

Polyurethane Electrospun Mats Strengthened and Toughened by Physically Blended Polyhedral Oligomeric Silsesquioxane

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ABSTRACT: In this work, polyfunctional polyhedral oligomeric silsesquioxane (POSS) with glycidyl ether groups was physically blended with end-capped polyurethane (PU) to improve the mechanical strength of PU electrospun mats. It was found that not only the tensile strength was elevated, but also the elongation-at-break was greatly improved. Fourier transform infrared spectroscopy results suggested that no chemical reaction happened, and there was no hydrogen bonding between POSS and PU, but the mobility of the PU chains was restricted. Wide-angle X-ray diffraction patterns showed that POSS aggregated inside the PU electrospun fibers. Scanning electron microscopy observation showed apparent die-swelling, indicating that the elasticity of PU chains was enhanced. This was always the result of strengthened chain–chain interactions. From the experimental observations, it was speculated that a physical polymer–particle network was established through attachment of PU chains onto the POSS nanoparticles and embedment of PU chains inside the POSS aggregates, which results in the simultaneous improvements in strength and extensibility. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40902.

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INTRODUCTION

Polyurethane (PU) electrospun mats are very promising in tissue engineering,^{1–3} protective clothes,^{4,5} biosensor,⁶ and filtration.⁷ However, the mechanical strength of the PU electrospun mats is always poor. It is of great necessity to improve their strength. Lots of materials, like surface-functionalized carbon nanotubes,^{8,9} organic clay,¹⁰ tumarline,¹¹ etc., were used to improve the mechanical strength of the PU electrospun mats. However, there are only few reports on PU/polyfunctional polyhedral oligomeric silsesquioxane (POSS) electrospun mats,¹² and no one has used POSS to reinforce the PU electrospun mats.

POSS is a nanosized organic–inorganic hybrid material.¹³ One important feature of POSS is that it has a hard, rigid, inorganic, and cage-like core. The other important feature is that its outer shell is composed of functional organic groups, which can form strong linkage with polymer matrix either through chemical bonds or through physical interactions. Such structural features make POSS a perfect candidate in reinforcing polymer materials.^{14–16}

However, the POSS with inert groups, such as the octacyclohexyl POSS or the octa-phenyl POSS, cannot form strong interactions with PU. They are not very suitable in polymer

reinforcement. On the other hand, the POSS with active groups, such as octa-amino POSS, may react too quickly with the PU with functional residues, like isocyanate groups. They are also not suitable in fabricating PU/POSS electrospun mats because the active POSS may cause serious gelation during electrospinning. It sounds to be a good choice to incorporate the active POSS onto the backbone of PU before electrospinning. However, it is always a time consuming process.^{17,18} The question is how to prepare PU/POSS electrospun mats in a simple way to fully utilize the advantages of POSS.

In this work, PU/POSS electrospun mats were prepared by physically blending polyfunctional glycidyl POSS with end-capped PU. It was supposed that the POSS with polar glycidyl groups could form polar–polar interactions with the PU, and the end-capped PU was inert to the functional POSS. In this way, the polyfunctional POSS was utilized as a kind of physical nanofiller instead of chemical crosslinker. It was found that the mechanical strength of the PU electrospun mats was remarkably improved through incorporation of POSS. More interestingly, the elongation-at-break of PU electrospun mats was also greatly improved. The physically blended POSS performed well in improving the mechanical performance of PU electrospun mats.

EXPERIMENTAL

Materials

PU (30 wt % solution in dimethyl formamide (DMF)) was kindly supplied by Anhui Anli Synthetic Leather Co. (China). The solution viscosity was 5×10^4 mPa·s at room temperature. POSS was synthesized according to the literature¹⁹ by the hydrolytic condensation of 3-glycidyloxypropyltrimethoxysilane catalyzed with tetramethylammonium hydroxide firstly in isopropyl alcohol and secondly in toluene. 3-Glycidyloxypropyltrimethoxysilane was purchased from Yuanye Biotech Co. (China). Tetramethylammonium hydroxide and anhydrous DMF (99.8%) were purchased from Sinopharm Group Co. (China).

Preparation of PU/POSS Electrospun Mats

A home-made electrospinning apparatus mainly composed of a high-voltage power supplier and a rolling collector was used. The power supplier (DW-P403-1ACDF) is a product of Tianjin Dongwen High Voltage Supply Co. (China).

Before electrospinning, PU/POSS composite solutions were prepared by mixing PU solution (30 wt % in DMF) with different amount of POSS solutions (20 wt % in DMF). The relative concentrations of POSS in the composites were set to be 2.5, 5, 10, and 20 phr. All the solutions, including POSS/DMF and PU/POSS/DMF composite solutions, were prepared at room temperature under magnetic stirring for 0.5–1 h mildly. The final concentration of the composite solutions was adjusted to 18 wt % by addition of small amounts of DMF.

During the electrospinning process, a high voltage (18 kV) was applied on the tip of the needle (inner diameter = 0.9 mm), and the distance between the needle tip and the collector was 15 cm. The electrospun mats obtained (thickness = 0.10 ± 0.02 mm) were named as PU2.5, PU5, PU10, and PU20, corresponding to the different concentrations of POSS (phr). Pristine PU was also electrospun into mats as control.

Characterizations

Wide-angle X-ray diffraction (WAXD) was performed on D/MAX 2500V (Rigaku, Japan) at a scanning speed of $2\theta = 4^\circ/\text{min}$. Fourier transform infrared (FTIR) spectra were obtained by using Nicolet iS10 instrument manufactured by Thermo Fisher Scientific (Waltham, MA). Surface morphology of the PU/POSS electrospun mats was observed on a SU8020 field-emission scanning electron microscope (Hitachi, Japan). Thermogravimetric analysis was performed on a TG 209 F3 (Netzsch, Germany) at N_2 atmosphere from 25°C to 800°C. The heating rate was 10°C/min. The sample mass was 6.71 mg for pristine PU, 7.37 mg for sample PU10, 6.73 mg for sample PU20, and 8.13 mg for POSS. An electronic universal testing machine (CMT-5000, Shenzhen Sans Testing Machine Co., China) was applied to measure the mechanical properties. All the tensile test specimens were cut into rectangle shape with a length of 40 mm and a width of 10 mm. The thickness of these samples was 0.1 ± 0.02 mm. The extension rate was 10 mm/min.

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectra of POSS, PU, PU10, and PU20 are shown in Figure 1. From the spectrum of PU shown in Figure 1(a), it can be read that there is no absorption band at 2270 cm^{-1} corresponding

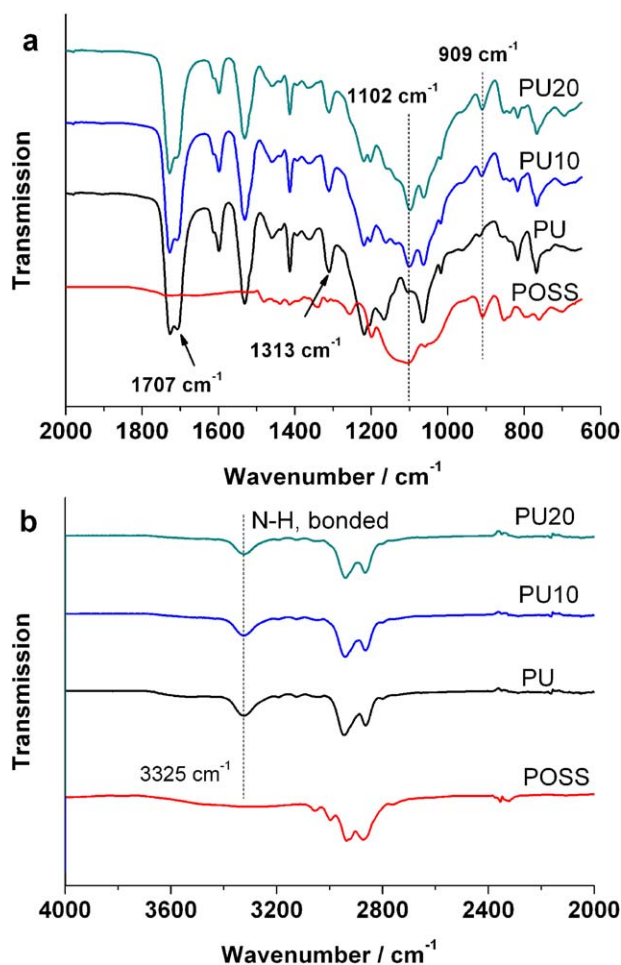


Figure 1. FTIR spectra of POSS, PU electrospun mat, and PU/POSS electrospun mats. (a) FTIR spectra in the wavenumber range of 2000–600 cm^{-1} , (b) FTIR spectra in the wavenumber range of 4000–2000 cm^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the $-\text{NCO}$ groups.^{20,21} The PU used was completely end-capped. There is an apparent absorption band at 1313 cm^{-1} , which corresponds to the $\text{O}-\text{CO}$ stretching of polyester.²² At the same time, the band corresponding to ether groups²³ at 1115 cm^{-1} is absent. It is concluded that the PU used is of polyester type.

On the FTIR spectrum of POSS in Figure 1(a), the absorption band at 1102 cm^{-1} is attributed to the $\text{Si}-\text{O}-\text{Si}$ in caged structure²⁴ and the band at 909 cm^{-1} is attributed to the glycidyl groups.²⁵ It confirms that the POSS is a glycidyl POSS. On the spectra of PU10 and PU20, it can be seen that both of the bands at 1102 and 909 cm^{-1} increase their strength with the increasing POSS concentration. Such results show that the POSS has been successfully incorporated into PU.

However, there are no new bands appearing in the range of $3400\text{--}3600 \text{ cm}^{-1}$ corresponding to the hydroxyl ($-\text{OH}$) groups²⁶ on the FTIR spectra of PU/POSS electrospun mats in Figure 1(b). It indicates that the glycidyl groups of POSS are not opened by the $\text{N}-\text{H}$ groups on PU. Besides, almost all the absorption bands corresponding to PU do not change their

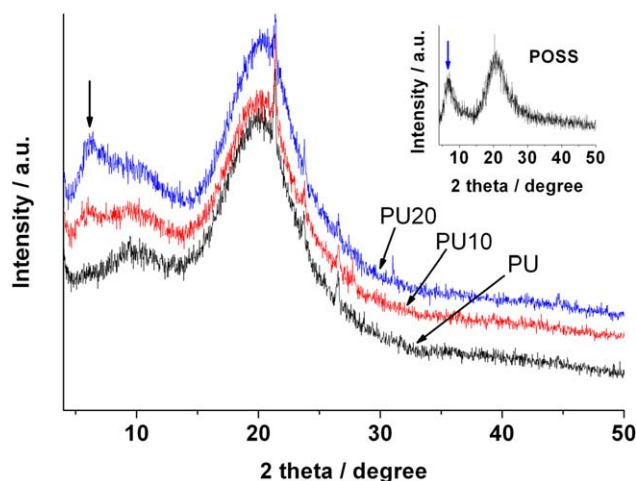


Figure 2. WAXD patterns of PU electrospun mat and PU/POSS electrospun mats. Inset: WAXD of POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

positions. There is no strong evidence that chemical reaction has happened between POSS and PU.

There is also no evidence that POSS has formed hydrogen bonds with PU. The absorption band at 1707 cm^{-1} , which corresponds to the hydrogen bonded C=O groups,²⁷ does not become stronger with the increasing POSS concentration [Figure 1(a)]. The absorption bands at 3325 cm^{-1} corresponding to the bonded N—H groups²⁸ do not become stronger too [Figure 1(b)].

Instead, both the bands at 1707 and 3325 cm^{-1} are slightly weaker. It indicates that the hydrogen bonding (between the N—H groups and the C=O groups) is not strengthened, but

weakened in the PU/POSS electrospun mats. Such a result suggests that the molecular motion of the PU chains is restricted. However, it is not understandable at present. More detailed structure analysis needs to be done.

WAXD Analysis

Figure 2 shows the WAXD pattern of PU, PU10, and PU20. The inset is the WAXD pattern of POSS. It can be read from the inset picture that there is a peak at $2\theta = 6.8^\circ$, corresponding to the paracrystalline structure of POSS.²⁹ On the WAXD pattern of PU10 and PU20, the same peak can also be found. Apparently, the peak height increases with the POSS concentrations. The WAXD pattern confirms that the POSS has been successfully incorporated into the PU electrospun mats. In addition, the POSS molecules aggregate in the PU electrospun fibers as they do in their original state.

Morphology Observations

The morphology of the PU and PU20 electrospun mats is shown in Figure 3. It can be seen from Figure 3(a) that the electrospun fibers of PU are straight, and the fiber size is as thin as $\sim 0.3\text{ }\mu\text{m}$ [Figure 3(b)]. However, the fibers of PU20 are distorted [as shown in Figure 3(c)], and the fiber size increases apparently. In Figure 3(d), it can be seen that some of the fibers are even thicker than $2\text{ }\mu\text{m}$. It is apparent die-swelling phenomenon. Such phenomenon is always caused by the increased elasticity of the polymer chains.³⁰

Fong and co-workers³⁰ have revealed that the fiber size of the polybutadiene rubber increases markedly from 1–2 to 5–10 μm as the concentration of spinning solution is higher than the critical chain entanglement concentration. The thicker PU electrospun fibers and distorted morphology in the present work are then thought to be the result of enhanced chain–chain

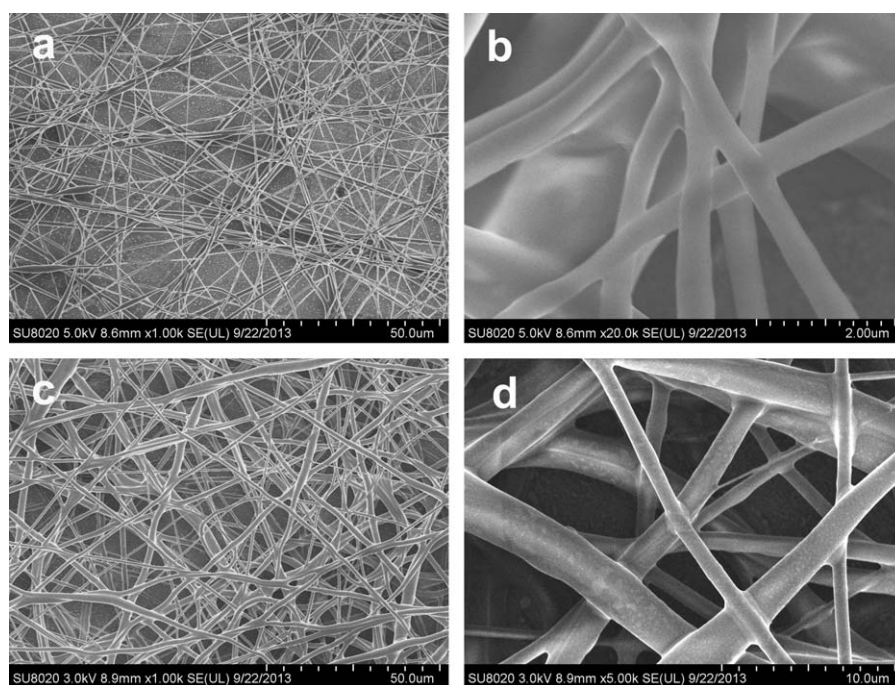


Figure 3. Scanning electron microscopy images of PU (a, b) and PU20 (c, d).

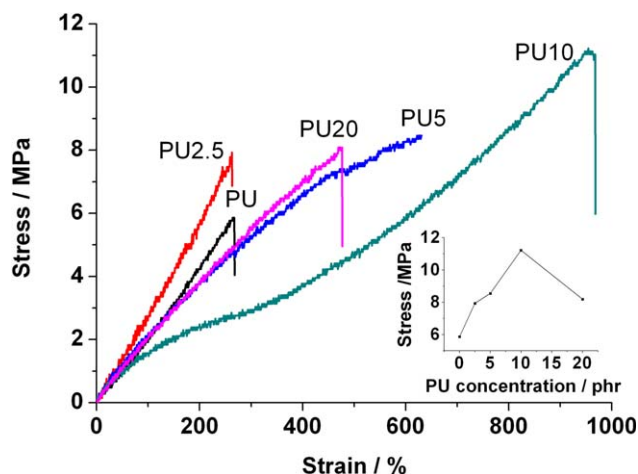


Figure 4. Stress–strain behaviors of PU and PU/POSS electrospun mats. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interactions and the enhanced elasticity of the PU chains. However, it is learnt from FTIR analysis that the hydrogen bonding between the PU chains are weakened by the POSS, and that the POSS does not react with PU or form hydrogen bonds with PU. The question is how the POSS can enhance the chain–chain interactions of PU.

On the fiber surfaces of PU20, some white dots can be seen [Figure 3(d)]. The size of the dots is about several hundred nanometers, coinciding with the size of POSS aggregates observed before.³¹ Recall the WAXD result that the POSS molecules aggregate inside the PU electrospun fibers. Consequently, the white dots are attributed to the POSS aggregates.

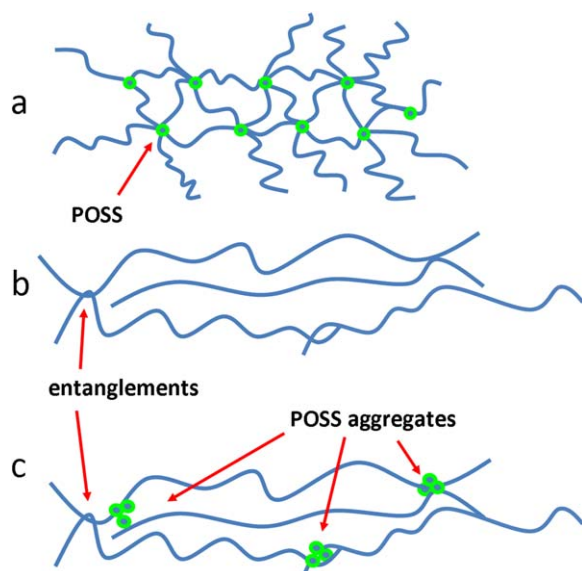


Figure 5. Illustration to chain–chain interactions (a) in chemically cross-linked PU/POSS products, (b) inside pristine PU electrospun fibers, and (c) inside PU electrospun fibers with physically blended POSS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Because the POSS aggregates are small, and the surface energy is considerably high, the PU chains have strong tendency to attach onto these small particles.³² In this case, the interaction of the PU chains might be strengthened. On the other hand, some of the PU chains might be embedded into the POSS aggregates during the formation of these aggregates. When studying polyethylene/carbon black composites, it was found that the carbon blacks could form aggregates in the polymer matrix.³³ Because the aggregates were not stable, they underwent destruction–reformation many times during the mixing process. Some polymer chains were inevitably embedded inside the aggregates.

Once the polymer chains are attached onto the surface of nanoparticles and are embedded inside the aggregates, a kind of polymer–particle dynamic network will be established.^{34,35} The result is that the mobility of polymer chains are restricted, and the elasticity of polymer chains is enhanced. Therefore, it is now understandable that POSS can have strong impact on the molecular motion of PU chains and the morphology of the PU electrospun fibers though there is no reaction and no hydrogen bonds between PU and POSS. It is all because of the small size of POSS molecules and their strong tendency to form

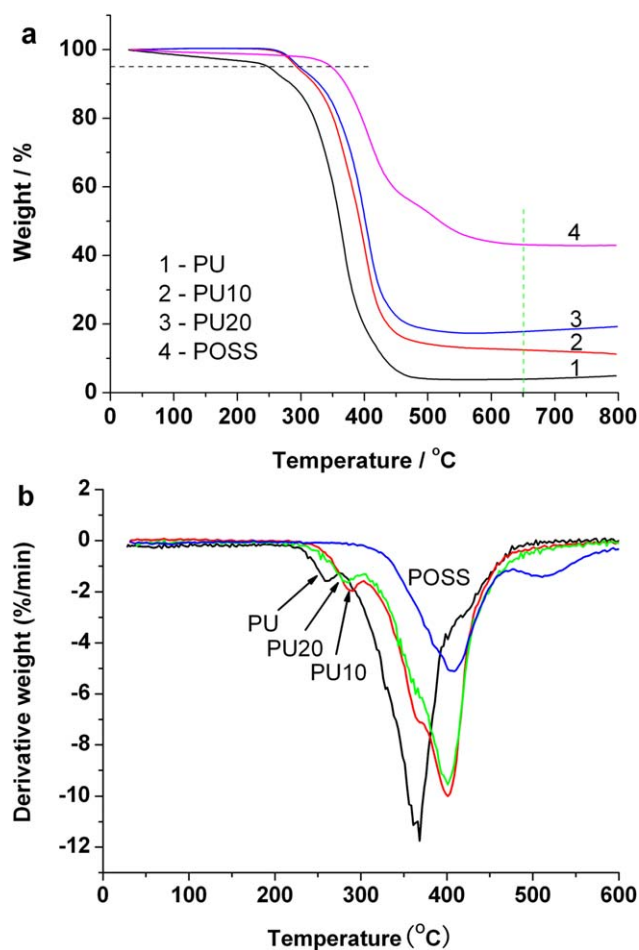


Figure 6. (a) Thermogravimetric diagrams (b) and differential thermal analysis diagrams of PU, POSS, and PU/POSS electrospun mats. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Thermogravimetric Data of PU, PU/POSS Electrospun Mats, and POSS

Sample	First stage decomposition temperature (°C)	5% mass loss temperature (°C)	Inflection temperature (°C)	Char yields (%)
PU	260.2	272.8	373.5	0.56
PU10	289.5	293.1	401.1	12.46
PU20	283.8	297.6	403.1	17.82
POSS	-	347.7	406.1	43.15

aggregates, which lead to a dynamic network composed of PU chains physically crosslinked by POSS.

Mechanical Performances

The typical stress–strain behavior of the PU and the PU/POSS electrospun mats is shown in Figure 4. With the POSS-to-PU ratio increasing, the strength of the electrospun mats increases gradually. It reaches the maximum as the POSS concentration is 10 phr (PU10). However, it is very interesting that the elongation-at-break of the PU/POSS electrospun mats increases simultaneously with the increasing tensile strength, which is quite different from the PU/POSS composites reported before.^{14,15,25,36} For PU10, the tensile strength increases by 91% (from 5.86 to 11.22 MPa), and the corresponding elongation-at-break increases from 266% to 954%. However, Zheng and co-workers²⁵ showed that the elongation-at-break of PU/POSS composite films dropped from 290% to 90% as the tensile strength increased from 2.1 to 6.3 MPa. Only in few reports can the simultaneous increment of strength and elongation-at-break of polymer/nanoparticle composites be found. In the study of Kim et al.,³⁶ they attributed such phenomenon to the network structure formed by the strong physical interactions between polyvinyl alcohol and ferritin.

It has been shown that the polymer chains are loosely oriented in the electrospun fibers.³⁷ This might lead to the early slip of PU chains in the electrospun fibers. Based on the experimental observations, the possible chain–chain interactions are proposed and illustrated in Figure 5 corresponding to the microenvironment inside the PU/POSS composite films, the PU electrospun fibers, and the PU/POSS electrospun fibers.

In the PU/POSS composite films [Figure 5(a)], the PU chains are short and densely crosslinked by the POSS. Although they can respond very quickly to the tensile stress, the extensibility is limited. Figure 5(b) shows the chain–chain interactions inside the PU electrospun fibers. The entanglements among the chains are very weak because the chains are loosely oriented. As a result, the chains may slip against each other very quickly right after the tensile strength is applied on. In Figure 5(c), the PU chains inside the electrospun fibers are physically linked together by the POSS like a polymer–particle network. The early slip between the PU chains is greatly hindered. Because the PU used is a commercial product with relative high molecular weight, they can be extended far more than those PU chains in the PU/POSS composite films, where the PU are always low-molecular-weight prepolymers. Consequently, the PU chains can burden much higher tensile stress and elongation than the unmodified PU electrospun mats.

It can be speculated that the chain–chain interactions of PU become stronger and stronger with the relative concentration of POSS increasing. Subsequently, the strength and the elongation-at-break of PU electrospun fibers/mats can be improved gradually, which is clearly shown in Figure 4. However, when the POSS concentration is as high as 20 phr, the movement of PU chains is restricted too seriously. The result is that the tensile strength and the elongation-at-break of PU/POSS electrospun mats become worse.

Thermostability

The thermal degradation diagrams of PU, POSS, and PU/POSS electrospun mats are shown in Figure 6. The data collected from the thermogravimetric analysis are listed in Table I. Obviously, the thermostability of the PU/POSS mats is much better than that of the pristine PU mat. The 5% mass loss temperatures ($T_{5\%}$) of the PU/POSS electrospun mats are 20°C–25°C higher than that of the pristine PU. In the former report,³⁸ it was thought that POSS was able to reduce the transport rate of reactive species and the diffusion rate of degradation products within the PU matrix by physical re-enforcement. We believe it also works here in the PU/POSS electrospun mats.

The corresponding temperatures of the peak of the first stage of decomposition extracted from derivative thermogravimetric curves are also improved remarkably through addition of POSS, which are listed in Table I. It can be seen that the first stage decomposition temperature of PU10 is higher than that of PU20, suggesting that the physical network inside PU10 is stronger than that in PU20.

CONCLUSIONS

In this work, physically blended PU/POSS composites were prepared and electrospun into mats. Very interestingly, the PU electrospun mats were strengthened and toughened simultaneously. Although there were no chemical reactions between PU and POSS and no hydrogen bonds between PU and POSS, the PU chain–chain interactions were still enhanced by the physically blended POSS. It was speculated that a polymer–nanoparticle dynamic network was formed through attachment of PU chains onto the POSS nanoparticles and embedment of PU chains inside the POSS aggregates. It was because the PU chains inside the electrospun fibers are loosely oriented with poor chain–chain interactions that the blended POSS was able to function as physical crosslinkers to lock up the PU chains.

In summary, a novel usage of POSS as physical nanofillers, not as chemical modifiers, was proposed in this work. The results were satisfying because the strength and the elongation-at-break of the PU/POSS electrospun mats were both improved at the same time.

It can be a good reference to the modification of polymer electrospun fibers/mats using other nanofillers. Because the layered double hydroxides are of nanometer size and plate-like structures, it is expected that the layered double hydroxides can function as well as, or even better than the POSS. Investigations are underway.

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