

The Properties of Modified Polysulfonamide Fabrics with Lamellar Magnesium Hydroxide Crystals

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ABSTRACT

Lamellar magnesium hydroxide crystals were prepared successfully on the surface of polysulfonamide fibers with carboxylic acid groups. The polysulfonamide fabrics with Mg(OH)₂ crystals were characterized by Scanning electron microscopy, Inductively coupled plasma atomic absorption spectrometer X-ray diffraction, Vertical flammability test and Thermalgravimetric analysis. The vertical flammability test showed that the damaged length of original polysulfonamide fabrics was 34mm, while that of the polysulfonamide fabrics with Mg(OH)₂ crystals (treated by 7.5% NaOH solutions) was 14mm. In addition, the Mg(OH)₂ crystals played a critical role in the improvement of thermal stability and heat insulation of polysulfonamide fabrics.

Keywords: Lamellar magnesium hydroxide, secondary growth, polysulfonamide fabrics, flame retardancy

INTRODUCTION

Inorganic coatings (metallic, ceramic, zeolitic or carbon-made) have increased research interest due to their high thermal, chemical, and mechanical stabilities and solvent-resistant properties, which make them suitable for various applications [1-4]. Moreover, fabrics coated with inorganic crystals have received special attention because the addition of the inorganic crystals can improve the properties of the fabrics obviously [5-7].

Mg(OH)₂, as a flame retardant, has been widely used in many polymers, electric cables, buildings, and decoration materials because of its smoke suppression property, flame retardancy and good thermal stability which allows higher processing temperature. If uniform Mg(OH)₂ crystals at the fiber surface are formed, such a char barrier can insulate the un-decomposed area from heat and fire, suppress combustion and eventually cause the composite to self-extinguish. However, although significant

progress has recently been made in the study of preparation and properties of Mg(OH)₂ crystals, the previous works seldom report the possibility for generating Mg(OH)₂ crystals on the fiber surface to improve fabric properties.

The secondary growth method, which can affect the growth direction of Mg(OH)₂ crystals and easily result in the lamella-like crystals, is the most commonly used for the growth of Mg(OH)₂ crystals [8]. We have successfully prepared lamellar Mg(OH)₂ crystals on cotton fabrics by the secondary growth method, which show better fire-proof properties. In this work, we further studied the growth of Mg(OH)₂ crystals on polysulfonamide (PSA) fibers, which need further improvement of the anti-flammability performance though possessing excellent thermal stability and mechanical properties. The morphology of crystals on the fiber surface was studied. In addition, the properties of treated PSA fabrics, including thermal conductivities, flammability, thermal stability, and tensile strength, were also investigated. We expect that our strategy to fabricate the fabrics with inorganic thin films will be of general interest and influence many other fields.

EXPERIMENTAL SECTION

Materials

The PSA fabrics were purchased from Shanghai Textile Research Institute. The molecular structure of PSA is shown in *Figure 1*. The warp and weft density of twill weave fabrics were 32 threads/cm and 21 threads/cm respectively, and they were either in warp or weft 19.7 tex. Magnesium chloride hexahydrate, aqueous ammonia (37%), sodium hydroxide, diethyl ether anhydrous, and polyvinylpyrrolidone (PVP, molecular weight = 1000 g/mol) were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. All the chemical reagents used in the experiment were analytical grade and used without further purification.

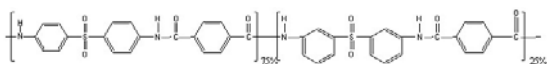


FIGURE 1. The molecular structure of PSA.

Introduction of Carboxylic Acid Groups on PSA Fibers

PSA fabrics were washed with anhydrous ether in a Soxhlet Extractor for ten cycles to remove the wax, grease and other chemicals before the surface treatment. The washed PSA fabrics were immersed in the NaOH solutions with different concentrations (the NaOH contents in weight percentage (w/w, %) were 2.5, 5.0, and 7.5, respectively) for 30 minutes, then took out and passed through a laboratory padder (Rapid Labortex Co., Ltd, Taiwan) at a nip pressure of 2 kg/cm² to reach an average pick-up of 60 % ~ 70 %. The fabrics were dried then at 80 °C for three minutes and cured at 180 °C for two minutes in a Mathis curing oven. Finally, the fabrics were washed extensively with double-distilled water.

Secondary Growth of Mg(OH)₂ Crystals on PSA Fibers

The Mg(OH)₂ stock solutions were prepared using PVP as dispersant (Mg(OH)₂ concentration: 3.13×10⁻³ mol/l) and a piece of treated PSA fabric was placed in a conical flask containing stock solutions. The secondary growth was performed following the same procedures according to the reference [8] and the secondary growth time was varied as one, three and seven days, respectively.

Measurement and Characterization

The amounts of Na⁺ and Mg²⁺ on the surface of PSA fibers were determined by inductively coupled plasma atomic absorption spectrometer (ZEE nit700, Analytik Jena AG, German). The amounts of carboxylic acid groups and Mg(OH)₂ seed crystals were calculated according to the amounts of Na⁺ and Mg²⁺, respectively (the coordination number between carboxylic acid groups and sodium ions was shown in Figure 2) [8].



FIGURE 2. The hydrolysis of amide linkages under the NaOH modification.

The morphology of the Mg(OH)₂ crystals on the PSA fibers was characterized with a Scanning electron microscopy (JSM-5600 LV SEM, JEOL, Tokyo, Japan). X-ray diffraction (XRD) patterns of the

original and treated PSA fibers were recorded using D/max-2550 PC (Rigaku), at an operating voltage of 40 kV and current of 200 mA. The samples were scanned over the range 2θ=10-60° and measurements were recorded at every 0.02° interval. Thermal analysis was carried out with TG209F1 (NETZSCH, Germany), at a temperature ranging from 25°C to 640°C under nitrogen atmosphere with heating rate of 10°C/min. The tensile strength of the PSA fabrics was measured using a Universal Testing Machine (Model H10K-S, Tinius Olsen, Inc., Horsham, PA, USA) equipped with an environmental chamber for temperature control in accordance with ISO 13934-1:1999. The flammability of the fabrics was evaluated through the vertical flammability test (A specimen of 15 cm (warp) × 5 cm (weft) was used) according to the standard ISO 6940:1984. The pictures of the samples were recorded by using a digital camera. The thermal conductivity of the fabrics was tested by using a DRL-II thermal conductivity cryoscopy (Xiangtan Xiangyi Instrument Co. Ltd., Hunan, P. R. China). All the samples were conditioned for 24h in the constant temperature and moisture room (23 ± 1 °C and 65 ± 1 %, respectively) before testing.

RESULTS AND DISCUSSION

Effect of NaOH Modification on the PSA Fibers and Mg(OH)₂ Lamellar Crystals Growth

SEM images of the PSA warp fibers before and after the NaOH treatment are shown in Figure 3. Before the modification, the fibers had a smooth surface as shown in Figure 3a. However, after the treatment, some amide bonds of PSA fibers were broken (Illustration in Figure 2). With the concentrations of sodium hydroxide increasing, the treated fibers surface became rougher and some cavities were created on the fibers' surface. Especially, for the fibers with 7.5% NaOH treatment, the surface was partly corroded and exfoliated. The negative charges on the fibers and positive charges of Mg(OH)₂ crystals under its isoelectric point, [9] would allow stronger electric force between the Mg(OH)₂ seeds in the stock solutions and the modified PSA fabrics surface. As shown in Table I, the amounts of Mg(OH)₂ crystals on the PSA fibers increased with the increase of carboxylic acid groups. The Mg(OH)₂ seeds in the solutions were absorbed on PSA fibers via electric forces, and this process followed the pseudo second-order kinetic model and Langmuir isotherm [9, 10].

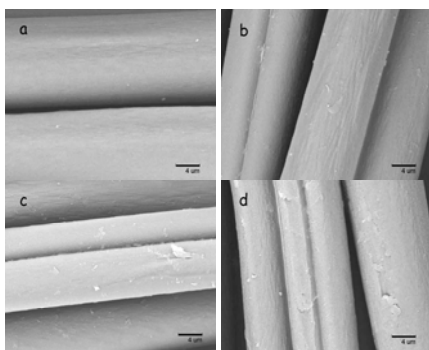


FIGURE 3. SEM images of PSA fibers before (a) and after the treatment with 2.5% (b), 5.0% (c) and 7.5 % (d) NaOH solutions.

The effects of NaOH treatment and growth time on the morphology of $Mg(OH)_2$ crystals are shown in Figure 4. Here, the fibers with 2.5% NaOH treatment had few active sites on the surface, resulting that the lamellar $Mg(OH)_2$ crystals hardly grew on the fiber surface after the one day' growth. Further, three days later, some $Mg(OH)_2$ crystals could be observed on the different fibers surface. The presence of the interconnected $Mg(OH)_2$ lamellar crystals show that

such crystals may result from growth within the cavities of the fibers. With longer growth time (seven days), it is worthy of noticing that the whole surface of the fibers was covered with a thick layer of lamellar $Mg(OH)_2$ crystals. With the presence of more negative charges on the fibers, the $Mg(OH)_2$ crystals on the fibers with 7.5% NaOH treatment show a more regular lamellar structure (Figure 4i) and a sharp increase in diameter ($3.2 \pm 0.7 \mu m$). Thus, the results presented here demonstrated that the ionic density and growth time had a critical effect on the morphology of $Mg(OH)_2$ crystals.

Figure 5 shows the XRD patterns of the original and treated PSA fibers after the secondary growth (seven days) process of $Mg(OH)_2$ crystals. The PSA fibers had the decreases of peak value and lower proportion of diffraction peak ($2\theta=16.5^\circ$) compared with the fibers treated with NaOH. The results show that NaOH treatment could effectively disturb the perfect arrangement of bonded sheets of PSA molecules, resulting from the para-sulfonamide block shifting to higher d-spacings.

TABLE I. Amounts of sodium hydroxide, carboxylic acid groups and $Mg(OH)_2$ covering on the PSA treated fibers.

Sodium hydroxide concentrations (%)	Sodium amounts (mg/g)	Carboxylic acid groups concentrations (mmol/g)	Magnesium hydroxide amounts (mg/g)	$Mg(OH)_2$ amounts after secondary growth (mg/g)
2.5	0.5420	0.0236	0.2531	28.018
5	0.6473	0.0281	0.2741	29.781
7.5	0.6845	0.0298	0.3024	31.194

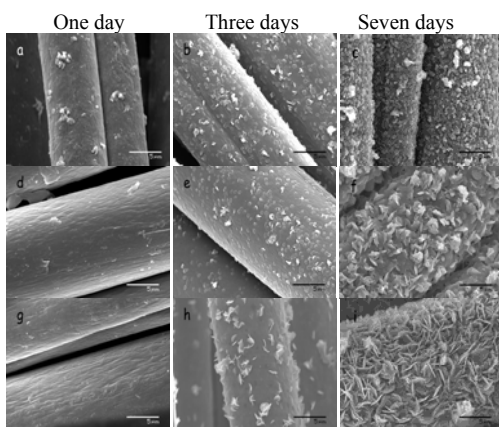


FIGURE 4. SEM images of lamellar $Mg(OH)_2$ crystals growing on the PSA fibers: 2.5% (a-c), 5.0% (d-f) and 7.5% NaOH treatment (g-i), respectively.

The sharp peaks could be indexed as hexagonal structured $Mg(OH)_2$ (JCPDS Card 86-0441) and there was no additional phase peak in the XRD pattern, indicating that the product had a high purity. Especially, the patterns of samples (7.5% NaOH treatment) indicate that $Mg(OH)_2$ crystals had an excellent lamellar structure in accordance with their morphology as seen from SEM images (Figure 4i). In addition, the calculation according to the Scherrer's equation (Table II) show that the $Mg(OH)_2$ crystals growing on the fibers with 7.5% NaOH treatment had the highest diameter-thickness ratio of the crystals (~ 1.6), which provided further evidence of the uniform lamellar structure.

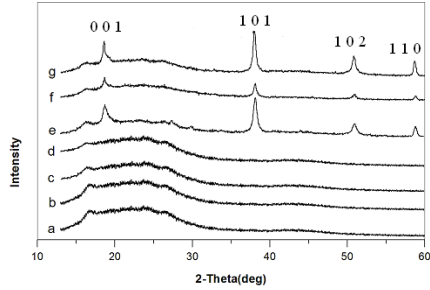


FIGURE 5. XRD patterns of original fibers (a), treated fibers with NaOH solutions (2.5% (b), 5.0% (c) and 7.5% (d) NaOH treatment) and PSA fibers (2.5% (e), 5.0% (f) and 7.5% (g) NaOH treatment) with Mg(OH)₂ crystals.

TABLE II. The size of Mg(OH)₂ crystals on treated PSA fibers after seven days' growth.

Sodium hydroxide concentrations (%)	Mg(OH) ₂ crystal size [001] (nm)	Mg(OH) ₂ crystal size [110] (nm)	Mg(OH) ₂ crystal size [101] (nm)
2.5	24.884	16.759	17.676
5.0	24.709	16.891	18.276
7.5	24.623	14.962	15.245

Effect of the Lamellar Mg(OH)₂ Crystals on the Flammability, Thermal Stability and Thermal Conductivities of the PSA Fabrics

The flammability of the original and treated PSA fabrics covered with Mg(OH)₂ layers was investigated using the vertical flammability test, and the flammability images are shown in Figure 6. The damaged length of original PSA fabrics was 34mm (Table III). With the addition of Mg(OH)₂ layers as a mass transport barrier to the volatile products generated during decomposition, the damaged length decreased dramatically. Especially, the damaged length of the PSA fabrics treated with 7.5% NaOH treatment, which was only 14mm. This was mainly due to the severe decomposition of Mg(OH)₂ crystals (H₂O and MgO) at high ignition temperature (above 800°C) [11]. It is important to note that water vapor makes the surface combustion difficult to proceed and MgO is also a good flame-proof material, which provides the better anti-flammability of PSA fabrics.

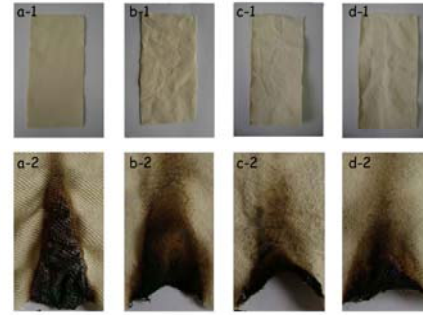


FIGURE 6. The images of treated PSA fabrics with Mg(OH)₂ crystals before (a-1, b-1, c-1 and d-1~ original, 2.5%, 5.0% and 7.5% NaOH treatment) and after (a-2, b-2, c-2 and d-2~ original, 2.5%, 5.0% and 7.5% NaOH treatment) the flammability test.

TABLE III. Thermal conductivity and flammability test results of the original and treated PSA fabrics with Mg(OH)₂ crystals.

	Thermal conductivity W/(m·k)	Damaged Length (mm)
Original PSA fabrics	0.083	34
PSA fabrics treated with 2.5% NaOH solutions (secondary growth for 7 days)	0.070	27
PSA fabrics treated with 5% NaOH solutions (secondary growth for 7 days)	0.066	20
PSA fabrics treated with 7.5% NaOH solutions (secondary growth for 7 days)	0.062	14

The TG curves of the original and treated PSA fabrics are shown in Figure 7. It was observed that the original PSA fabrics exhibited a pronounced weight loss step in the temperature range of 460-640°C. However, for the PSA fabrics with Mg(OH)₂ crystals, there were two main degradation process. The first onset endothermic decomposition temperature was 323°C attributed to the decomposition of Mg(OH)₂ crystals, [11,12] while

the other onset endothermic decomposition temperature rose to 440°C corresponded to the decomposition of PSA fibers. The total weight loss of treated PSA fabrics (2.5%, 5% and 7.5% NaOH solutions) with Mg(OH)₂ layers at the range of 323-640°C was 50.8%, 49.0% and 46.1% respectively, which was lower than that of the original PSA fabrics (54.2%). These results demonstrate that the addition of Mg(OH)₂ crystals could provide the further improvement of thermal stability of PSA fabrics.

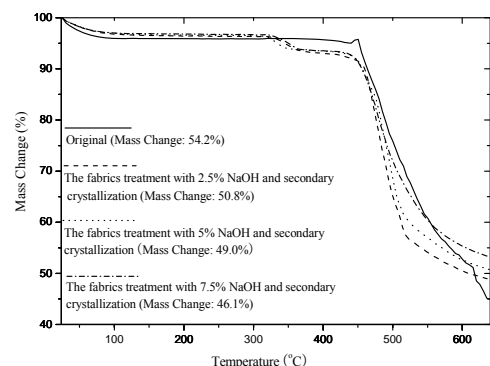


FIGURE 7. TG curves of the original and treated PSA fabrics with Mg(OH)₂ crystals.

The thermal conductivity, which is related to the steady-state temperature distribution, is an important parameter in estimating the effectiveness of heat transfer in materials [13]. *Table III* shows that the PSA fabrics with Mg(OH)₂ crystals had lower thermal conductivities compared to the original fabrics and the amounts of Mg(OH)₂ crystals on the fiber surface could affect the heat transfer process. We observed that the treated fabrics (7.5% NaOH treatment) with Mg(OH)₂ crystals showed the lowest thermal conductivity (0.062), which exhibited the best effectiveness of heat insulation. Thus, the Mg(OH)₂ layers as a superior insulator, especially assembling in the porosity of the degraded fibers, could provide the formidable improvement of thermal conductivity of PSA fabrics.

Mechanical Properties of PSA Fabrics with Mg(OH)₂ Lamellar Crystals

The tensile strength data of different PSA fabrics are shown in *Table IV*. Here, the warp tensile strength was higher than that weft mainly due to the difference of Yarn density. After the concentrations of 2.5%, 5.0% and 7.5% NaOH treatment, the weft values had 1.56%, 6.77% and 11.85% decrease while the warp values had 8.64%, 11.69% and 13.95% decrease compared to the original fabrics. It is

noteworthy that, through the presence of the porosity in the fibers, the loading capacity of the fabrics with Mg(OH)₂ crystals was improved and almost equal to the original PSA fabrics. This can be explained by the fact that the crystal growth in the fabric brakes can provide strong bonding effects between Mg(OH)₂ crystals and the degraded fibers and improve tensile strength and as a result the mechanical properties of the fabrics with Mg(OH)₂ crystals were not obviously decreased compared to the original PSA fabrics.

TABLE IV. Tensile strength of the original, treated PSA fabrics and PSA fabrics with Mg(OH)₂ crystals.

	Tensile strength (N)	
	Weft	Warp
Original PSA fabrics	768	1018
The fabrics treated with 2.5% NaOH solutions	756	930
The fabrics treated with 5% NaOH solutions	716	899
The fabrics treated with 7.5% NaOH solutions	677	876
PSA fabrics treated with 2.5% NaOH solutions (secondary growth for 7 days)	765	985
PSA fabrics treated with 5.0% NaOH solutions (secondary growth for 7 days)	758	928
PSA fabrics treated with 7.5% NaOH solutions (secondary growth for 7 days)	750	902

CONCLUSIONS

In summary, the results presented in this work show that lamellar Mg(OH)₂ crystals can be assembled on the surface of PSA fibers after the NaOH modification and secondary growth process. The vertical flammability test data show that the damaged length of original fabrics was 34mm, while that of the fabrics with Mg(OH)₂ crystals (7.5% NaOH treatment) was 14mm. We also demonstrate the growth of Mg(OH)₂ crystals on the fibers had an obvious improvement in the thermal stability and heat insulation of the fabrics. Moreover, the bonding effects between Mg(OH)₂ crystals and the degraded fibers improved the tensile strength of NaOH treated fabrics, and the mechanical properties of the fabrics with Mg(OH)₂ crystals only had a slight decrease compared to the original fabrics. These findings may have various implications on creating new fabrics with inorganic films.

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REFERENCES

- [1] S. L. Wee, C. T. Tye, S. Bhatia, Sep Purif Technol 2008; 63: 500-516.
- [2] E. Romero, J. Molina, A. I. Río, J. Bonastre, F. Cases, Textile Res J 2011; 81: 1427-1437.
- [3] C. I. Su, C. C. Peng, C. Y. Lee, Textile Res J 2011; 81: 730-737.
- [4] K. Qi, X. Wang, J. H. Xin, Textile Res J 2011; 81: 101-110.
- [5] T. Suchada, A. O'R. Edgar, Y. Nantaya, Colloids Surf A 2009; 349: 170-175.
- [6] Y. Qing, X. D. Wang and Z. L. Wang, Nature 2008; 451: 809-813.
- [7] R. Wang, J. H. Xin, X. M. Tao, W. A, Chem Phys Lett 2004; 398: 250-255.
- [8] Q. H. Mao, L. P. Zhang, H. Xu, H. T. Cao, Z. P. Mao, et al, Surf Interface Anal 2011; 43: 903-912.
- [9] V. A. Philips, J. L. Kolbe, H. Opperhauser, J Cryst Growth 1977; 41: 228-234.
- [10] J. C. Yu, A. Xu, L. Zhang, R. Song, L. Wu, J Phys Chem B 2004; 108: 64-70.
- [11] A. Genovese, R. A. Shanks, Polym Degrad Stab 2007; 92: 2-13.
- [12] B. V. L'vov, A. V. Novichikhin, A. O. Dyakov, Thermochim Acta 1998; 315: 135-143.

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