

Thermal stability and mechanical properties of hybrid materials based on nitrocellulose grafted by aminopropylisobutyl polyhedral oligomeric silsesquioxane^{*)}

Xiaomei Yang¹⁾, Yiliang Wang¹⁾, Yuanyuan Li¹⁾, Zhipeng Li¹⁾, Tianyou Song¹⁾,
Xiu Liu¹⁾, Jianwei Hao^{1),**)}

DOI: [dx.doi.org/10.14314/polimery.2017.576](https://doi.org/10.14314/polimery.2017.576)

Abstract: The need for improvement in nitrocellulose (NC) storage safety and convenience of application requires an increase in NC thermal stability and enhancement of its mechanical properties. To this aim, hybrid materials were synthesized by grafting NC with aminopropylisobutyl polyhedral oligomeric silsesquioxane (amino-POSS) using isophorone diisocyanate (IPDI) as a crosslinking agent. The structure and elemental composition of the resulting products were confirmed by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (¹H NMR and ²⁹Si NMR), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). It was found, based on the silicon mapping using energy dispersive X-ray spectroscopy (EDS), that amino-POSS was well dispersed in NC matrix. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies showed that hybrid amino-POSS-NC materials have higher thermal decomposition activation energy (E_a) compared to NC control sample. According to TGA results, the temperatures of 5 % weight loss ($T_{5\%}$) and 50 % weight loss ($T_{50\%}$) as well as the residual masses at 240 °C ($CR_{240^\circ C}$), were increased as a result of NC modification with amino-POSS. As can be seen from the digital and scanning electron microscopy (SEM) images, the char layers of amino-POSS-NC hybrid materials after burning in air became more compact with increasing amino-POSS content. XPS studies have shown an increased content of the graphitized carbon in the char residues of the modified samples. The results of DSC, TGA, SEM and XPS studies have directly proved the enhancement of the thermal stability of amino-POSS-NC hybrid materials. In addition, tensile strengths and Young's moduli of amino-POSS-NC hybrid materials were increased gradually with the amino-POSS content in the uniaxial tensile tests. All these results show that the proposed modification of nitrocellulose improves the safety of manufacture and use of this material.

Keywords: nitrocellulose, hybrid material, aminopropylisobutyl polyhedral oligomeric silsesquioxane, thermal stability, mechanical properties.

Stabilność termiczna i właściwości mechaniczne materiałów hybrydowych na bazie nitrocelulozy szczepionej oligomerycznym wielofunkcyjnym aminopropylizobutylosilsekwioxanem

Streszczenie: Poprawa bezpieczeństwa przechowywania nitrocelulozy (NC) wymaga zwiększenia jej stabilności termicznej, a wygoda używania poprawy właściwości mechanicznych. W tym celu zsyntetyzowano materiały hybrydowe, w których NC szczepiono oligomerycznym wielofunkcyjnym aminopropylizobutylosilsekwioxanem (amino-POSS) stosując jako środek sieciujący izoforonodizocyanian (IPDI). Strukturę i skład otrzymanych materiałów potwierdzono za pomocą spektroskopii w podczerwieni z transformacją Fouriera (FT-IR), jądrowego rezonansu magnetycznego (¹H NMR i ²⁹Si NMR), dyfraktometrii rentgenowskiej (XRD) oraz spektroskopii fotoelektronów rentgenowskich (XPS). Na podstawie wyników badań mapowania Si, otrzymanych metodą spektroskopii dyspersji energii promieniowania rentgenowskiego (EDS), stwierdzono, że amino-POSS został dobrze zdysper-

¹⁾ Beijing Institute of Technology, School of Materials Science and Engineering, National Engineering Technology Research Center of Flame Retardant Materials, Beijing 100081, PR China.

^{*)} This material was presented at 9th International Conference MoDeSt 2016, 4–8 September 2016, Cracow, Poland.

^{**)} Author for correspondence; e-mail: hjw@bit.edu.cn

gowany w matrycy NC. Badania stabilności termicznej przeprowadzone za pomocą różnicowej kalorymetrii skaningowej (DSC) wykazały, że materiały hybrydowe typu amino-POSS-NC charakteryzują się większymi wartościami energii aktywacji rozkładu termicznego (E_a) niż próbka kontrolna NC. Zgodnie z wynikami analizy termogravimetrycznej (TGA) wartości temperatury ubytku 5 % ($T_{5\%}$) i 50 % ($T_{50\%}$) masy próbki oraz pozostałości masy w temperaturze 240 °C ($CR_{240\text{ °C}}$) zwiększały się na skutek modyfikacji NC za pomocą amino-POSS. Według fotografii cyfrowych i fotografii wykonanych metodą skaningowej mikroskopii elektronowej (SEM) warstwy węglowe powstałe po spaleniu materiałów hybrydowych w powietrzu wraz ze zwiększeniem zawartości amino-POSS stawały się coraz bardziej zwarte, a wyniki badań XPS wykazały, że tworzyło się coraz więcej węgla w postaci grafitu. Wszystkie wyniki DSC, TGA, SEM i XPS dowodzą poprawy stabilności termicznej materiałów hybrydowych amino-POSS-NC. Stwierdzono także, że wytrzymałość na rozciąganie i moduł Young'a podczas prób jednoosiowego rozciągania materiałów hybrydowych rosną ze zwiększaniem się zawartości amino-POSS. Wyniki wszystkich przeprowadzonych badań dowodzą, że zaproponowana modyfikacja NC poprawia bezpieczeństwo wytwarzania i użytkowania tych materiałów w porównaniu z niemodyfikowanym NC.

Słowa kluczowe: nitroceluloza, materiał hybrydowy, oligomeryczny wielofunkcyjny aminopropylolizobutylosilseskwioxan, stabilność termiczna, właściwości mechaniczne.

Nitrocellulose (NC) is the nitrate ester of cellulose [1], which comes from the nitration of the natural material. It can be used in various applications based on the different nitrogen contents [2, 3]. The main applications of NC with low nitrogen content [4] are in the fields of coatings [5], printings [6], membranes [7], magnetic filtrations [8], and others [9, 10]. Although NC products present many outstanding features (*e.g.*, transparency and fast drying [11]), the poor thermal stability limits their application because NC has spontaneous ignition property and it is susceptible to combust [12, 13] (high burning rate, no residual char [14]). Additionally, the poor mechanical properties of NC [15] also restrict the down-stream products. In terms of the storage safety and the usage requirements, it is essential to endow NC with good thermal stability and mechanical properties, which can be realized by introducing some additives or reactive modifiers into NC.

During the past decades, various additive modifiers, such as diphenylamine (DPA) [16], malonanilide dimers [17] and 1,4-diaminoanthraquinone (DAAQ) [18], have been used to improve the thermal stability of NC. In addition, inorganic salts [19] are also used to increase the thermal stability and prolong the induction time period of NC. However, the migration and poor compatibility are the main problems associated with the additive modifiers prepared in this manner. Compared with the additive modifiers, reactive modifiers are usually incorporated into the backbone of the polymer matrix, increasing the thermal stability in an efficient way [20].

Great scientific interest in polyhedral oligomeric silsesquioxane (POSS) has been stimulated by the smallest known silica particles with the specific cage-like molecular structure with inorganic silicon-oxygen core (Si_8O_{12}) and eight variable organic vertex groups [21, 22]. The organic substituents endow the POSS with good dispersion and miscibility, which is the key to tailor a wide variety of nano- and micro-structured organic/inorganic hybrid materials [23]. In general, the forma-

tion of a ceramic layer on the surface of the materials by POSS thermal degradation resulted in a protective physical barrier, strongly improving the thermal stability [24]. The incorporation of POSS into polymers would enhance obviously their mechanical properties [25], yet retaining the processibility and commodity [26]. Furthermore, POSS derivatives also possess various chemical side groups [27], *e.g.*, aminopropylisobutyl polyhedral oligomeric silsesquioxane (amino-POSS), which can facilitate its chemical incorporation into a given polymer *via* chemical method [28].

To the best of our knowledge, using chemical method to graft POSS onto NC has not been reported yet. Thus, in the present study, in aim to improve the thermal stability and mechanical properties of NC, amino-POSS will be grafted onto NC by using isophorone diisocyanate (IPDI) as a linkage, giving rise to a series of amino-POSS-NC hybrid materials containing different amino-POSS contents. IPDI is an aliphatic ring with one primary and one secondary isocyanate group, which has unequal reactivity at different temperatures [29]. We will mainly study the influence of amino-POSS content on the thermal stability and mechanical properties of NC materials.

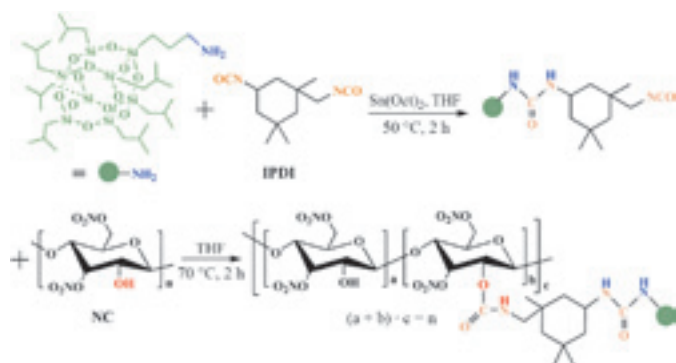
EXPERIMENTAL PART

Materials

Nitrocellulose (NC, nitrogen content ~ 11.91 wt %) was kindly provided by Baoding BaoFeng Nitrocellulose Co., Ltd (Hebei, China). All NC was pre-treated to remove residual water in a freeze dryer at -80 °C for 48 h and stored in a desiccator before use.

Isophorone diisocyanate (IPDI) and tin(II) 2-ethylhexanoate [$\text{Sn}(\text{Oct})_2$] were purchased from Alfa Aesar.

Aminopropylisobutyl polyhedral oligomeric silsesquioxane (amino-POSS, 99.98 %) was purchased from Hybrid Plastics.



Scheme A. The synthetic route of amino-POSS-NC hybrid materials

Tetrahydrofuran (THF) and *n*-hexane were purified by distillation over CaH₂.

All other reagents were obtained from Beijing Chemical Works and used as received.

Preparation of amino-POSS-NC hybrid materials

Sn(Oct)₂ (volume conc. = 0.0013 g/cm³) was added to a three-necked flask containing amino-POSS in THF (30 cm³). Then, stoichiometric amount of IPDI with 10 cm³ THF was dropped into the flask. The stirring was continued at 50 °C for 2 h. Subsequently, appropriate amount of NC solution (in 30 cm³ THF) was added to the mixture and then the mixture was heated up to 70 °C. The reaction was kept for additional 2 h. All above operations were carried out under a nitrogen atmosphere. At last, the amino-POSS-NC hybrid materials were precipitated in a 5-fold amount of *n*-hexane for three times. After drying, light yellow solids were obtained. The synthetic route of preparation of NC grafted with amino-POSS are presented in Scheme A, and the detailed recipes are listed in Table 1. The yields of syntheses performed using 8.9 wt %, 22.1 wt % and 31.2 wt % amino-POSS-NC are 86.9 %, 84.7 % and 87.6 %, respectively.

The NC control and amino-POSS-NC hybrid material films were obtained through mixing NC or amino-POSS-NC hybrid materials with butanone solution (0.1 g/cm³). The mixtures were casted to polytetrafluoroethylene substrates, allowed to evaporate at ambient temperature for 48 h, and then dried at 50 °C in a vacuum oven for another 24 h. The average thickness of the resulting films was 1 mm, which can be controlled by the amount of solution used.

Methods of testing

Fourier transform infrared spectroscopy (FT-IR) was applied in the range of 4000–400 cm⁻¹ with Bruker Tensor-27 FT-IR spectrometer at room temperature using the KBr disk method.

Nuclear magnetic resonance (¹H NMR and ²⁹Si NMR) spectra were recorded at room temperature on AV400 (Bruker) NMR instrument with DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal standard.

Table 1. Preparation of NC control sample and amino-POSS-NC hybrid materials

Sample symbol	NC, wt %	IPDI, wt %	Amino-POSS, wt %
NC (control sample)	100	0	0
H1	89.3	1.8	8.9
H2	73.5	4.4	22.1
H3	62.5	6.3	31.2

X-ray diffraction analysis (XRD) was performed using an X'pert PRO diffractometer system. CuK_α radiation was used with a copper target over the 2θ range of 5–40° at a speed of 10 °/min.

X-ray photoelectron spectroscopy (XPS) was applied using a PHI Quantera II SXM at 25 W, under a vacuum of 2.6 · 10⁻⁷ Pa with AlK_α X-ray source. Furthermore, the weight content of Si (Si %) for each amino-POSS-NC hybrid material was calculated according to equation:

$$\text{Si \%} = \frac{C_A(\text{Si}) \cdot M(\text{Si})}{C_A(\text{C})M(\text{C}) + C_A(\text{O})M(\text{O}) + C_A(\text{N})M(\text{N}) + C_A(\text{Si})M(\text{Si})} \cdot 100\% \quad (1)$$

where: C_A(C), C_A(O), C_A(N), C_A(Si) – the atomic concentrations of C, N, O and Si elements on the surface and the char residues of amino-POSS-NC hybrid material, respectively; M(C), M(O), M(N), M(Si) – the relative atomic mass of C, O, N and Si elements.

The spectrometer was calibrated using the binding energy of adventitious carbon as 284.6 eV.

Differential scanning calorimetry (DSC) was carried out on Netzsch 200 PC instrument. All the samples were heated from room temperature to 200 °C at the heating rate of 2, 5, 7 or 10 °C/min with a continuous N₂ flow rate of 60 cm³/min. The sample mass in the pan was around 5.0 mg.

Thermogravimetric analysis (TGA) was performed using Netzsch TG 209 with a continuous flow of a N₂ atmosphere. Samples (~ 3.0 mg) were heated from 50 °C to 240 °C at a rate of 10 °C/min. The following parameters were determined: initial decomposition temperature based on 5 % mass loss (T_{5%}), middle decomposition temperature based on 50 % mass loss (T_{50%}) and char residues under 240 °C (CR_{240 °C}).

Scanning electron microscopy (SEM) was applied by using Hitachi S-4700 SEM apparatus. In addition, the distribution of Si atoms was obtained by energy dispersive X-ray spectroscopy (EDS) Si mapping.

Uniaxial tensile tests were carried out on Instron 1185 at 25 °C with a crosshead speed of 5 mm/min. Rectangular tensile bars measuring 50 mm × 10 mm × 1 mm were obtained above using a fresh razor blade.

RESULTS AND DISCUSSION

Chemical structure characterization

The FT-IR spectra of NC (control sample) and amino-POSS-NC hybrid materials are presented in Fig. 1a. Two characteristic peaks at 1661 cm^{-1} and 1284 cm^{-1} are attributed to NO_2 asymmetric and symmetric stretching vibrations, respectively, while the group at 840 cm^{-1} is related to the O- NO_2 vibrations [30]. The increase in the peak intensity at 1661 cm^{-1} for amino-POSS-NC hybrid materials is

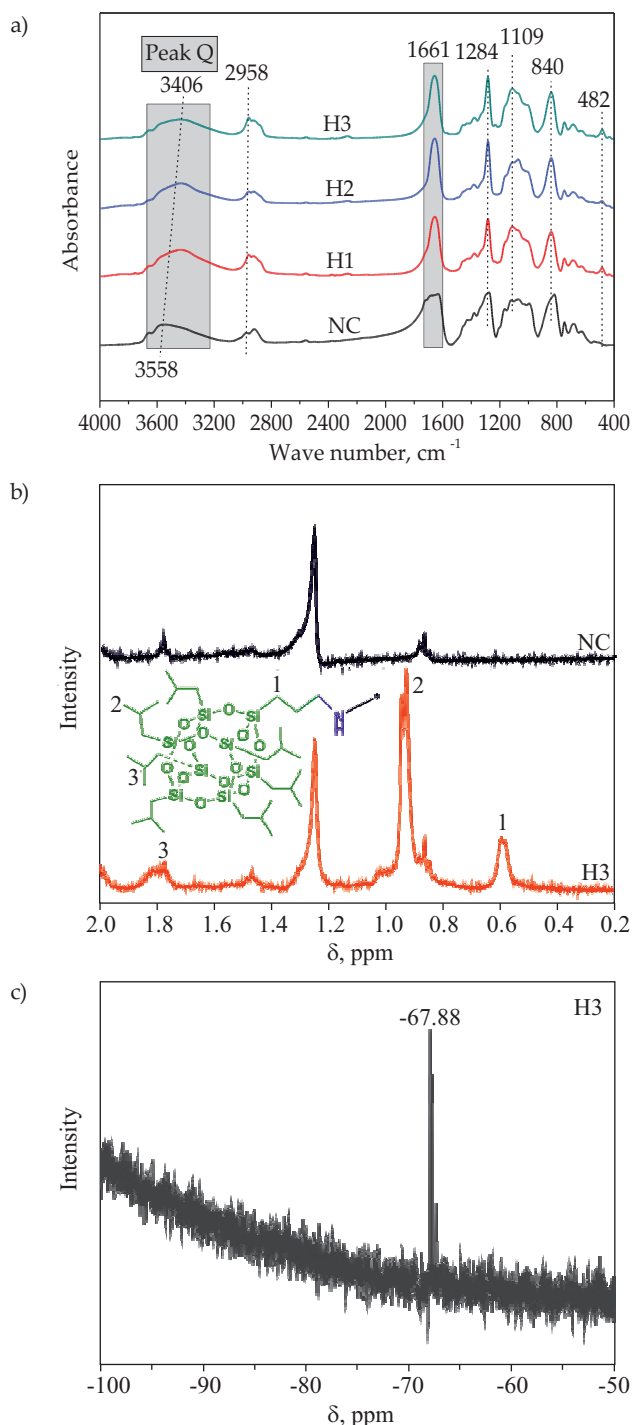


Fig. 1. Spectra of NC (control sample) and amino-POSS-NC hybrid materials: a) FT-IR, b) ^1H NMR, c) ^{29}Si NMR

also attributed to the C=O stretching vibration (amide I). The successful grafting of amino-POSS onto NC can be confirmed by the appearance of dominant Si-O-Si stretching vibration at 1109 cm^{-1} and 482 cm^{-1} [31, 32]. The intensity of the bands of saturated C-H bonds is increased when compared with NC control, further indicating the introduction of amino-POSS. In addition, the peak Q in Fig. 1a shifts from 3558 cm^{-1} (NC) to 3406 cm^{-1} (H3). It is because the peak corresponding to asymmetric stretching vibration of N-H in amide, near 3400 cm^{-1} [33] is formed, and the introducing of amino-POSS with significant steric hindrance may impair the interaction of intermolecular hydrogen bond of NC.

The ^1H NMR spectra of NC and H3 amino-POSS-NC hybrid material are shown in Fig. 1b. The resonance peaks at 0.58 ppm (peak 1), 0.93 ppm (peak 2), and 1.80 ppm (peak 3) are caused by seven isobutyl hydrocarbon substituents of the amino-POSS [34]. The multiple resonances at peak 2 ($\delta\ 0.8\text{--}1.0\text{ ppm}$) and peak 1 ($\delta\ 0.58\text{ ppm}$) in H3 amino-POSS-NC hybrid material correspond to the chemical shifts of methyl (CH_3) and methylene (CH_2) of amino-POSS, respectively. Moreover, the enhanced peak 3 ($\delta\ 1.80\text{ ppm}$) is methine (CH) group of amino-POSS [31]. These results give a further proof of the grafting reaction.

The ^{29}Si NMR spectrum of H3 amino-POSS-NC hybrid material is shown in Fig. 1c. The signal of Si (-67.88 ppm) was detected indicating the successful synthesis of amino-POSS-NC.

The XRD patterns of NC, H3 amino-POSS-NC hybrid material and amino-POSS are presented in Fig. 2. Both NC and H3 samples show a wide, amorphous diffraction peak at $2\theta \approx 20^\circ$, which is attributed to the characteristic peak of NC [35]. As compared with NC control sample, H3 amino-POSS-NC shows a diffraction peak at $2\theta \approx 9^\circ$ after washing with *n*-hexane for removing the unreacted substances, indicating that the amino-POSS is grafted onto NC. Notably, this peak is related to the local order among amino-POSS molecules of the Si-O-Si caged structure [36].

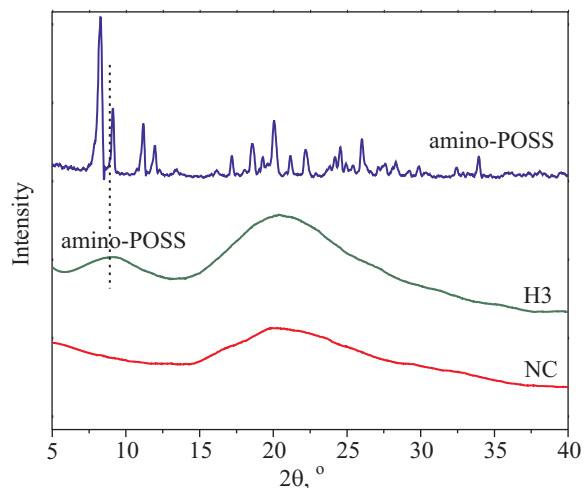


Fig. 2. XRD spectra of NC, H3 amino-POSS-NC hybrid material and amino-POSS