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SYNTHESIS, MORPHOLOGY AND THERMAL PROPERTIES OF THE POSS-CONTAINING POLYURETHANE NANOCOMPOSITES

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A series of nanocomposites based on polyurethane matrix (PU) have been synthesized using 1,2-propanediolisobutyl polyhedral oligomeric silsesquioxanes (POSS) as functionalized nanofiller. The effect of POSS content (0–10 % by weight) on the structure and properties of the created nanocomposites have been investigated. The polymer matrix (PU network) was synthesized from adduct of trimethylolpropane (TMP) and toluene 2,4-diisocyanate (TDI), and oligoetherglycol with $M_w = 5000 \text{ g/mol}^1$. FTIR analysis was used for investigation of 1,2-propanediolisobutyl-POSS incorporation possibility into PU matrix. The FTIR spectra of neat POSS, neat TDI-TMP adduct and model system adduct+POSS before curing and after curing were analyzed. The FTIR-ATR data obtained evidence that the POSS structure is chemically incorporated into the PU matrix during process of nanocomposites preparation. The thermal behaviour of POSS-containing nanocomposites by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was investigated. From the DSC data the glass transition temperature (T_g) of the nanocomposites was found to be increased with increasing of POSS content. Overall the results of thermal properties investigation of POSS-containing nanocomposites demonstrate that the created nanocomposites are significantly more thermally stable in compare with native matrix. The morphology of POSS-containing nanocomposites by SEM was analyzed. The incorporation of the POSS nanoparticles into PU matrix was found results in the formation of more ordered structure. Consequently the POSS introduced into PU matrix acts as nanostructuring agent. As a result the nanocomposites with more ordered structure are formed, so leading to obtaining of materials with improved thermal stability.

Keywords: polyurethane, polyhedral oligomeric silsesquioxanes, nanocomposite, morphology, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis

INTRODUCTION

Nanocomposites are a unique class of materials where a little quantity of nanofillers can significantly improve their properties [1–5]. Polyurethanes (PUs) are often used as polymer matrices for nanocomposites preparation due to their wide variety of physical and chemical properties [6–9]. The incorporation of polyhedral oligomeric silsesquioxane (POSS) macromer into the polyurethane matrix was found results in improving of the permeability of gas transport [10], increasing of the conduction and the permittivity [11]. The addition of POSS into the PU's polymers leads to enhancement of their thermal stability [12, 13], also to improving of the mechanical properties [14, 15] due to the reinforcement effect of the nanoparticles. The increasing of resistance of the nanocomposites against oxidation was also detected by authors [14, 16] due to incorporation of POSS to the systems. These favorable effects are evident mainly when the functionalized POSS

particles are integrated into polymer chains via a chemical reaction.

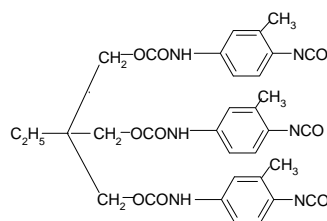
In our study, 1,2-propanediolisobutyl-POSS (POSS) was used as a functionalized nanofiller for PU matrix. The presence of two reactive hydroxy groups in peripheral substituent of POSS allows it to react with diisocyanates so resulting in embedding of the POSS particles into the main polymer chain of the nanocomposites [17–19].

The objective of the present study was the creation of nanocomposites based on polyurethane matrix and 1,2-propanediolisobutyl polyhedral oligomeric silsesquioxane (POSS), and investigation of the effects induced by the POSS content on the morphology and thermal properties of the nanocomposites.

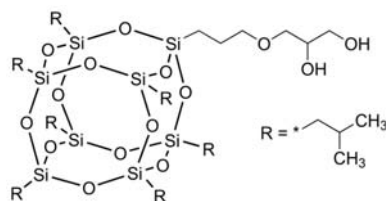
MATERIALS

1,2-propanediolisobutyl polyhedral oligomeric silsesquioxane (POSS) was purchased from Sigma-Aldrich Inc. Trimethylolpropane (TMP) and

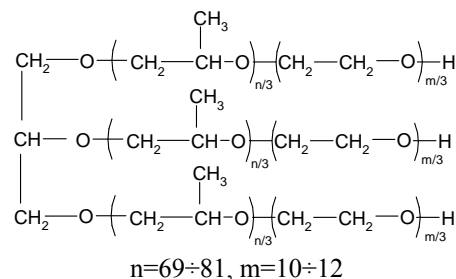
toluene 2,4-diisocyanate (TDI) were obtained from Merck. The reagents were of high purity and used as received. The oligoetherglycol with $M_w = 5.000 \text{ g/mol}^{-1}$ (Laprol 5003) was obtained from commercial sources and dried with liquid nitrogen under vacuum at 75–80 °C for 5 h before



Adduct TMP-TDI



POSS



Laprol 5003

Preparation of PU/POSS nanocomposites.

PU network used as polymer matrix was synthesized by two-step polymerization. In the first stage, the adduct of trimethylolpropane with toluene 2,4-diisocyanate (the adduct TMP-TDI) was obtained as described before [20]. Second step was the synthesis of three-dimensional polyurethane. Polyurethane network was obtained from a mixture of Laprol 5003 and adduct TMP/TDI (ratio 1:2 g-eq.) at 80 °C in nitrogen atmosphere. POSS (1 or 10 wt. %) was added as a functionalized nanofiller at the second stage of PU network synthesis. The stoichiometric ratio NCO/OH=1.5/1 was in all cases. The mixture was poured out on Petri dishes and cured at 70 °C for 2 h and post-cured at 80 °C for 24 h. The obtained nanocomposite films with ~1 mm thickness were post-cured for 2 h at 100 °C and then were held at 80 °C for 36 h in vacuum 10^{-5} Pa to remove residual solvent. The nanocomposites were named PUX, where X denotes the content of POSS in the samples. For example, PU1 indicates that the POSS content in the nanocomposite is 1 % by weight.

Neat PU also was synthesized for investigation and comparison of the results.

METHODS

Fourier transform infrared spectroscopy (FTIR). FTIR spectra of neat POSS, neat adduct TMP-TDI and model adduct+POSS (see below for details) were recorded using a TENSOR 37 FT-IR spectrometer (BRUKER, USA, Germany) in the spectral range of 4000–400 cm^{-1} (with resolution of

use. Ethyl acetate was used as a solvent and its purification was done by distillation in vacuum.

The molecular structures of neat components constituents of the nanocomposites are presented below.

0.8 cm^{-1}). The samples (thin films) of PU, PU1, and PU10 were presented in the ATR module.

Differential scanning calorimetry (DSC).

DSC was undertaken using a TA Instruments Q1000, on samples (cut thin film samples) of 10–15 mg in hermetically-sealed aluminium pans. Experiments were conducted at the heating rate of 20 °C min^{-1} in the temperature range –90 °C to 200 °C under nitrogen. The glass transition temperature (T_g) was taken as the midpoint of the curve at the change in heat capacity.

Thermogravimetric analysis (TGA). TGA was undertaken using a TA Instruments Q500 in hermetically-sealed aluminium pans. In a dry nitrogen atmosphere, the samples (about 5–6 mg) were heated from ambient temperature to 700 °C at the heating rate of 20 °C min^{-1} . The initial thermal degradation temperature was taken as the onset temperature at which a mass loss of 5 wt. % occurs.

Scanning electron microscopy (SEM).

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6060 LA (Tokyo, Japan) at the accelerating voltage of 30 kV and using a detector of secondary electrons. The samples were cut into strips, before being submerged in liquid nitrogen for 5 min and fractured as quickly as possible. Then the samples were warmed to room temperature and fixed to an SEM stub. The fracture surface of samples was coated with gold in vacuum to prevent accumulation of static charge and to increase the resolution. All measurements were done at 20 °C and at magnification of $\times 15000$.

RESULTS AND DISCUSSION

FTIR analysis of incorporation of 1,2-propanediolisobutyl-POSS into PU matrix.

A model system adduct+POSS was created by mixing of the adduct of TDI-TMP and POSS in the molar ratio NCO/OH = 1.5/1 for the FTIR investigation of the possibility of POSS incorporation into PU matrix. This model allows us to investigate the potential of the hydroxy groups of POSS to react with diisocyanates of

adduct TDI-TMP in our system. A given amount of POSS (10 wt. %) was dissolved in ethyl acetate and added to the adduct. The composition was carefully mixed and coated in glass NaCl. The mixture was cured at the 80 °C within 3 days.

In Fig. 1 the FTIR spectra of neat POSS, neat TDI-TMP adduct, and model system adduct+POSS before curing and after curing are presented.

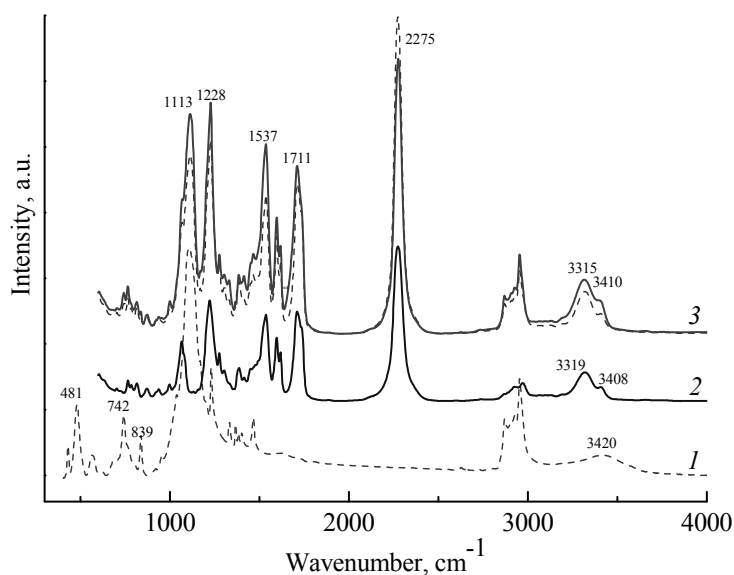


Fig. 1. FTIR spectra of: 1 – neat POSS; 2 – neat adduct TDI-TMP; 3 – model system adduct+POSS before (dot) and after curing (straight line)

In the FTIR spectrum of POSS the strong absorption band at 1108 cm^{-1} is observed (Fig. 1, curve 1) which could be attributed to the asymmetric stretching mode of $\nu_{\text{as}}(\text{Si-O-Si})$ in caged structure [21–23] and it is always accompanied with the corresponding symmetric stretching counterpart mode $\nu_{\text{s}}(\text{Si-O-Si})$ in the spectral region from 400 to 480 cm^{-1} (at 481 cm^{-1}) [21, 22, 24, 25] and corresponding bending vibrations $\delta_{\text{s}}(\text{O-Si-O})$ at 565 cm^{-1} [25, 26]. The band at 742 cm^{-1} is attributed to the stretching vibration in the $\text{Si-C}(\text{H}_2)$ isobutyl groups of POSS [25, 27] and accompanied by CH_2 (2871 and 2926 cm^{-1}) and CH_3 (2908 and 2955 cm^{-1}) stretching [28] and corresponding deformational modes (1465, 1402, 1384, 1230, and 839 cm^{-1}) [23, 25, 29]. The broad band at 3420 cm^{-1} is attributed to the stretching mode of $\nu(\text{OH})$ [30].

The characteristics of absorption bands of neat adduct (urethane units peaks) (Fig. 1, curve 2) are at 3408 (free N–H stretching), 3319 (hydrogen-

bonded N–H stretching), 1730 (free C–O stretching), 1711 (H-bonded C–O stretching), 1537 (N–H bending), and 1233 cm^{-1} (N–CO–O asymmetric stretching) [29, 31]. The broad bands in the range from 2856 to 2951 cm^{-1} are assigned to the saturated C–H symmetric and asymmetric stretching vibrations of methylene groups [29].

In Fig. 1. (curve 3) the spectrum of model system adduct+POSS before (dot) and after curing (straight line) are presented. We could observe that the band of isocyanate group ($-\text{NCO}$ stretching, 2275 cm^{-1}) of the model adduct+POSS decreased with the curing process. Conversely, urethane units bands increased and redistributed. So, we can conclude that the additional urethane linkages are formed in the model adduct+POSS that means the hydroxyl groups of POSS are capable to react with diisocyanates of adduct TDI-TMP in our system.

The proposed structure of cured model adduct of TDI-TMP+POSS is shown in Fig. 2.

FTIR-ATR analysis. Chemical structure of the POSS-containing nanocomposites.

In Fig. 3 the FTIR-ATR spectra of the nanocomposite films with different POSS content after curing are presented. The isocyanate band at 2275 cm^{-1} corresponding to the -NCO stretching vibrations (Fig. 2, curves 2, 3) has completely disappeared when the curing process finalizes in the neat PU and also in the nanocomposites (Fig. 3, curves 1–3).

For the POSS-containing nanocomposites, PU1 and PU10 (Fig. 3, curves 2 and 3), not only the characteristic bands of urethane units (see

above), but also the absorption bands at 1108 and 743 cm^{-1} for Si-O-Si and Si-C stretching vibrations and corresponding bending modes at 839 and 1465 (1332) cm^{-1} , respectively, were observed. Furthermore, it can be seen that the characteristic silsesquioxane bands increase their intensity with the increasing POSS content. These results show that the POSS has been successfully incorporated into PU chain. It is confirmation that the POSS cube structure is chemically incorporated into the PU matrix rather than there being a physical mixture [32].

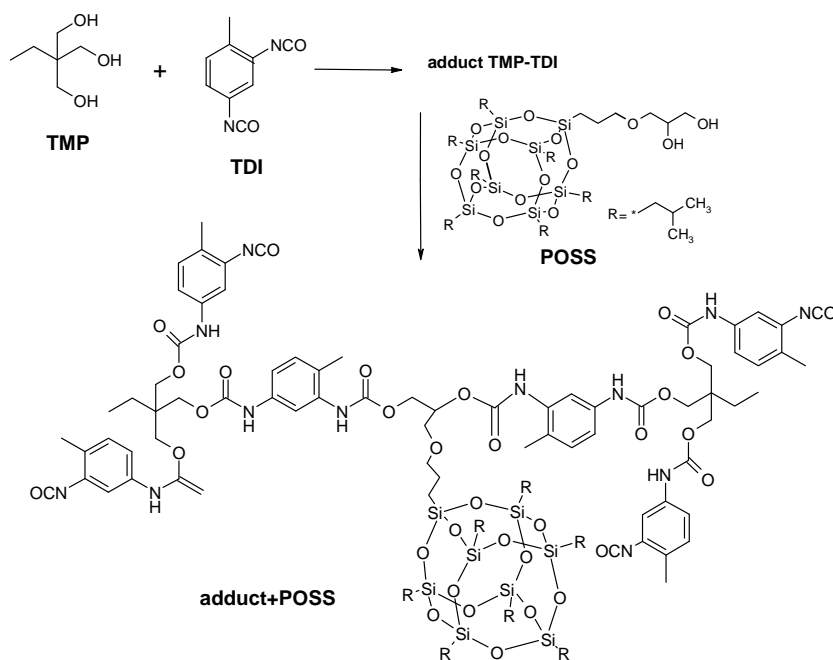


Fig. 2. The proposed structure of cured model adduct of TDI-TMP +POSS

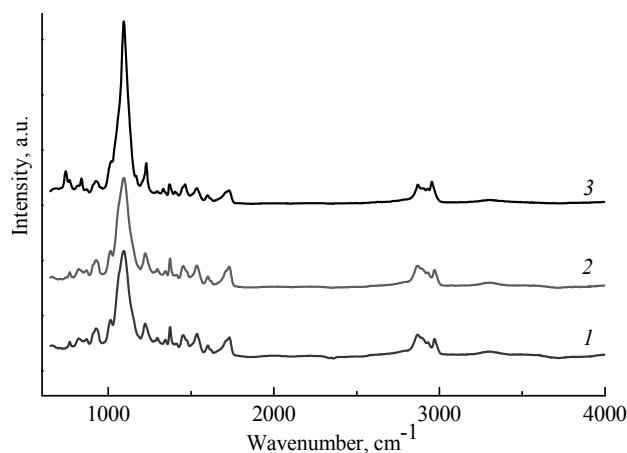


Fig. 3. FTIR spectra of: 1 – neat PU, 2 – PU1, 3 – PU10

The thermal behaviour of POSS-containing nanocomposites.

DSC thermograms of the PU/POSS nanocomposites (POSS content 1 and 10 wt. %) as well as thermogram of the neat PU are presented in Fig. 4 a.

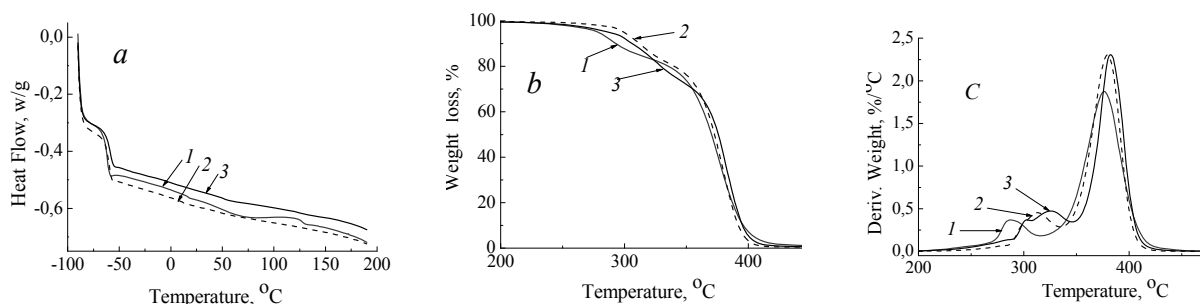


Fig. 4. DSC (a) and TGA (b, c) thermograms of neat PU and PU/POSS nanocomposites under inert atmosphere (N_2) at the heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$

The thermal behavior of PU/POSS nanocomposites was observed using TGA. The results of investigation are presented in Fig. 4 b, c. The TGA curves for all the samples displayed similar degradation profiles: for all the samples degradation was observed in two steps: around $280\text{--}300\text{ }^\circ\text{C}$ and above $380\text{ }^\circ\text{C}$, indicative of the soft and hard segments in the polyurethane. Maximum values of the thermal decomposition temperatures, $T_{d(max)}$, defined as the second maximum of the TGA curves, are shifted towards higher temperatures with increasing POSS content: from $376\text{ }^\circ\text{C}$ for neat PU to 379 and $382\text{ }^\circ\text{C}$ for PU1 and PU10, respectively. According to the TGA data (Fig. 4 b), addition of 1 wt. % of POSS

Fig. 4 a shows the second DSC scans of the investigated samples. From the DSC data the glass transition temperature (T_g) of the nanocomposites was found to be increased with increasing of POSS content: from $T_g = -61.13\text{ }^\circ\text{C}$ (neat PU) to $T_g = -59.76\text{ }^\circ\text{C}$ and $T_g = -58.76\text{ }^\circ\text{C}$ (PU1 and PU10, respectively).

results in increase in onset degradation temperature (T_{onset}) from $270\text{ }^\circ\text{C}$ for native PU to $294\text{ }^\circ\text{C}$ for the nanocomposite.

Overall, the results of thermal properties investigation of POSS-containing nanocomposites demonstrate that the created nanocomposites are significantly more thermally stable in comparison with native polymer matrix (PU network). The thermal stability of the nanocomposites increases with amount of POSS in the systems.

The morphology of POSS-containing nanocomposites. Fig. 5 shows the SEM cross-sectional images of the nanocomposites (fractured surfaces) with different POSS content in comparison with image of neat polymer matrix.

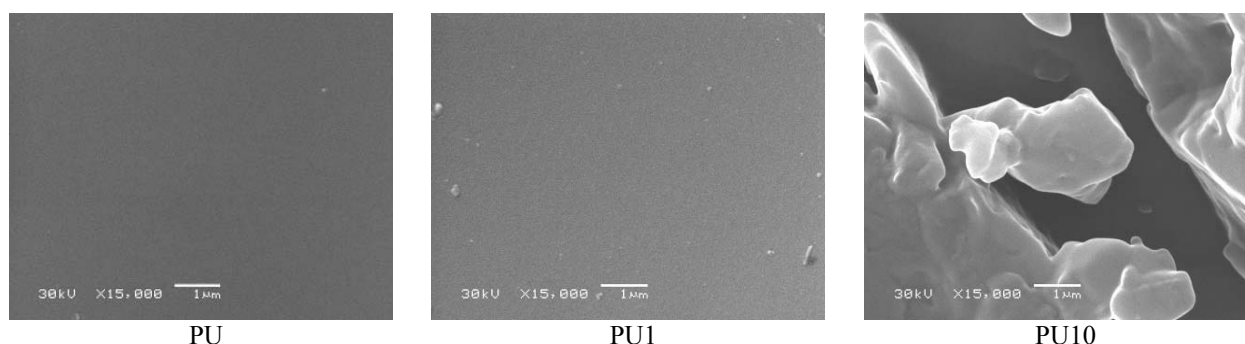


Fig. 5. SEM cross-sectional images of PU and PU/POSS nanocomposites (at magnification $\times 15000$)

It has been found that comparatively homogeneous structure of neat PU matrix becomes more segregated in the nanocomposites with

increasing POSS content. The POSS particles aggregation in the form of rectangular microdomains for PU10 with the maximum POSS

content was observed. Obviously, the POSS introduced into PU matrix acts as a nanostructuring agent. As a result, the nanocomposites with more ordered structure are formed so leading to obtaining of materials with improved thermal stability.

CONCLUSIONS

The nanocomposites based on polyurethane matrix (PU) and 1,2-propanediolisobutyl polyhedral oligomeric silsesquioxane (POSS), using as a functionalized nanofiller, have been synthesized. The chemical structure, morphology, and thermal properties of the created nanocomposites have been investigated. The data obtained evidence that the POSS cube structure is chemically incorporated into the PU matrix during

process of nanocomposites preparation. The incorporation of the POSS nanoparticles into PU matrix leads to the formation of more ordered structure, the POSS acts as a nanostructuring agent.

The incorporation of the POSS nanoparticles into PU matrix also significantly affects the thermal stability of the nanocomposites. The increasing in thermal stability of the nanocomposites with amount of POSS in the systems has been detected.

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Синтез, морфологія та термічні властивості POSS-вмісних поліуретанових нанокompозитів

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Синтезована серія нанокompозитів на основі поліуретанової матриці (ПУ) із використанням 1,2-пропандіолізобутилполіедрального олігомерного сілсесквіоксану (POSS) як функціонального нанонаповнювача. Досліджено вплив вмісту POSS на структуру та властивості створених нанокompозитів. Полімерна матриця (ПУ сітка) синтезована на основі адукту триметилпропану (ТМП), толуїлен-2,4-діізоціанату (ТДІ) та олігоетергліколю з $M_w = 5000$ г/моль⁻¹. Модельна система на основі адукту ТМП з ТДІ була використана для дослідження можливості вбудовування POSS в поліуретанову сітку із застосуванням FTIR спектроскопії. Структура та морфологія POSS-вмісних нанокompозитів досліджена методами FTIR-ATR спектроскопії та SEM. Термічні властивості досліджені методами ДСК та ТГА. Показано, що введення POSS в ПУ матрицю призводить до підвищення термічної стабільності створених нанокompозитів.

Ключові слова: поліуретан, поліедральний олігомерний сілсесквіоксан, нанокompозит, морфологія, Фур'є інфрачервона спектроскопія, диференційна скануюча калориметрія, термогравіметричний аналіз

Синтез, морфология и термические свойства POSS-содержащих полиуретановых нанокомпозитов

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Синтезирована серия нанокомпозитов на основе полиуретановой матрицы (ПУ) с использованием 1,2-пропандиолизобутилполиэдрального олигомерного силсесквиоксана (POSS) как функционального нанонаполнителя. Исследовано влияние содержания POSS на структуру и свойства созданных нанокомпозитов. Полимерная матрица (ПУ сетка) синтезирована на основе аддукта триметилпропана (ТМП), толулен-2,4-диизоцианата (ТДИ) и олигоэфиргликоля с $M_w = 5000 \text{ г/моль}^{-1}$. Модельная система на основе аддукта ТМП с ТДИ была использована для исследования возможности встраивания POSS в полиуретановую сетку с применением FTIR спектроскопии. Структура и морфология POSS-содержащих нанокомпозитов исследована методами FTIR-ATR спектроскопии и SEM. Термические свойства исследованы методами ДСК и ТГА. Показано, что введение POSS в ПУ матрицу приводит к повышению термической стабильности созданных нанокомпозитов.

Ключевые слова: полиуретан, полиэдральный олигомерный силсесквиоксан, нанокомпозит, морфология, Фурье инфракрасная спектроскопия, дифференциальная сканирующая калориметрия, термогравиметрический анализ

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