

Modification of Cellulose Fabrics with Reactive Polyhedral Oligomeric Silsesquioxanes to Improve Their Shape-Memory Performance

Kongliang Xie, Xu Liu, Yanli Zhang

Modern Textile Institute, Donghua University, 1882 West Yan-An Road, Shanghai, 200051, People's Republic of China

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ABSTRACT: Reactive polyhedral oligomeric silsesquioxane (R-POSS) containing multi-*N*-methylol is a functional and attractive starting monomer for new reinforcement materials. R-POSS has excellent potential as a nanosized core for starburst dendrimers and highly reactive multi-*N*-methylol. R-POSS can be used for cellulose fabric finishing to improve its shape-memory performance. Factors affecting the crosslinking reaction of the cellulose with R-POSS were investigated. The physical properties and morphological structure of the cellulose fabrics modified with R-POSS are discussed with respect to the crease recovery angle, the whiteness index, micro-Fourier transform infrared spectroscopy, and scanning electron microscopy. The results show that the crease recovery angle of the fabric

modified with R-POSS obviously increased. With increasing R-POSS concentration, the crease recovery angle of the modified fabric sharply increased. R-POSS readily crosslinked to cellulose and improved the elastic recovery of the cellulose fabrics. The surfaces of the cellulose fibers modified with R-POSS were smooth and full. The inclusion of R-POSS with dimethylol dihydroxyl ethylene urea to modify the cellulose showed very interesting results. It showed a good combination of an increase of crease recovery angle and a decrease in tensile strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1872–1877, 2010

Key words: crosslinking; mechanical properties; nanotechnology; resins

INTRODUCTION

Cellulose fiber is an excellent natural polymer biomaterial, but it also suffers from some inferior properties, such as a low resiliency.^{1–5} When cotton fabrics are twisted or rubbed when they are washed or worn, the cellulose macromolecules shift and undergo plastic deformation. Consequently, the fabric shrinks and wrinkles. *Shape memory* refers to the ability of cellulose materials to remember or keep their shape on demand, even after rather severe deformation. A number of attempts have been made to improve cellulose resiliency for shape-memory purposes.^{6–8} Crosslinking agents containing *N*-methylol groups, such as dimethylol dihydroxyl ethylene urea (DMDHEU) and dimethyl dimethylol dihydroxyethylene urea, have been proven to be the most effective compounds for finishing cellulose fabrics.^{7,9,10} When cellulose fabrics are crosslinked with DMDHEU, the crease recovery angles (CRAs) of the finished cellulose fabrics significantly increase. The finished cellulose materials have excellent shape memory. Cellulose to which crosslinking has been introduced has improved elastic recovery because of

the inhibition of slippage between the molecules when forces are applied. However, because of the problem of formaldehyde release, some nonformaldehyde crosslinking compounds or polymers are developed. Poly(carboxylic acid)s, especially 1,2,3,4-butanetetracarboxylic acid and citric acid, have been widely investigated. Sodium hypophosphite is used as a catalyst for the formation of an anhydride intermediate of 1,2,3,4-butanetetracarboxylic acid. Excellent wrinkle recovery in treated cellulose fabrics is obtained. However, its disadvantages are that it can cause a shade change of dyed fabrics and that it brings about eutrophication in rivers because of the phosphorus in it.^{11,12}

For both dimethyloldihydroxyethylene urea and poly(carboxylic acid)s as crosslinking agents for cellulose fabrics, the major disadvantage is the significant loss in tensile strength. Some new materials, such as β -cyclodextrin, nano-SiO₂, poly(*N*-vinyl-2-pyrrolidone), and aliphatic urethane, have been applied as additional agents to overcome this disadvantage.^{13–18} However, reports on novel crosslinking monomers are lacking. Polyhedral oligomeric silsesquioxane (POSS) has a nanometer-sized confined structure with a cubic silica core and can be functionalized with a variety of organic compounds. POSS can be effectively incorporated into polymers by copolymerization, grafting, or even blending through traditional processing methods.^{19–25} The nanoeffect has been

Correspondence to: K. Xie (klxie@dhu.edu.cn).

demonstrated for unusual strength, high surface energy, surface reactivity, and high thermal stability.^{4,26,27} Reactive polyhedral oligomeric silsesquioxane (R-POSS) containing multi-*N*-methylol groups is a novel active monomer that possesses a high reactivity. After cellulose fabrics are treated with a crosslinking monomer containing POSS nanoparticles, their physical properties are improved.

In this study, novel R-POSS was used to improve the shape-memory properties of cellulose fabrics. The structure of R-POSS is shown in Scheme 1.

The factors affecting the crosslinking reaction of the cellulose with R-POSS were investigated. The physical properties and morphological structure of the cellulose modified with R-POSS are discussed. The physical properties of cellulose fabrics modified with the inclusion of R-POSS and DMDHEU are also discussed.

EXPERIMENTAL

Materials

R-POSS was obtained from the National Engineering Research Center for the Dyeing and Finishing of Textiles (Shanghai, China). DMDHEU was obtained from Handa Chemical Co. (Shanghai, China). Scoured and bleached cellulose (cotton) fabrics were obtained from Jinqiu Textile Co. (Shaoxing, China). Other chemicals were obtained from Shanghai Chemical Reagent Plant (Shanghai, China).

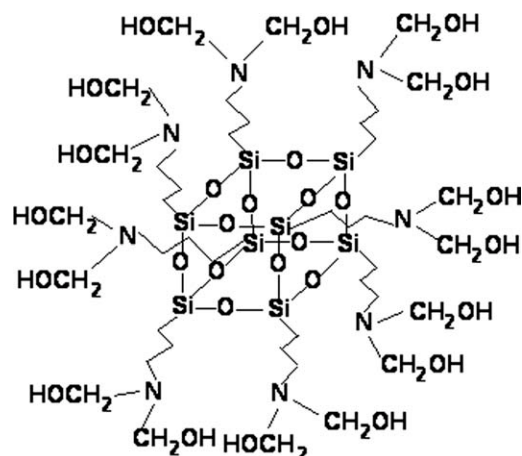
Modification of the cellulose fabrics with R-POSS

R-POSS was diluted with distilled water to a certain concentration. Citric acid and MgCl₂ as catalysts were used in the crosslinking reaction. The mixtures were sufficiently mixed by stirring at room temperature.

The cellulose fabrics were padded with the R-POSS mixtures to give an 80% wet pickup. The dry temperature and time were 95°C and 3 min, respectively. After drying, the fabrics were cured for a specified time at a certain temperature.

Measurements

The dry CRA was determined according to ASTM D 1296-98. The values of CRA in both the warp and weft directions were determined. The samples were conditioned at 20°C and 65% relative humidity for at least 24 h before testing. The tensile strengths of the modified samples were tested according to ASTM D 2256-98. The Commission Internationale de l'Éclairage whiteness index was tested according to AATCC test method 110-1989. The fabrics' color yield (K/S , where K is the absorption coefficient of the substrate and S is the scattering coefficient of the substrate) was determined with a Datacolor SP600⁺



Scheme 1 Chemical structure of R-POSS.

spectrophotometer (Lawrenceville, NJ). The absorbance was measured in the visible spectrum region from 400 to 700 nm, and the reflectance at the wavelength of maximum absorption (R) was used to calculate the color yield of the fabrics with the Kubelka–Munk equation:

$$K/S = \frac{(1 - R)^2}{2R} \quad (1)$$

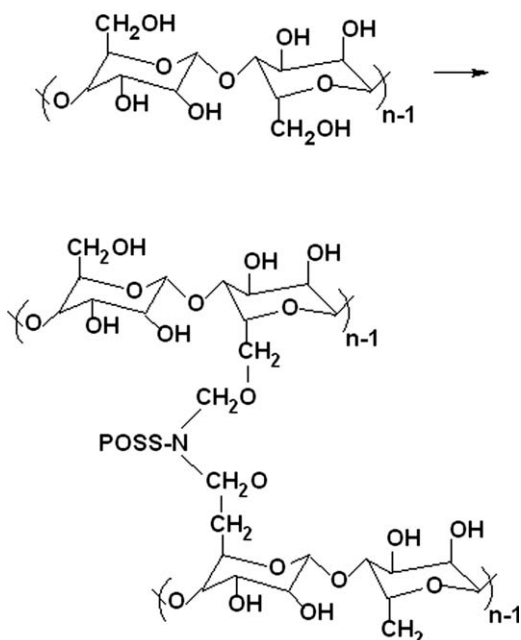
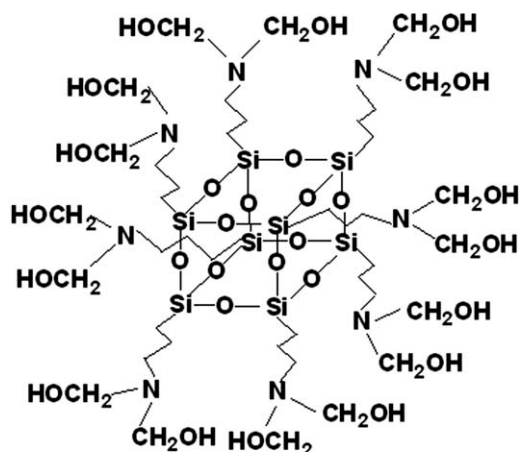
Micro-Fourier transform infrared (micro-FTIR) spectra of the samples were measured by the OMNI Sampler of a Nexus 670 FTIR Raman spectrometer (Nicolet Analytical Instruments, Madison, WI) with a single attenuated total reflection (ATR) reflecting method. For scanning electron microscopy (SEM) analysis, the samples were sputtered with gold and then examined with a JSM 5600LV scanning electron microscope (JEOL, Tokyo, Japan), operated at 15 kV.

RESULTS AND DISCUSSION

Effects of the curing temperature and curing time on the crosslinking reaction of the cellulose fabrics with R-POSS

R-POSS is a novel functional and highly reactive POSS. It is an attractive starting monomer and has a corner-capping framework of condensed POSS trisilanol. R-POSS has excellent potential as a nanosized core for starburst dendrimers and highly reactive multi-*N*-methylol. The highly reactive multi-*N*-methylol of R-POSS can be used to modify cellulose fibers and form a network structure. The crosslinking reaction of cellulose and R-POSS is shown in Scheme 2. In the crosslinking reaction, POSS particles are dispersed in the cellulose host matrix, bonding to the cellulose through covalent bonds.

The effect of the curing temperature on the crosslinking reaction of cellulose fabrics with R-POSS was investigated with 0.1% citric acid, 1.5% (w/w)



Scheme 2 Crosslinking reaction of cellulose and R-POSS.

MgCl_2 , and a curing time of 1.5 min. The results are shown in Table I. A curing temperature of 120°C resulted in a small increase in CRA. With increasing curing temperature, the CRA of the modified samples significantly increased. When the curing temperature reached 150°C, the CRA of modified samples increased to 168.15° (that of the control sample was 104.71°). It was clear that the elastic recovery properties of the modified samples improved significantly because of the crosslinking reaction of the cellulose fabrics with R-POSS. The cellulose macromolecules contained large amounts of hydroxyl groups. The chemical structure of R-POSS had numerous highly reactive *N,N*-dimethylol groups. They could be used to crosslink the cellulose macromolecules and form a network structure. The shape-memory performance of the cellulose materials was attributed to the slippage being inhibited among the cellulose

TABLE I
Effects of the Curing Temperature on the Physical Properties of Modified Cellulose Fabrics with R-POSS (1.6% w/w R-POSS)

Sample	Curing temperature (°C)	CRA: W + F (°)	Whiteness	Tensile strength (N)	
				Warp	Weft
Control		104.71	73.93	303.3	747.6
1	120	113.96	74.37	282.9	738.2
2	130	127.14	74.53	276.3	695.9
3	140	145.02	72.30	272.6	667.4
4	150	168.15	68.15	223.8	598.5
5	160	171.5	64.40	195.4	526.7

W + F = Warp and filling.

macromolecules because of the crosslinking reaction. Meanwhile, the whiteness index and tensile strength of the modified cellulose samples decreased. The decrease in the tensile strength of the modified cellulose samples was that the slippage between the cellulose macromolecules was inhibited because of the crosslinking reaction. This was in agreement with previous studies.^{7,10,11}

The effect of the curing time on the crosslinking reaction with 0.1% citric acid, 1.5% MgCl_2 (w/w), and a curing temperature of 150°C is shown in Table II. The effect of the curing time on the crosslinking reaction was also obvious. With increasing curing time, the CRA of the modified samples increased noticeably (from 104.71 to 173.67°). However, when the curing time exceeded 1.5 min, the whiteness index decreased obviously. As shown in Tables I and II, the crosslinking reaction between cellulose and R-POSS with a curing temperature of 150°C and a curing time of 1.5 min was reasonable.

Effect of the catalyst concentration on the crosslinking reaction of the cellulose fabrics with R-POSS

The concentration of MgCl_2 as a catalyst affected the crosslinking reaction of the cellulose fabrics with R-POSS. The effect of the catalyst concentration on

TABLE II
Effects of the Curing Time on the Physical Properties of Modified Cellulose Fabrics with R-POSS (1.6% w/w R-POSS)

Sample	Curing time (min)	CRA: W + F (°)	Whiteness	Tensile strength (N)	
				Weft	Warp
Control		104.71	73.93	303.3	747.6
1	0.5	135.41	72.36	295.4	653.2
2	1.0	158.57	70.18	258.1	634.7
3	1.5	168.15	68.15	223.8	598.5
5	2.0	173.67	63.62	210.3	588.4

TABLE III
Effects of the Catalyst Concentration on the Physical Properties of Modified Cellulose with R-POSS

Sample	MgCl ₂ (% w/w)	CRA: W + F (°)	Whiteness	Tensile strength (N)	
				Weft	Warp
Control		104.71	73.93	303.3	747.6
1	0.5	119.94	72.35	283.9	694.2
2	1.0	134.02	70.63	257.2	632.7
3	1.5	168.15	68.15	223.8	598.5
4	2.0	169.21	67.23	206.0	587.3

the crosslinking reaction with 0.1% citric acid, 1.6% R-POSS, a curing temperature of 150°C, and a curing time of 1.5 min are shown in Table III. These results indicate that when the concentration of MgCl₂ exceeded 1.0% (w/w), the CRA of modified samples increased significantly. So, an MgCl₂ concentration of 1.5% was needed to improve the crosslinking reaction of the cellulose fabrics with R-POSS.

Effect of the R-POSS concentration on the physical properties of the cellulose fabrics with R-POSS

As a property of the crosslinking agent, the R-POSS concentration had a very important effect on the physical properties of the cellulose fabrics. The effect of the R-POSS concentration on the physical properties of the modified cellulose with R-POSS is shown in Table IV. The crosslinking reaction conditions were 1.5% MgCl₂, 0.1% citric acid, a curing temperature of 150°C, and a curing time of 1.5 min. When the R-POSS concentration was 0.4%, the CRA of the modified sample increased obviously. With increasing R-POSS concentration, the CRA of the modified sample increased further. This demonstrated that R-POSS possessed a high active ability. It could readily crosslink with cellulose and improve the elastic recovery of the cellulose fabrics.

After the cellulose fabrics were modified with R-POSS, the *K/S* of the modified samples was tested. The *K/S* curves of samples are shown in Figure 1. The figure shows that *K/S* of the modified

TABLE IV
Effects of the R-POSS Concentration on the Physical Properties of Modified Cellulose with R-POSS

Sample	R-POSS (% w/w)	CRA: W + F (°)	Whiteness	Tensile strength (N)	
				Weft	Warp
Control	0	104.71	73.34	303.3	747.6
1	0.4	131.80	71.03	255.2	712.5
2	0.8	143.35	69.10	248.3	687.3
3	1.2	156.62	68.84	236.8	635.8
4	1.6	168.15	68.15	223.8	598.5
5	2.0	179.26	68.01	222.5	581.7

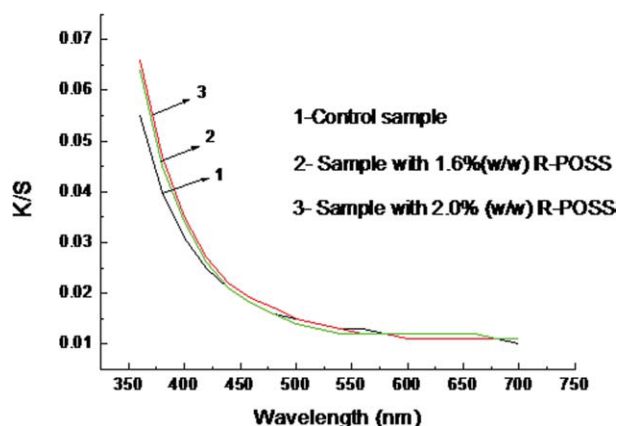


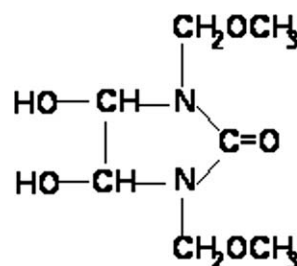
Figure 1 *K/S* curves of the control cellulose sample and cellulose samples modified with R-POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

samples had a small increase at a wavelength of 360–420 nm. This indicates that the modified samples emerged with a little thermal yellowing. This was in agreement with the decrease in the whiteness index.

Inclusion of R-POSS with DMDHEU

DMDHEU is the most effective compound for the finishing of cellulose fabrics. The structure of DMDHEU is shown in Scheme 3.

The inclusion of R-POSS with DMDHEU for finishing cellulose fabrics was also investigated. Usually, cellulose fabrics modified with DMDHEU are regarded as having good shape-memory performances because of their excellent elastic properties. The ingredients of the finishing solution and the physical properties of the modified cellulose samples are shown in Table V. The crosslinking reaction was carried out with 1.5% MgCl₂, 0.1% citric acid, a curing temperature of 150°C, and a curing time of 1.5 min. The results in Table V are very significant. When 20% DMDHEU was applied to finish the cellulose fabric, the CRA of the modified cellulose sample reached 212.7°, and the tensile strengths decreased to 178.37 (weft) and 455.67 (warp). The CRA of the



Scheme 3 Chemical structure of DMDHEU.

TABLE V
Composition of the Inclusion of R-POSS with DMDHEU and the Physical Properties of the Modified Cellulose Fabrics

Sample	R-POSS (% w/w)	DMDHEU (% w/w)	CRA: W + F (°)	Tensile strength (N)	
				Weft	Warp
Control	0	0	104.71	303.3	747.6
1	0	20	212.7	178.37	455.67
2	0.4	19.6	212.1	222.35	511.92
3	0.8	19.2	197.7	229.35	526.43
4	1.6	18.4	190.53	244.97	548.12
5	2.4	17.6	172.1	260.93	577.19

modified cellulose sample with DMDHEU significantly increased, but the retentions of the tensile strength reached 58.8% (weft) and 60.9% (warp). This was in agreement with previous studies.^{11,12} When 0.4% R-POSS was added to the DMDHEU solution (19.6%), the CRA of the modified cellulose sample also reached 212.1°, but the retentions of tensile strength were 73.4% (weft) and 68.5% (warp). This could be attributed to the cellulose matrix modified with POSS. Inorganic POSS nanoparticles crosslinked among the organic cellulose macromolecules improved the plastic properties of the cellulose materials. The cellulose containing POSS nanoparticles may have decreased the loss of tensile strength. It further indicated that R-POSS was crosslinked in the cellulose matrix and formed novel organic–inorganic hybrid materials. Table V also indicates that compared with the sample treated with 20% MDHEU, with increasing R-POSS concentration in the inclusion solution of DMDHEU, the CRA of the modified cellulose samples slightly decreased, and the tensile strength increased.

Chemical structure and morphology of cellulose modified with R-POSS

To further characterize the chemical structure and morphology of cellulose modified with R-POSS, the micro-FTIR spectra and SEM of the samples were measured. The micro-FTIR spectra and SEM micrographs of the control sample and modified cellulose with 1.6% R-POSS at a curing time 1.5 min and a temperature 150°C are shown in Figures 2 and 3, respectively. The micro-FTIR spectra of the cellulose exhibited bands at 3470 cm^{-1} assigned to $-\text{OH}$ vibrations. The $-\text{OH}$ vibration peaks at 3470 cm^{-1} of the cellulose modified with R-POSS obviously became lower. This demonstrated that the amount of $-\text{OH}$ of the cellulose modified with R-POSS decreased. This reconfirmed that R-POSS was able to form covalent bonds with cellulose

SEM analysis was used to characterize changes in the surface morphology of the cellulose samples.

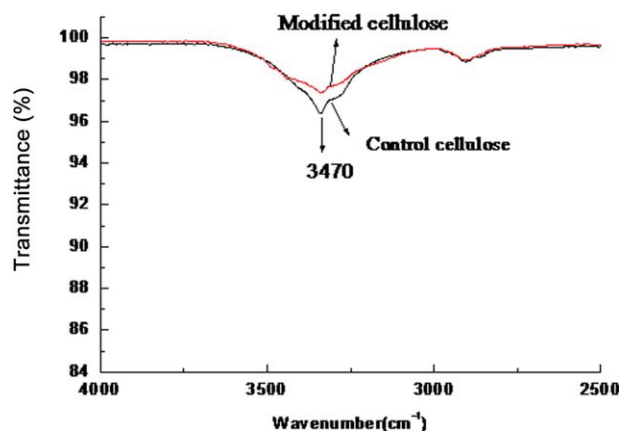


Figure 2 FTIR spectra of the control cellulose sample and cellulose sample modified with R-POSS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Representative SEM micrographs of the samples taken at a magnification of 1000 \times are shown in Figure 3. Figure 3(a) shows the SEM micrograph of the control sample, and Figure 3(b) shows the SEM micrograph of

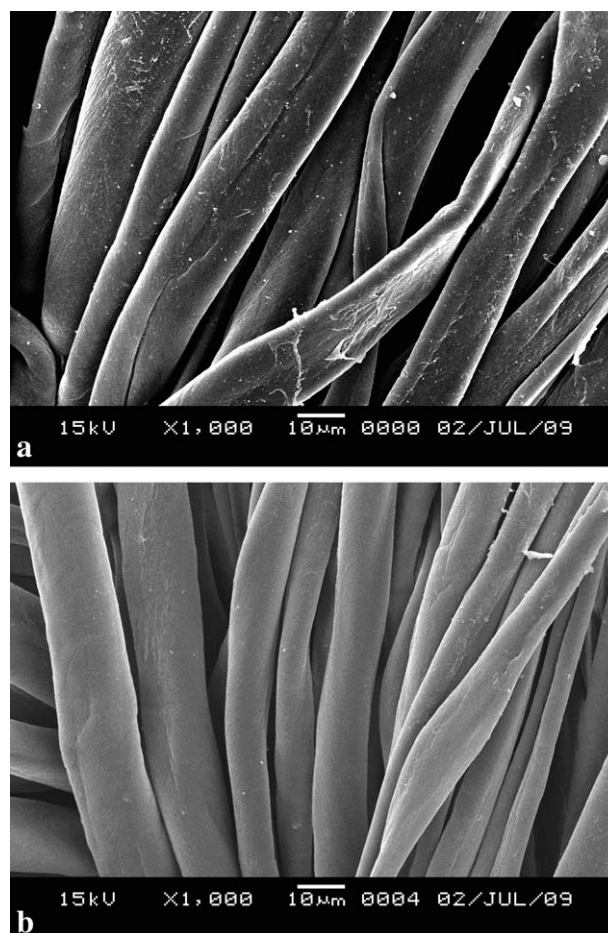


Figure 3 SEM micrographs of the cellulose samples: (a) the control cellulose sample and (b) the cellulose sample modified with R-POSS.

cellulose with R-POSS. As shown in Figure 3(a,b), the surface of the cellulose fibers modified with R-POSS were smooth and full. Compared with control cellulose fibers, the cellulose fibers modified with R-POSS imparted excellent elastic surfaces.

CONCLUSIONS

R-POSS as a crosslinking agent readily crosslinked with cellulose and improved the elastic recovery properties of the cellulose fabrics. It was used for cellulose fabric finishing in shape memory. Cellulose was modified with 1.5% $MgCl_2$, 0.1% citric acid, a curing temperature of 150°C, a curing time of 1.5 min, and an R-POSS concentration of 1.6%; the CRA of the modified sample was significantly improved. With increasing R-POSS concentration, the CRA of the modified fabric increased further. When the inclusion of R-POSS with DMDHEU was applied, the CRA of the modified cellulose fabric increased, and the loss of tensile strength decreased. The surface of the cellulose fibers modified with R-POSS was smooth and full. Cellulose fibers modified with R-POSS imparted an excellent elastic surface. R-POSS as a crosslinking agent has the potential for application in the improvement of the physical properties of biocellulose materials.

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