Microencapsulation and Application of Fluorine-Free Water Repellent Agent-AH102

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ABSTRACT: Fluorine-free water repellent agent, AH102, was microencapsulated by interfacial polymerization with polyurethane as shell material to restrict its hydrolysis and improve its dispersibility in water. The appearance of the resultant microcapsules was characterized with optical microscope and scanning electron microscope. Chemical structure of microcapsules was identified with Fourier-transforming infrared spectrometer. The size and size distribution of the microcapsules were determined by laser particle size analyzer. The thermal property of the microcapsules was investigated by thermogravimetric analysis. The stability and dispersibility of the microcapsules in aqueous medium were characterized by evaluating the static water contact angles of the treated cotton fabrics with the emulsions of unencapsulated and microencapsulated AH102 at different storage intervals. The results showed that AH102 was successfully encapsulated and its stability and dispersibility in water were greatly improved. As expected, the emulsion of the microencapsulated AH102 became more stable than that of the unencapsulated one at water repellence to cotton fabric with increasing storage intervals. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 330–335, 2011

Key words: microencapsulation; polyurethane (PU); fluorine-free water repellent agent; dispersibility; stability

INTRODUCTION

Recently, concern has been raised regarding the ecological persistence and toxicity of a number of chemicals including perfluorooctanoic sulfonate and perfluorooctanoic acid, which are associated with fluorochemical (FC) finishing,[1] while research to determine the long-term impact of such chemicals still ongoing, it seems advisable to begin considering the utility of various alternatives to such finishing options. In addition to environmental concerns being raised, identification of a viable alternative could provide a significant cost savings considering the relatively high cost of FC finishes.

Among alternatives, commercially available AH102, a kind of fluorine-free water repellent agent containing long-chain alkyl and acid anhydride groups has good water repellence to cotton fabrics. Unfortunately, it is difficult to be dispersed in water and will hydrolyze due to the acid anhydride groups of AH102, i.e., its stability in aqueous solution cannot meet the demand on application.

To solve the problems mentioned above, a process of microencapsulation was used. Microencapsulation is a process of enveloping microscopic amounts of matter in a thin film of polymer, which forms a solid shell.[2] The core/shell structure allows isolation of the encapsulated substance from the surroundings and thus protects it from any degrading factors such as water. The encapsulated substance can be liberated by fusion or dissolution of the impermeable shell or by diffusion across a porous shell.[3,4] It is meaningful to perform microencapsulation with a polyurethane (PU) shell for two main reasons. First, it is expected that PU-shelled microcapsules will be compatible with the final PU coating on textiles and also with other polymeric matrices. Second, the PU shell will not have negative effect on water repellence of the core material encapsulated.

Therefore, to restrict its hydrolysis and improve its dispersibility in aqueous solution, AH102 was encapsulated with the PU shell by the interfacial polymerization of toluene-2,4-diisocyanate (TDI) and polyethylene glycol 400 (PEG 400) in this work.

EXPERIMENTAL

Materials

Toluene-2,4-diisocyanate (TDI) and polyethylene glycol with a number average molecular weight of 400

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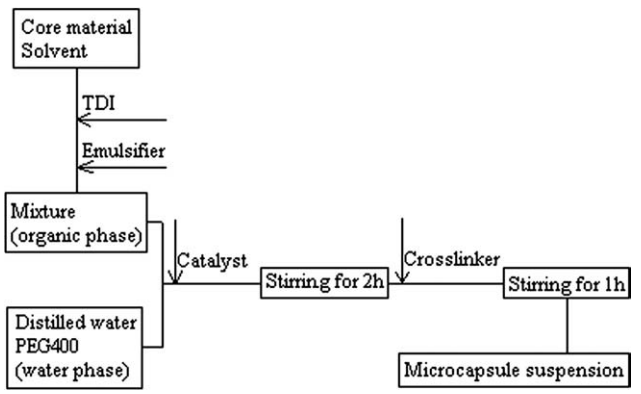

Figure 1 Schematic diagram of microencapsulation of AH102.

g/mol (PEG 400) used as reactants for obtaining PU shell to encapsulate were purchased from Shanghai Rongrong chemicals Co. and Sinopharm Chemical Reagent Co., respectively. AH102 used as core material to be encapsulated was kindly provided by Kefeng Co.,China. Dichloromethane (DCM) used as solvent, dibutyltin dilaurate (DBTL) used as catalyst, and ethylene diamine (EDA, anhydrous) used as crosslinking agent were all purchased from Shanghai Boer Chemical Reagent Co. Emulsifier 2201 (nonionic) was obtained from Xingtai Lantian Fine Chemicals Co. All chemicals were reagent grade and used as received. Scoured, mercerized and bleached woven cotton fabric (plain weave, 130 g/m^2) was used as a substrate.

Microencapsulation of AH102

An interfacial polymerization method was used for the microencapsulation.[5–8] AH102 was encapsulated with the PU shell by the interfacial polymerization of TDI and PEG 400. The encapsulating procedure is shown in Figure 1. Briefly, first, 1.7 g AH102 was added into 1.7 g DCM and mixed uniformly, and added 2.5 g TDI and 6 g Emulsifier 2201 under agitation, respectively, the mixture obtained above was as organic phase, meanwhile, aqueous phase was obtained by dissolving 4.6 g PEG 400 in 103 mL distilled water, and then the organic phase was added into the aqueous phase under agitation, and dropped 0.08 mL catalyst DBTL and kept stirring for 2 h at ambient conditions [chemical reaction herein involved shown in Fig. 2(a)], and then dropped 0.8 mL crosslinking agent EDA and continued to stir for 1 h [chemical reaction herein involved shown in Fig. 2(b)], and the microcapsule slurry was obtained. Lastly, the microcapsules were obtained by filtrating the slurry, and washing with acetone and distilled water, respectively, and vacuum drying at 60°C for 2 h. The detailed preparing conditions are given in Table I.

Treatment of cotton fabrics with the microencapsulated and unencapsulated AH102 emulsions

Cotton fabrics were immersed into the corresponding emulsions for 1 min and then padded with an automatic padder (Rapid Labortex Co., Taipei,

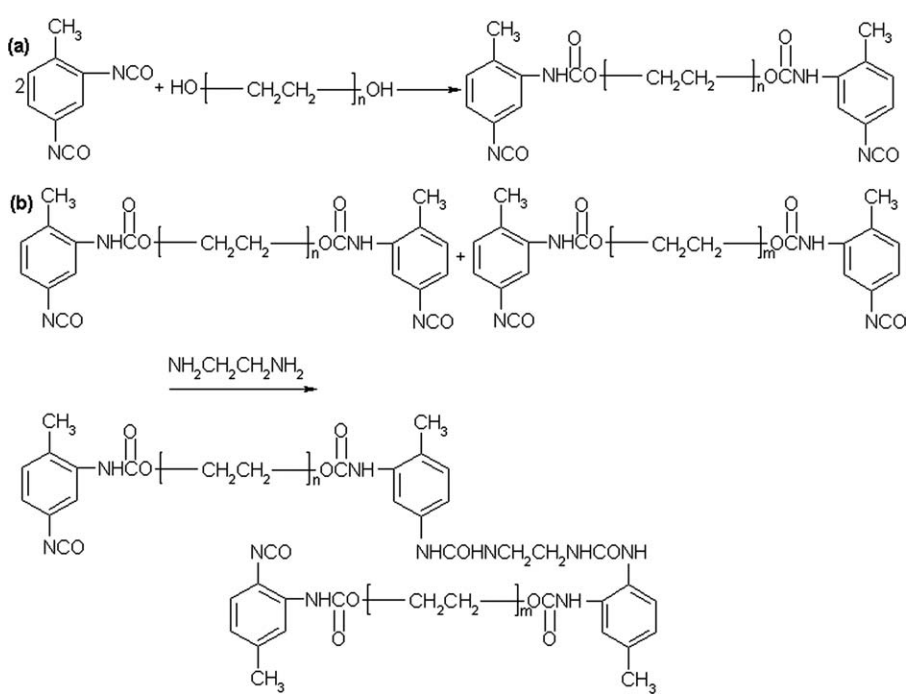

Figure 2 Chemical reactions involved in the preparation of microcapsules, (a) polymerization reaction; (b) crosslinking reaction.

TABLE I
Formulation of Microencapsulation of AH102

AH102/g	TDI/g	PEG 400/g	Emulsifier 2201/g	DCM/g	DBTL/mL	EDA/mL	Distilled water/mL	Dispersion rate/r/min
1.7	2.5	4.6	6	1.7	0.08	0.8	103	1000

Taiwan) with a nip pressure of 1.0 kg/cm^2, and then dried at 100°C for 2 min and cured at 160°C for 2 min.

Characterization of the microcapsules

Fourier-transforming infrared (FTIR) spectra were obtained by Nicolet-380 Fourier transform infrared spectrometer (Thermo Electron Corporation, USA) in transmission mode to identify the chemical structure of the specimens, which were prepared by grinding the solid samples with potassium bromide powder (KBr) and pressing the mixture into a tablet or by attaching the liquid samples to a KBr disc. The scanning number was 32 and the resolution was 4 cm$^{-1.}$

Average diameter and size distribution of the resultant microcapsules were determined by LS13320 Particle Size Analyzer (Beckman Coulter Inc., USA).

The appearance of the microcapsules was observed by E400POL optical microscope (NIKON, Japan). A drop of microcapsule suspension was placed on a microscope slide, diluted with distilled water, and examined at a magnification of 1000. Meanwhile, to measure the mean size of microcapsules by optical microscopy, samples of the microcapsules were selected at random from different locations on a glass slide and diameters of 100 particles were measured. The sampling procedure was repeated three times and the average value was reported as the diameter of microcapsules.

Surface morphology of the microcapsule powder was observed by JSM-5600 LV scanning electron microscope (JEOL, Japan). The sample was sputter coated with gold and examined at an accelerating voltage of 15 keV.

Thermogravimetric analysis (TGA) of the microcapsules was carried out using TG209 F1 Thermogravimetric Analyzer (NETZSCH Corporation, Germany). The weight of all samples were kept within 5–10 mg. Samples in an open Pt pan were examined under a nitrogen atmosphere with a flowing rate of 40 mL/min at temperature ranging from room temperature to 800°C at a linear heating rate of 10°C/min.

The stability and dispersibility of AH102 in aqueous solution were indirectly characterized by evaluating the static water contact angles of the treated cotton fabrics with the unencapsulated and microencapsulated AH102 emulsions at different storage intervals measured with JY-82 contact angle tester (Beijing Hake Testing Instruments Corporation). The emulsions was stored in clean containers and sealed with PE film in room temperature. At a set interval, the emulsions were used to treat cotton fabrics and measured the corresponding contact angles.

RESULTS AND DISCUSSION

Microscopic analysis

Morphological observation is important for verifying the result of the microencapsulation. The optical microscopic image of PU-shelled microcapsules containing AH102 is shown in Figure 3(a), and as a control sample, the optical microscope image of just the PU particle without AH102 was also provided as shown in Figure 3(b). It can be seen from their optical microscopic images that the microcapsules are approximately spherical in shape with a mean diameter of about 6 μm ($\sigma = 2.324$), whereas the PU particles are irregularly in shape and adhere to each other together, and the particles size is smaller than the microcapsules. From the comparison of the two, it is confirmed that AH102 has been microencapsulated by PU.

To have a general view of the microcapsule powder, SEM micrograph of the microcapsule powder was taken as shown in Figure 3(c). It can be seen from Figure 3(c) that the microcapsules are nearly spherical in shape and congregate together, and their outer surfaces are compact.

Size and size distribution of microcapsules

The size and size distribution of microcapsules have a great impact on the handle of treated fabrics and play a vital role in quality control of finished product, so the size and size distribution are typically two important parameters for the obtained microcapsules. To obtain the detailed information of size and size distribution of the microcapsules, a diluted microcapsule suspension was examined and analyzed by laser particle size analyzer, the resultant statistical histogram and statistical report of size distribution of the microcapsules based on differential volume are shown in Figure 4 and Table II, respectively. The size distribution of the microcapsules is slightly broad as shown in Figure 4, which is mainly attributed to the geometric forms of the core material droplets formed in the emulsification stage, thus

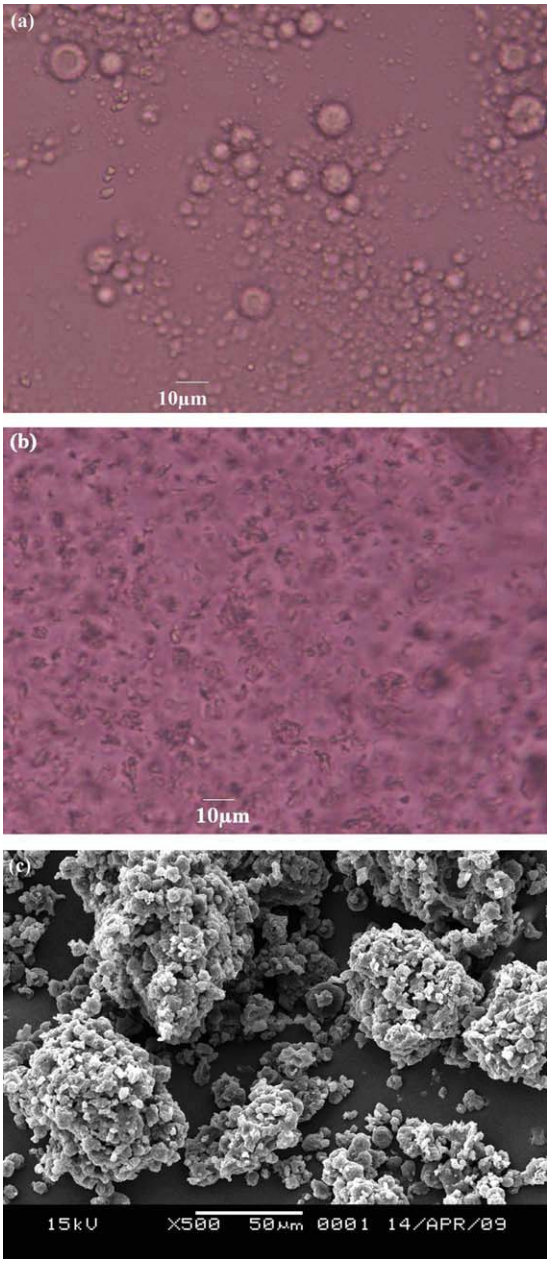

Figure 3 Optical microscopic images of (a) microcapsules, (b) polyurethane (PU) particles; (c) SEM image of the microcapsule powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersion rate of the stirrer for making the emulsion is critical, and emulsifier content is also important for keeping the body of AH102 droplets in shape. The average diameter of microcapsules is 5.807 μm ($\sigma = 4.601$) almost in agreement with the one by the microscopic analysis, the median, which is the particle diameter at which half of the volume percent is larger and half is smaller, is 4.604 μm, and the mode is 5.355 μm, which is the value corresponding to the channel center with the maximum volume percent, given in Table II. It can also been seen from Table II that d_{10}, d_{50}, and d_{90} are 1.734 μm, 4.604 μm, and 12.64 μm, respectively, which implies that 10% of particle size in volume percent is lower than 1.734 μm, 50% is lower than 4.604 μm and 90% is lower than 12.64 μm. The kurtosis of size distribution of microcapsules is a leptokurtic distribution as given in Table II, which suggests that most of the particle sizes are close to the mean size. The results mentioned above also suggest that dispersion rate of 1000 r/min, and emulsifier content of 5% (wt %) are appropriate for the preparation of microcapsules used to treat textiles, as testified by Saihi et al.[9] that microcapsules with a diameter of smaller than 50 μm is appropriate for treating textiles with a good homogeneity and acceptable mechanical properties.

Fourier-transforming infrared spectra

Besides morphological characterization, the chemical structure of microcapsules should be identified. FTIR spectra of PU shell, AH102, and microcapsules are presented in Figure 5. For AH102, its FTIR spectrum exhibits asymmetrical stretching vibration of —CH_2 at 2922 cm^{-1}, symmetrical stretching vibration of —CH_2 at 2854 cm^{-1}, deforming vibration of C—H at 1465 cm^{-1} and 1413 cm^{-1}, stretching vibration of C—C at 1378 cm^{-1}, asymmetrical and symmetrical stretching vibration of C—O at 1222 cm^{-1} and 1066 cm^{-1}, respectively, and characteristic absorption peak of acid anhydride group at 1862 cm^{-1} and 1785 cm^{-1}.Meanwhile, the spectrum of PU shell reveals board stretching mode of N—H at 3294 cm^{-1}, stretching vibration of —CH_2 at 2922 cm^{-1}, stretching vibration of C=O at 1642 cm^{-1}, stretching vibration of benzene ring at 1540 cm^{-1} and 1473 cm^{-1}, and asymmetrical and symmetrical stretching vibration of C—O at 1224 cm^{-1} and 1100 cm^{-1}, respectively. Clearly, in the spectrum of the broken microcapsules, all the characteristic peaks of AH102 and

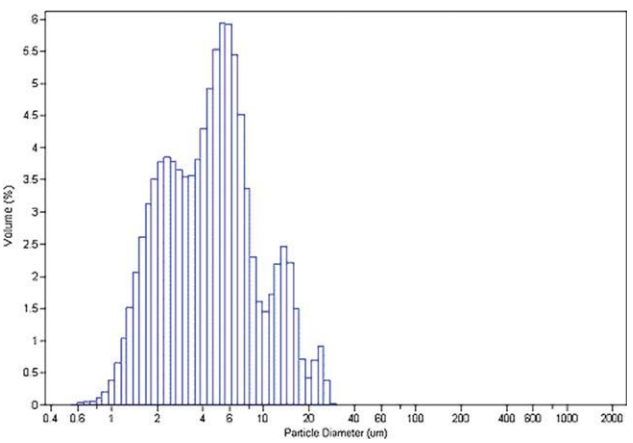

Figure 4 Size distribution of microcapsules based on differential volume. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Size Statistics Report of Microcapsules

Mean/μm	Median/μm	Mode/μm	d_{10}/μm	d_{50}/μm	d_{90}/μm	S.D. /μm	Kurtosis
5.807	4.604	5.355	1.734	4.604	12.64	4.601	Leptokurtic

PU shell appear, which implies that AH102 has been encapsulated by PU shell.

Thermogravimetric analysis

The thermal property of microcapsules is also an important performance parameter in application, thus the TGA of the obtained microcapsules was carried out. From the pyrolytic behaviors shown in Figure 6, it is clearly seen that TG curve of AH102 displays only a phase of weight loss from 230 to 300°C with a weight loss of ~ 94%, and reaches a maximum weight loss rate of 15%/min at 273°C. The residue is approximatively zero at 450°C. For PU shell, there are three stages of weight loss within the temperature range of interests. The first one with a weight loss of ~ 3% from 25 to 100°C should be attributed to evaporation of the absorbed water. The second one with a weight loss of ~ 80% from 274°C to 417°C should be due to the depolycondensation reaction of PU, and attains a maximum weight loss rate of ~ 4%/min at 321°C. The third one is between 445°C and 528°C with a weight loss of ~ 8%. The residue is 4.76% at 695°C. Thermal degradation of PU-shelled microcapsules containing AH102 is a combination of the contributions made by PU and AH102, thus TG curve of microcapsules also shows three steps of weight loss. The first one with a weight loss of ~ 5% from 25°C to 100°C should be resulted from elimination of the absorbed water. The second one is between 246°C and 413°C with a weight loss of ~ 77%, achieving a maximum weight loss rate of ~ 6%/min at 331°C. The third one is between 421°C and 636°C with a weight loss of ~ 17%. The residue is 0.68% at 695°C. The above analysis suggests that the thermal stability of PU-shelled microcapsules containing AH102 increased as a result of thermally stable urethane formed by the reaction of isocyanate and hydroxyl,[10] which also gives us a hint to apply the microcapsules in high temperature conditions.

Stability and dispersibility of the microcapsules in aqueous solution

To evaluate the stability and dispersibility of PU-shelled microcapsules containing AH102 in aqueous solution, an indirect characterization method by measuring the static water contact angles of the treated cotton fabrics with the unencapsulated and microencapsulated AH102 emulsions at different storage intervals was used. Because the stability and dispersibility of AH102 in aqueous solution play a key role in the water repellence of the treated fabrics, good stability and dispersibility lead to high and stable water repellence. As a control sample, the water contact angles of the treated cotton fabrics with just the PU dispersion were also measured. The obtained results were represented in Figure 7.

Because of the hydrolysis of acid anhydride groups of AH102, the water repellence of the treated cotton fabrics with the unencapsulated AH102 emulsions at different storage intervals (0 h, 24 h, and

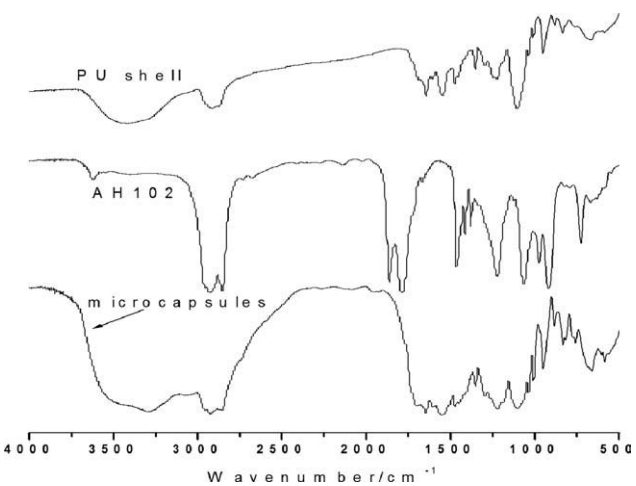

Figure 5 FTIR spectra of PU shell, AH102, and microcapsules.

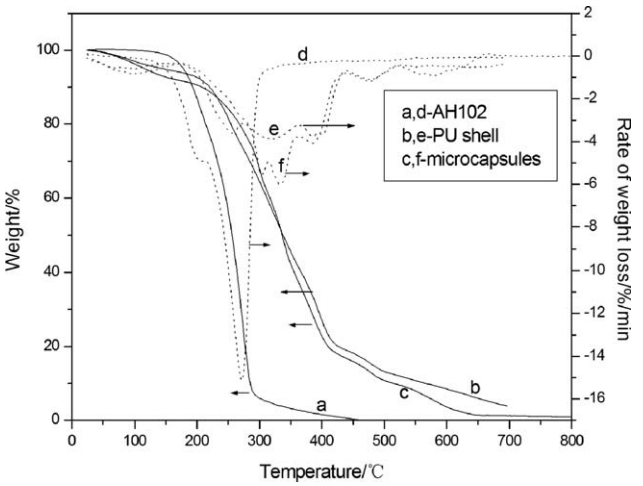

Figure 6 TG and DTG curves of AH102, PU shell and microcapsules.

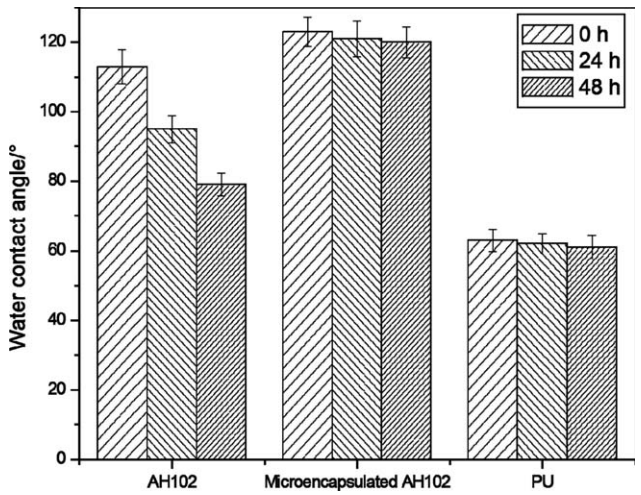

Figure 7 Water contact angles of the treated cotton fabrics with the unencapsulated and microencapsulated AH102 emulsions at different storage intervals.

48 h) are varying and with increasing storage intervals of the emulsions, the water contact angles of the treated cotton fabrics reduced, whereas the water contact angles of the treated cotton fabrics with the microencapsulated AH102 emulsions at different storage intervals (0 h, 24 h, and 48 h) are almost invariable, which suggests that the emulsion of microencapsulated AH102 becomes more stable than that of the unencapsulated one, which could be attributed to the restriction of the hydrolysis of acid anhydride groups of AH102. It can also be seen from Figure 7 that the water contact angles of the treated cotton fabrics with the emulsions of microencapsulated AH102 at different storage intervals are correspondingly higher than those with the unencapsulated one, which implies that the dispersibility of AH102 was enhanced by microencapsulation, while the treated cotton fabrics with just the PU dispersion almost have no repellence, the water contact angles are all lower than 90°. Based on the above results obtained, it is testified that microencapsulation is an effective and useful method for the restriction of hydrolysis and the improvement of dispersibility of AH102 in water.

CONCLUSIONS

Fluorine-free water repellent agent, AH102 was successfully encapsulated with PU shell by the interfacial polymerization of TDI and PEG 400, the resultant microcapsules are approximately spherical in shape, with a mean diameter of about 6 μm, onset pyrolytic temperature at 230°C. The application to water repellent finishing of cotton fabric indicated that the stability and dispersibility of the microencapsulated AH102 in water were greatly improved and the water repellence of the treated cotton fabric with the microencapsulated AH102 emulsion is higher and more stable than that with the unencapsulated one. Thus, it is verified that microencapsulation is an effective and novel method for the restriction of hydrolysis and the improvement of dispersibility of AH102 in aqueous solution.

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