

# Synthesis and surface properties of fluorinated inorganic-organic materials for nylon 6

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**Abstract.** We applied poly(methacrylic acid), PMAA, a stain blocker for nylon fiber, to an inorganic-organic material. We also developed a fluorinated inorganic-organic material (PMAA / tetraethoxysilane, TEOS /2-perfluorooctylethyltriethoxysilane, 17F), and applied it to nylon 6. When the silicate contents in the inorganic-organic materials were 85.5~98.3 mass%, pencil scratch hardness and stain resistance were improved. The materials showed a low surface free energy ( $11 \text{ mJ m}^{-2}$ ), equivalent to that of a typical fluorochemical finishing agent, poly(perfluorooctylethyl acrylate)(P17FA).

**Key words:** nylon 6, fluorinated inorganic-organic, sol-gel process, stain resistance

## 1. Introduction

In the last decade, inorganic or inorganic-organic materials prepared by the sol-gel process have been applied in various fields [1-4]. The sol-gel process offers a low temperature synthesis route to prepare advanced materials, and is particularly important in thin film coatings on glass substrates. This coating technology also has potential in the preparation of advanced organic materials. The inorganic-organic materials prepared by the sol-gel method are useful for improving the surface of organic polymers such as the surface hardness of the materials [5]. There are few reports on surface modification of the polymers by inorganic-organic materials using poly(methacrylic acid), PMAA. The reason is that the inorganic-organic materials have a poor mutual interaction with polymer substrates and PMAA acts as an acid catalyst in the sol-gel process.

We have modified the surface of nylon 6 fabrics to improve stain resistance [6]. Nylon polymers are organic materials which have excellent properties, e.g. flexibility and hydroscopy for fibers and textiles. However, their weak point is that they are easily stained by acid dyes such as Acid Red 40, including juice and wine, because there are amino end groups in the nylon. Therefore, a stain blocker, PMAA, to prevent this staining is usually used in nylon 6 fabrics, so called stain resistant fabrics.

In this study, we applied PMAA to inorganic-organic materials prepared by the sol-gel process as an organic component. We also developed a fluorinated inorganic-organic material with high stain resistance for nylon 6. In this paper, we report on the synthesis and surface properties of inorganic-organic materials with the stain resistance for nylon 6.

## 2. Experimental

### 2.1. Preparation of hydrophobic inorganic-organic materials

PMAA and poly(methyl methacrylate), PMMA were of a commercial origin (Minnesota Mining & Manufacturing Co.(FX-668F (solid content 29.6 mass%)) and Katayama Kagaku Co., respectively).

Their average molecular weights were  $55,000 \text{ gmol}^{-1}$  and  $150,000 \text{ gmol}^{-1}$ , which were determined by a Shodex gel permeation chromatography System 11 using THF as a developing solvent and standard polystyrene. Commercially available tetraethoxysilane, TEOS (Shin-Etsu Chemical. Co.), n-decyltriethoxysilane, 17H, and 2-perfluorooctylethyltriethoxysilane, 17F (Azmax, Co.) were used as raw materials of alkoxysilanes. Ethanol, THF, and nitric acid were reagent grade.

The sols from various proportions of TEOS/PMAA and hydrophobic TEOS/PMAA were prepared as follows: TEOS and PMAA were added to a solution of ethanol and water containing a nitric acid. When other hydrophobic alkoxysilanes (17H or 17F) were used in this sol-gel process, 1.0 mol% of them to TEOS was added to the sol. The mixture was stirred at room temperature for 16 hrs. The solid content of these mixtures was 27.6 mass%. The  $\text{SiO}_2$  contents were calculated by converting all of the TEOS to  $\text{SiO}_2$ . The detailed conditions used to prepare inorganic-organic materials are listed in Tables 1 and 2.

Hydrophobic inorganic-organic films with the stain resistance for nylon 6 were formed on nylon 6 films by the dip coating method (dipping time: 20 min). Heating treatment of this coating film at  $110^\circ \text{C}$  for 15 min formed a hard gel film.

**Table1. Preparation conditions of inorganic-organic films.**

No.	Component/(g) PMAA/TEOS/EtOH/H <sub>2</sub> O/HNO <sub>3</sub>	SiO <sub>2</sub> (mass%)	Appearance
1	0/4.3/7/4.18/0.05	100	Transparent
2	0.002/4.3/7/4.19/0.05	99.8	Transparent
3	0.021/4.3/7.06/4.18/0.05	98.3	Transparent
4	0.21/4.3/7.75/3.99/0.05	85.5	Transparent
5	0.48/4.3/8.14/4.32/0.05	72	Opaque
6	1.1/4.3/11.44/2.61/0.05	53	Opaque
7	2.1/4.3/11.81/4.99/0.05	37	Opaque
8	4.3/4.3/12.47/10.22/0.05	23	Opaque
9	4.3/1.84/5.88/10.22/0.05	11	Transparent
10	4.3/0/0.96/10.22/0	0	Transparent

**Table 2. Preparation conditions of hydrophobic inorganic-organic films.**

No.	Component/(g)	SiO <sub>2</sub>	Appearance
	PMAA/PMMA/TEOS/17H/17F/EtOH/THF/H <sub>2</sub> O/HNO <sub>3</sub> (mass%)		
1	0.021/0/4.3/0/0/7.06/0/4.18/0.05	98.3	Transparent
2	0/0.021/4.3/0/0/0/7.18/4/0.05	98.3	Opaque
3	0.021/0/4.3/0.064/0/7.06/0/4.18/0.05	98.3	Transparent
4	0.021/0/4.3/0/0.13/7.06/0/4.18/0.05	98.3	Transparent

### 2.2. Characterization of the inorganic-organic materials

Surfaces of the inorganic-organic materials were characterized by the contact angles of water and n-hexadecane, by a Shimadzu ESCA-750 X-ray photoelectron spectroscopy (XPS) and by a Perkin-Elmer 1760X attenuated total reflection infrared spectroscopy (IR-ATR). The peak area in the region of 1100–1250 cm<sup>-1</sup> in the reflection IR spectrum was defined as the C-F values on the surface which shows the amounts of fluorines. The C-F value below 20 show background values for PMAA/SiO<sub>2</sub> and PMMA/SiO<sub>2</sub> films without fluorine components.

The micro structures of the hydrophobic inorganic-organic films with stain resistance for nylon 6 were observed by a JEOL JSM-5300 scanning electron microscope. The surface hardness of the films was determined by a pencil scratch hardness instrument using the JIS K-5401 method. The stain resistance was determined by an AATCC-175 method.

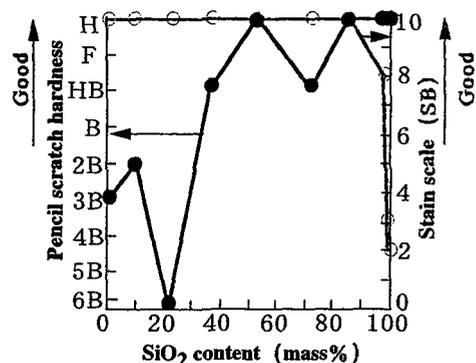
### 3. Results and Discussion

Novel inorganic-organic materials including PMAA were prepared by the sol-gel method under the conditions shown in Tables 1 and 2. Figure 1 shows the pencil scratch hardness and stain resistance of inorganic-organic films prepared by varying the ratio of TEOS to PMAA.

The interface between silica and PMAA was changed by altering the ratio of TEOS to PMAA. When the SiO<sub>2</sub> content was more than 99.8 mass%, transparent films with a relatively high hardness were formed and no macroscopic phase separation occurred. However, their stain resistance for nylon 6 became low. This means the amount of stain blocker PMAA was insufficient to combine with the amino end groups of nylon 6.

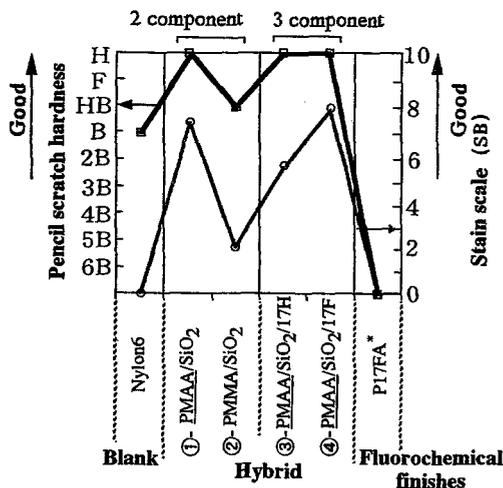
When the SiO<sub>2</sub> content was 23–72 mass%, the film was opaque by macroscopic phase separation and its pencil scratch hardness fell to roughly 6B–HB. Under other conditions transparent films were also prepared. The most suitable inorganic-organic film with high stain resistance and transparency was prepared when the SiO<sub>2</sub> content was 85.5–98.3 mass%.

The contact angles for the hybrid films ①–④ prepared from PMAA (or PMMA), TEOS, 17H and 17F were 51°, 69°, 104°, and 109° with water and 17°, 45°, 28°, and 71° with n-hexadecane, respectively.



**Fig. 1 Pencil scratch hardness and stain resistance of inorganic-organic films using PMAA.**

Figure 2 shows the pencil scratch hardness and the stain-resistance of hydrophobic inorganic-organic films, compared with two component films (PMAA/SiO<sub>2</sub> and PMMA/SiO<sub>2</sub>). Each transparent inorganic-organic film with PMAA on nylon 6 showed a higher stain resistance and pencil scratch hardness than the simple nylon 6 and poly(perfluorooctylethyl acrylate), P17FA.



**Fig. 2 Pencil scratch hardness and stain resistance of hydrophobic inorganic-organic films.**

(\*P17FA : polyperfluorooctylethylacrylate)

Figure 3 shows typical SEM photographs of fluorinated inorganic-organic film (Hybrid-④) with stain resistance and nylon 6 blank. The surface of the Hybrid-④ film was smooth and homogeneous, compared with nylon 6. However, a few cracks were observed on the inside of the film. Hybrid-④ film had flexibility with nylon 6, and its adhesion was also good.

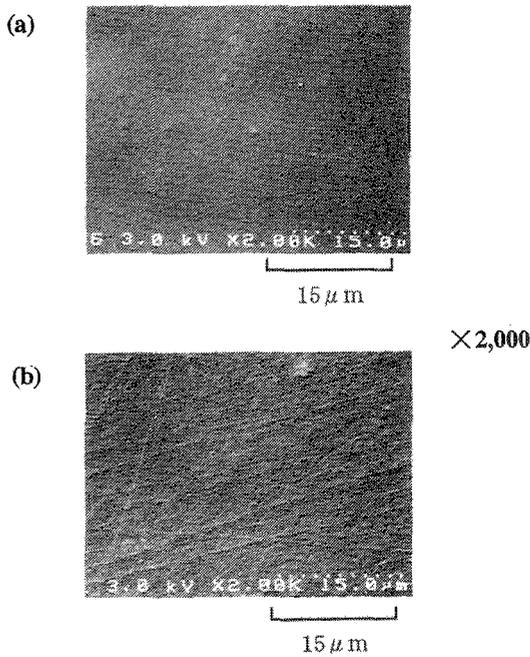


Fig.3 SEM photographs of : (a) fluorinated inorganic-organic film (Hybrid-④) and (b) nylon 6.

On the other hand, the Hybrid-② film obtained from TEOS and PMMA was opaque and showed a low stain resistance for nylon 6 even if the SiO<sub>2</sub> content is same as that of the Hybrid-④ film. These results show that PMMA in the inorganic-organic materials does not react with amino end groups of nylon 6, and is not useful as a inorganic-organic stain blocker.

Figure 4 shows the surface free energy [7-9] and the fluorine content of the various inorganic-organic films and typical fluorochemical finishing agent, P17FA. The fluorinated inorganic-organic films on nylon 6 (Hybrid-④ film) showed low surface free energy, equivalent to that of P17FA, in spite of the ca. 6.7 mass% fluorine.

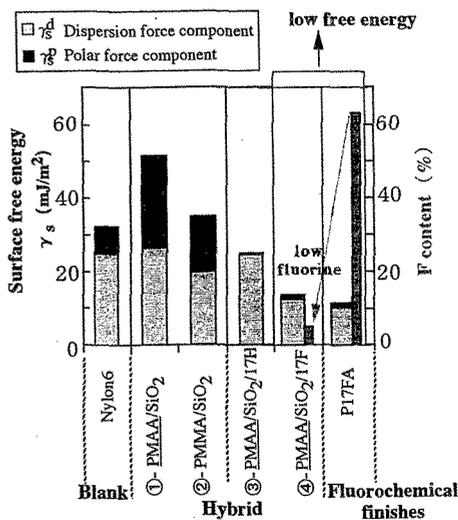


Fig.4 Surface free energy and fluorine contents of inorganic-organic films, nylon 6, and fluorochemical finishing agent.

In general, the surface sensitivity of polymer surfaces can be characterized by various instruments. For example, the contact angle analysis shows a surface sensitivity of ~1 nm, which responds to direct contact with the liquid phase. The XPS is a useful analytical tool for surface depth profiles up to ~10 nm to determine the wettability of the surface, and the IR-ATR spectroscopy detects the excitation of vibration of materials in a layer with a thickness of up to ~1000 nm [10].

Figure 5 shows the fluorine concentrations, C-F and F<sub>1s</sub>/C<sub>1s</sub>, on inorganic-organic films and fluorochemical finishing agent determined by the XPS and IR-ATR analyses, respectively. It was found that many fluorine components were concentrated on the surface of the fluorinated inorganic-organic film, more than that of P17FA, by the XPS analysis. Very little fluorine concentrated below the surface on the hybrid film observed by the IR-ATR and XPS analyses. This suggests that the silicate phase under ca. 10 nm depth of the hybrid film is dominant.

The film thickness for the Hybrid-④ was calculated to 770nm from its density, since no peaks of N1s in the hybrid films were detected by the XPS. However, the thickness of the Hybrid-② film using PMMA could not be determined because of its ruggedness.

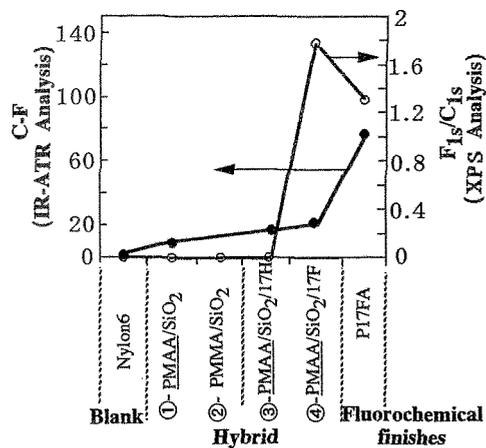
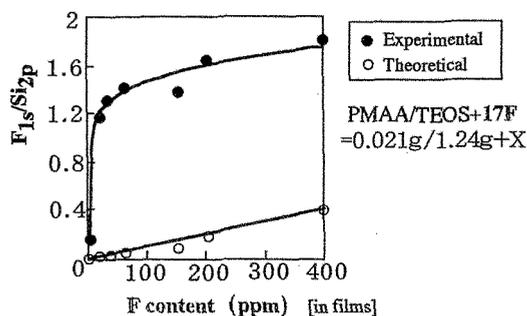


Fig.5 Fluorine concentration (C-F and F<sub>1s</sub>/C<sub>1s</sub>) of inorganic-organic films and fluorochemical finishing agent.

Figure 6 shows the relationship of the fluorine surface concentration and fluorine content of the Hybrid-④ film. The results show that the fluorine concentrated on the surface in spite of the low fluorine content in the film.



**Fig.6 Fluorine surface concentration and fluorine content of the fluorinated inorganic-organic film(Hybrid-④).**

#### 4. Conclusion

We applied PMAA, a stain blocker for nylon fiber, to inorganic-organic materials, and the following conclusions were obtained:

- (1) The transparent inorganic-organic films with 85.5 ~98.3 mass%  $SiO_2$  prepared from TEOS/PMAA have high pencil scratch hardness and stain resistance.
- (2) The inorganic-organic films prepared from TEOS and PMMA became opaque, and exhibited low stain resistance even if the  $SiO_2$  content is the same as that of the TEOS/PMAA series.
- (3) The fluorinated inorganic-organic materials prepared from TEOS, PMAA, and P17FA showed low surface free energy, higher pencil scratch hardness and the highest stain resistance for nylon 6.
- (4) The IR-ATR and XPS analyses show that the fluorine components were concentrated on the surface of the fluorinated inorganic-organic films.

#### 5. References

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