NOTE

Removal of Carbon Black Particles from Polymer Substrates in Water/Ethanol Mixtures

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Abstract: The removal of the carbon black (CB) particles from the polymer substrates was investigated in water/ethanol mixtures. As substrates, the films and the fibrous assemblies of polyethylene, nylon 6 and cellulose acetate were used. The ultrasonic wave was applied as a mechanical action for cleaning. The detergency of the CB particles for the films and the fibrous assemblies was assessed with the quartz crystal microbalance (QCM) technique and the reflectometry, respectively. The detergency for the films was discussed with the wetting force calculated from the experimentally determined contact angle on the substrate and surface tension of the water/ethanol mixture.

Key words: detergency, carbon black, quartz crystal microbalance, reflectometry, wetting force

1 INTRODUCTION

In recent years, the textile cleaning technology such as the washing media¹⁻³⁾, the washing machine⁴⁾ and the detergents^{5,6)} has been developed from a viewpoint of the environmental conservation. In order to improve this technology, the techniques for evaluating the detergency are needed to be established. There are many evaluations such as the visual observation^{7,8)}, the reflectometry⁹⁾, the image processing¹⁰⁾ and the particle counting¹¹⁾. The quantitative evaluations of detergency have also been carried out by the X-ray intensity¹²⁾, the IR spectroscopy¹³⁾, the liquid chromatograph¹⁴⁾ or the gas chromatograph¹⁵⁾. However, it takes much time and experience for measuring the amount of the contaminants. In the previous studies, the quartz crystal microbalance (QCM) has been used as a device to estimate the detergency of oily and particulate contaminants^{16,17)}. The QCM is widely utilized as a sensor to measure the deposited amount on its electrodes. It has been reported that the detergency processes of the protein and the organic contaminants can be monitored by the QCM technique^{18,19)}.

In the present study, the CB particles deposited on the polymer substrates were ultrasonically cleaned in water/ethanol mixtures as the detergent solution. As substrates, we selected the films and the fibrous assemblies of three polymers which are commonly used as

textile materials. The detergency for the films evaluated by the QCM technique was compared with that of the fibrous assemblies evaluated by the reflectometry. The obtained detergency was discussed on the basis of the wetting force acting on the film surface.

2 EXPERIMENTAL

2.1 Materials

The spherical carbon black (CB) particle (pyrolyzed at 1100°C, a mean diameter of 260 nm, the gravity of 1.86 g/cm³, Tokai Carbon Co., Ltd., Japan,) was used as a model particulate soil.

Three polymer samples, polyethylene, nylon 6 (Scientific Polymer Products Inc., USA) and cellulose acetate (Kishida Chemicals, Japan), were used for the preparation of the polymer films onto the QCM (AT-cut, the fundamental resonance frequency of 9MHz, a gold electrode area of 63.6 mm², USI System Co., Japan). The fibrous assemblies used were the polyethylene mesh (Kansai Iseikatu Kenkyukai, Japan) and the woven plain fibrous assemblies of nylon 6 (Japanese Standard Associations, Japan) and cellulose acetate (Nakao Filter Media Corporation, Japan).

All chemicals were extrapure grade and used without further purification. The water was purified using a water

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purification system (the resistivity of 18.2 M Ω cm, Direct-Q UV, MILLIPORE, USA).

2.2 Preparation of polymer films on QCM

For the preparation of the polymer films, polyethylene, nylon 6 and cellulose acetate were dissolved in xylene (2 g/dm³), phenol/benzene (1/3 of volume ratio, 10 g/dm³) and acetone (10 g/dm³), respectively. After dropping the polymer solution onto the gold electrodes, the QCM was rotated at 8000–9000 rpm for 2 s. The thickness of the polymer films was obtained from the resonance frequency change of the QCM due to the spin-coating using the Sauerbrey equation²⁰. The calculated thickness of polyethylene, nylon 6 and cellulose acetate were 78 nm, 33 nm and 55 nm, respectively, which were enough to prevent the effect of the gold support on the surface property¹⁶. The mean roughness of polyethylene, nylon 6 and cellulose acetate was determined to be 6.17 nm, 1.98 nm and 2.57 nm, respectively¹⁶. The film surfaces were regarded as flat planes, since the film roughness was sufficiently small compared with the diameter of the CB particle. To estimate the wettability of the films, the water contact angle on the film surface was measured by the sessile drop method as mentioned in the section 2.3. It was found that the contact angles on polyethylene, nylon 6 and cellulose acetate were 99.6°, 73.3° and 67.3°, respectively¹⁶.

2.3 Contact angle and surface tension measurement

The contact angle on the polymer film surface and the surface tension of the detergent solution were measured using a video contact angle system (VCA Optima-EX, AST Products, Inc., USA). For experimental convenience, the contact angle at 1 s after placing a drop on the polymer film was measured¹⁷. The surface tension of the solution was determined by the pendant drop image analysis using the Laplace equation²¹.

2.4 Evaluation of detergency

2.4.1 Particle removal from polymer films

Prior to the removal experiments, the CB particles were deposited onto the polymer film surfaces. The particles were dispersed in water with applying ultrasonic waves. Preliminary experiments were carried out to find the optimum CB concentrations considering the requirements for the uniform distribution of the CB particles deposited on the substrates and the detectable frequency range of the QCM. As a result, the particle concentration of the dispersion was 0.05 g/dm³ for the polyethylene and cellulose acetate, and 0.2 g/dm³ (containing 1 mmol/dm³ hydrochloride acid) for nylon 6. The QCM was perpendicularly immersed in the aqueous dispersion of 0.015 dm³ with stirring at 100 rpm for 2 h. The QCM pulled out of the dispersion was dried in air and kept in the desiccator with silica gel overnight. The deposited amount of the CB particles, M_D , was obtained

from the frequency change of the QCM due to the particle deposition. The obtained M_D for polyethylene, nylon 6 and cellulose acetate were 1300 ± 500 ng, 1600 ± 500 ng and 2300 ± 300 ng, respectively. Then, the QCM was cleaned in the water/ethanol mixtures of 0.015 dm³ containing 1 mmol/dm³ sodium chloride for 20 min²² using an ultrasonic cleaning system (the frequency of 36 ± 0.5 kHz, CA-6400FM, KAIJO Corporation, Japan). The power of the ultrasonic waves was controlled within 5 ± 1 mV by monitoring with a sonic sensor (HUS-5, Honda Electronics Co., Ltd., Japan). The amount of particles removed from the polymer film, M_R , was calculated from the frequency change of the QCM due to the cleaning. The detergency was expressed by M_R/M_D .

2.4.2 Particle removal from fibrous assemblies

The fibrous assembly (50×50 mm²) was immersed in 0.1 dm³ CB particle/ethanol dispersion (0.5 g/dm³) with applying ultrasonic waves for 5 min. After pulling out of the ethanol dispersion, the soiled fibrous assembly was dried in air and kept in a desiccator overnight. The 4 reflectance measurements on each side of the fibrous assembly were carried out on 5 layers of the fibrous assembly by a spectrophotometer (the wavelength of 460 nm, U-3010, HITACHI, Japan). The Kubelka-Munk function²³ of the soiled fibrous assembly, $(K/S)_S$, were 1.05 ± 0.1 , 0.55 ± 0.1 and 1.64 ± 0.5 for polyethylene, nylon 6 and cellulose acetate, respectively. The soiled fibrous assembly was washed in the water/ethanol mixture of 0.1 dm³ with applying ultrasonic waves of 5 mV in power for 20 min and dried in air. The reflectance of the washed fibrous assembly was obtained as described above. The detergency for the fibrous assembly, D , was calculated by the equation²³,

$$D(\%) = \frac{(K/S)_S - (K/S)_W}{(K/S)_S - (K/S)_O} \times 100 \quad (1)$$

where subscripts O, S and W refer to the original, the soiled and the washed fibrous assemblies, respectively.

3 RESULTS AND DISCUSSION

3.1 Detergency

The detergency for the films and the fibrous assemblies is plotted against the ethanol concentration in Fig. 1. It was observed that the detergency for nylon 6 and cellulose acetate was higher than that for polyethylene in both cases of the films and the fibrous assemblies. The detergency for the fibrous assemblies was found to be much lower compared with that for the films, because the mechanical action by ultrasonic waves was not effective for the geometrically complicated substrates²⁴.

The detergency for polyethylene film considerably increased with increasing ethanol concentration. On the

Fig. 1 The Detergency of the Carbon Black Particles for the Polyethylene Films (●), Nylon 6 Films (▲), Cellulose Acetate Films (■), Polyethylene Fibrous Assemblies (○), Nylon 6 Fibrous Assemblies (△) and Cellulose Acetate Fibrous Assemblies (□) as a Function of the Ethanol Concentration.

other hand, the detergency for nylon 6 and cellulose films was not dependent on ethanol concentration. The detergency for the fibrous assemblies was observed to decrease by the addition of 10 vol% ethanol and slightly increase at the high ethanol concentrations. It seems likely that the detergency calculated from the surface reflectance on the fibrous assembly is affected by the particle size change with the ethanol concentration²⁵. Therefore the stability of the CB particle was optically investigated in water and water/ethanol (10 vol%). The obtained results showed that the stability of the CB particles was low in water and increased by the addition of ethanol. This demonstrates that the addition of ethanol causes the change in the CB particle size.

For the QCM technique, the obtained detergency is reliable, because it can be determined directly from the amount of particles deposited on the substrate.

3.2 Effect of ethanol concentration on contact angle and surface tension

The contact angle on the polymer film, θ_s , and the surface tension of the detergent solution, γ_L , are shown in Fig. 2 as a function of the ethanol concentrations. It was observed that θ_s decreased with increasing ethanol concentration. The measured θ_s was found to be the largest for the polyethylene film, followed by nylon 6 film and cellulose acetate film. The surface tension of the solution decreased with increasing ethanol concentration.

3.3 Effect of wetting force on detergency

It is considered that the penetration of the solution into the interface between the particle and the substrate results in reducing the adhesion force and promoting the

Fig. 2 The Advancing Contact Angles of the Detergent Solution on the Polyethylene Films (●), Nylon 6 Films (▲) and Cellulose Acetate Films (■) and the Surface Tension of the Detergent Solution (▽) as a Function of the Ethanol Concentration.

particle removal. Figure 3 shows the relationship between the detergency for the films and the wetting force, $\gamma_L \cos \theta_s$, calculated from the experimentally determined contact angle and surface tension. It was observed that the detergency increased with increasing wetting force. It was clear that the detergency for the films assessed with QCM technique were strongly dependent on the wetting force. It was also found that the detergency for nylon 6 film and cellulose acetate film was large (see Fig. 1) because of its large wetting force.

Fig. 3 The Relation between the Detergency of the Carbon Black Particles for the Polyethylene Films (●), Nylon 6 Films (▲) and Cellulose Acetate Films (■) and the Wetting Force on the Film Surface.

4 CONCLUSION

The removal of the CB particles from the films and the fibrous assemblies was investigated in water/ethanol mixtures. The detergency for the films and the fibrous assemblies was assessed with the QCM technique and the reflectometry, respectively. The CB particle was found to be removed easily from nylon 6 and cellulose acetate compared with polyethylene in both cases of the film and the fibrous assembly. The detergency for the polyethylene film increased with increasing ethanol concentration. A good relation was found between the detergency and the wetting force for the films, suggesting that the liquid penetration into the interface between the particle and the substrate took an important role in detergency.

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