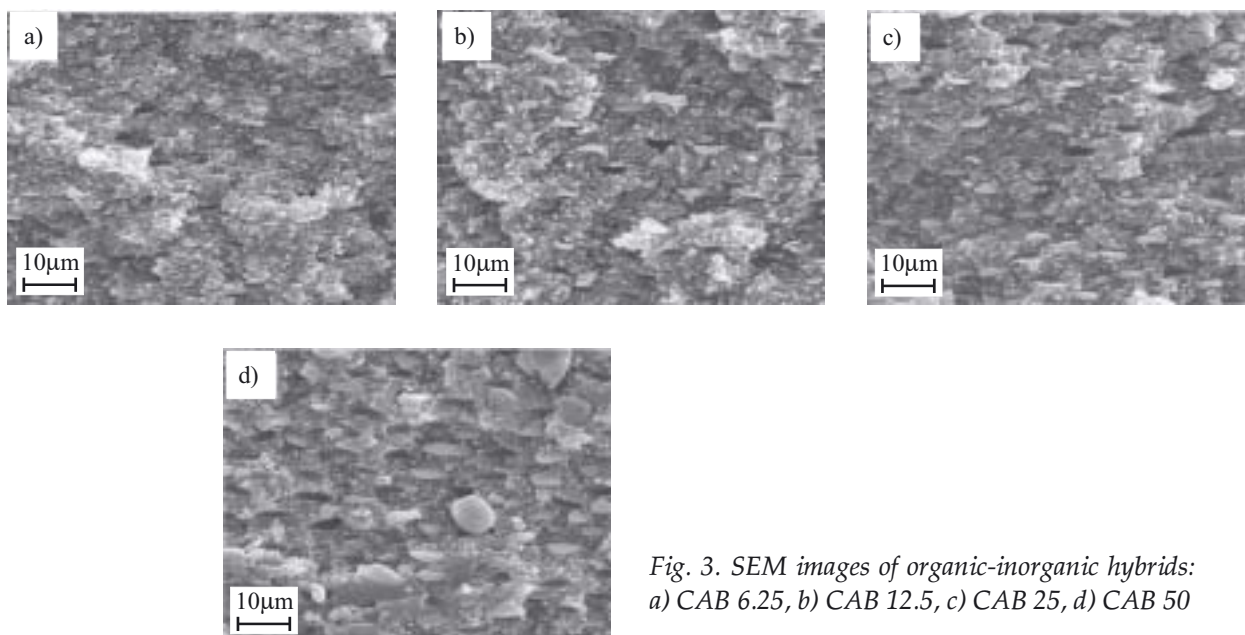

Fig. 3. SEM images of organic-inorganic hybrids: a) CAB 6.25, b) CAB 12.5, c) CAB 25, d) CAB 50

facial adhesion between the organic and inorganic phase.

The obtained organic-inorganic hybrids exhibit good transparency in comparison with unmodified CAB.

CONCLUSIONS

In this paper we describe for the first time the syntheses of CAB organic-inorganic hybrids obtained *via* sol-gel process using solution casting technique. The results of IR analysis and ^{29}Si NMR revealed the successful formation of silica network within CAB matrix. ROSi(OSi)$_3$ are the main structures that build inorganic phase network due to the incomplete condensation during the sol-gel process. Silanol groups in silica may form hydrogen bonds among SiO$_2$ particles and esters groups of CAB chains. SEM images showed uniformly distributed silica particles, debonded from the organic matrix. The number of inorganic particles increases with the higher amount of TEOS used for the synthesis. Cellulose acetate butyrate hybrids exhibit good transparency in comparison with a neat polymer. The CAB organic-inorganic hybrids are promising materials for packaging applications.

REFERENCES

1. Brinker C. J., Scherer G. W.: "Sol-Gel Science", Academic Press Inc., San Diego 1990, Chap. 3.
2. Kickelbick G.: "Hybrid Materials. Synthesis, Characterization, and Applications", WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2007, Chap. 1, 2 and 4.
3. Hüsing N., Schubert U.: *Angew. Chem., Int. Ed*. 1998, **37**, 22.
4. Chiang C. L., Ma C. C. M., Wu D. L., Kuan H. C.: *J. Polym. Sci., Part A: Polym. Chem.* 2003, **41**, 905.
5. Hajji P., David L., Gerard J. F., Pascault J. P., Vigier G.: *J. Polym. Sci., Part B: Polym. Phys.* 1999, **37**, 3172.
6. Sanchez C., Ribot F., Lebeau B.: *J. Mater. Chem.* 1999, **9**, 35.
7. Hofacker S., Mechtel M., Mager M., Kraus H.: *Prog. Org. Coat.* 2002, **45**, 159.
8. Sforca M. L., Yoshida I. V. P., Nunes S. P.: *J. Membrane Sci.* 1999, **159**, 197.
9. Kickelbick G.: *Prog. Polym. Sci.* 2003, **28**, 83.
10. Schubert U.: *New J. Chem.* 1994, **18**, 1049.
11. Słomkowski S.: *Polimery* 2006, **2**, 85.
12. Chruściel J., Leśniak E., Fejdyś M.: *Polimery* 2008, **11—12**, 817.
13. Tamaki R., Chujo Y.: *Appl. Organometal. Chem.* 1998, **12**, 755.
14. Babooram K., Francis B., Bissessur R., Narain R.: *Comp. Sci. Tech.* 2008, **68**, 617.
15. Yano S., Iwata K., Kurita K.: *Mater. Sci. Eng.* 1998, **6**, 75.
16. Reisfeld R.: *Polimery* 2006, **2**, 95.
17. Polish Pat. Appl. P-380939 (2006).