Fabrication of thermo-regulating cotton fabric with enhanced flame retardancy via layer-by-layer assembly

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Abstract

The lack of thermo-regulation functionality and high flammability of cotton fabrics greatly restrict their application in high-performance fields. Herein, we report a versatile layer-by-layer (LbL) assembly strategy for introducing to cotton fabrics a multilayered coating consisted of phase change microcapsules and ammonium polyphosphate, endowing them with thermo-regulating and flame retardancy. The coated fabrics were characterized by limiting oxygen index (LOI), scanning electron microscopy (SEM), thermogravimetry (TG), differential scanning calorimetry (DSC) and infrared thermal imaging. The fabric deposited with 20 bilayers (MCPM/APP-20) showed improved flame retardancy with a LOI of 24.4% and residual carbon of 34.24%. It also shows a melting enthalpy of 30.16 J/g, which transferred to a temperature difference of 6.4 ℃ compared with pristine cotton. The functional endowed by the LbL assembly was reasonably durable, with melting enthalpy and residual carbon of MPCM/APP-20 reduced to 17.14 J/g and 19.82% after 30 laundering cycles. These results suggest that LbL assembly was a convenient way for functionalization of cotton fabrics.

Introduction

Cotton is the most important natural substrate for textile and clothing industry because of its excellent wearability and for being bio-degradable and renewable(Fang et al. 2015). Nevertheless, apparels made from plain cotton fabrics cannot provide adequate protection to wearers in specific scenarios such as fire hazards or extreme weather conditions(Masood et al. 2020). Researchers had been working lately to impart thermo-regulating functionality to cotton fabrics by introducing phase change materials (PCMs) (Kumar et al. 2014; Scacchetti et al. 2017; Sun and Iqbal 2017).

PCMs are thermal energy storage materials that can absorb and release thermal energy during phase transition (Liu et al. 2020; Ma et al. 2015a; Qiao et al. 2020). However, bulk PCMs transform into liquids at higher temperature which confined their applications(Jin et al. 2013; Wang et al. 2016). This problem could be solved by microencapsulation of phase change materials. Microencapsulated PCMs (MPCM) have a higher heat transfer area per unit volume and tolerate volume changes during phase change processes without their enthalpies being much compromised(Mohaddes et al. 2014; Su et al. 2017; Vitorino et al. 2014; Zhao and Zhang 2011).

MPCM could be conveniently introduced to cotton fabrics using conventional finishing methods(Iqbal and Sun 2018; Prajapati and Kandasubramanian 2019; Sun and Iqbal 2017). Alay et al(Alay Aksoy et al. 2017). constructed a cotton-based thermal regulating fabric that showed up to 3.1 °C difference to pristine cotton fabric by incorporating a MPCM via the pad-dry-cure method. Saraç et al.(Saraç et al. 2019) fabricated stretch denim-based and cotton-based thermal regulating fabrics, whose latent heats were 10.1 J/g and 14.9 J/g, respectively, via knife-coating technique. MPCM had also been introduced to fabrics by coating(Su et al. 2020), printing(Sánchez et al. 2010), grafting(Benmoussa et al. 2018), exhaustion(Bonet et al. 2012) and spinning(Iqbal and Sun 2014; Li et al. 2013; Li et al. 2014). However, durability of the thermo-regulating function imparted by these methods was generally poor.

Moreover, these fabrics became susceptible to fire hazard due to intrinsic flammability of paraffin wax, commonly applied as the phase change core. Using flame-retardant MPCMs is a good approach to conquer this deficiency(Qiu et al. 2015). Demirbağ et al.(Demirbağ and Aksoy 2016) imparted flame-retardancy to MPCMs via introducing clay nano-particles (Clay-NPs) into the gelatin/sodium alginate shell, and observed improvement in flame retardancy of finished cotton fabrics (burning time increased from 19.24 s to 34.48 s). Nevertheless, the preparation of flame-retardant MPCMs was complex and the durable property were also unsatisfactory.

Layer-by-Layer (LbL) assembly technique as a facile, versatile and cost-effective strategy had been used to prepare functional fabrics, such as flame retardant(Carosio et al. 2015; Fang et al. 2019), anti-ultraviolet(Liu et al. 2012; Saini et al. 2020), hydrophobic(Li et al. 2019b; Xue et al. 2020), and anti-bacterial(Ali et al. 2020; Bashari et al. 2020). In this paper, we introduced MPCM and ammonium polyphosphate onto cotton fabrics via the LbL technique, to improve their thermo-regulating performances and flame retardant properties. The treated fabrics were examined for thermo-regulating performance, flame retardant property, thermal stability and durable properties. The results indicated that highly durable thermo-regulating and flame-retardant cotton fabrics could be obtained by this facile and cost-effective strategy.

Materials And Methods

Materials

Woven cotton fabrics were supplied by the Luthai Textile Co., Ltd, China., n-octadecane, acetic acid, hydrochloric acid (HCl) and ethanediamine were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Ammonium polyphosphate (APP), isophorone diisocyanateand (IPDI) and sodium hydroxide (NaOH) were provided by Adamas Co., Ltd. Chitosan (high viscosity) was supplied by Macklin Biochemical Co., Ltd, Shanghai. Glycidyltrimethylammonium chloride (CHTAC) was purchased from Energy Chemical Co., Ltd. All chemicals were used as received.

Preparation of MPCM

Phase change microcapsules were prepared by interfacial polymerization using a procedure modified from our previous report (Zhu et al. 2020). IPDI (2.00 g) and n-octadecane (6.00 g) were mixed in a 100 mL beak at 60 ℃ and used as the oil phase. An aqueous suspension of regenerated nanochitin (RCh, 48.0 g, 0.15 wt%) was added in as the aqueous phase. A stable Pickering emulsion was obtained by emulsifying the mixture for 3 min using a homogenier ((IKA T18, Germany)) at 9000 rpm. Subsequently, the emulsion was stirred at 200 rpm and heated to 70 ℃ for 2 hours, after which a solution of ethanediamine (27.0 g, 2.00 wt%) was dropped in. More ethanediamine was added as a more concentrated solution (21.6 g, 10.0 wt%) over a course of 4 hours. Then, stirring was lowered to 100 rpm and the mixture was cooled to ambient temperature. Finally, microcapsules were collected through filtration and dried for 24 hours at ambient temperature.

Cationization of cotton fabric

Cotton fabric (5.0 g) was impregnated in a mixed solution of 18.8 g/L CHTAC and 9.0 g/L NaOH, at a liquor ratio of 1:30. The mixture was stirred for 1 h at 70 ℃. Subsequently, the fabric was washed using deionized water and dried in oven at 60 ℃ to yield the positively charged cotton fabric.

Preparation of the APP solution and the MPCM solution

APP (1.5 g) was dissolved in deionized water (33.5 g). The mixture was stirred until transparent, after which 2 M NaOH (7.5 mL) was added. Then, the pH was adjusted to 10 with 2 M HCl to obtain the 3.0 wt % APP solution. Zeta potential of the APP solution was measured and the results showed that a maximum negative potential of -30.8mV was recorded at pH=10 (Fig. S1, Supporting Information).

Chitosan (1.00 g), acetic acid (1.00 g) and MPCMs (2.00 g) were combined and added in deionized water (96.0 g) with stirring to obtain the 2.0 wt% MPCM solution.

Thermo-regulating and flame-retardant treatment of cotton fabric

The process to impart the thermo-regulating and flame-retardant coating on cotton fabrics is illustrated in Fig. 1. In detail, the positively charged cotton fabrics were successively impregnated in 3.0 wt% APP solution and 2.0 wt% MPCM suspension for 10 min, respectively. The samples were dried at 60 ℃ after each immersion. By repeating this process in a cyclic manner, multilayered fabrics (MPCM/APP-n) were obtained, where n represents the cycle number.

Characterizations

Malvern Zetasizer (Nano-ZS, UK) was used to test the Zeta potential of samples. The measurements were repeated three times. The morphology of MPCMs and the cotton fabrics were characterized by scanning electron microscopy (SEM, TM3030, Hitachi, Japan). Before the test, all the samples were coated with gold. Limiting oxygen index (LOI) of fabrics was determined using an oxygen index testing instrument (5801A, Suzhou Vouch Testing Technology Co., Ltd, China), referring to ASTM D2863 standard. The chemical composition of the treated cotton fabrics was analyzed using FT-IR spectroscopy (PerkingElmer Spectrum-Two, USA) over the wavenumber range from 400-4000 cm^{-1}. Thermogravimetry was performed on a thermal analyzer (TG, 209F1, Netzsch, Germany) to observe the thermal decomposition behavior of MPCMs and cotton fabrics. All samples were heated from 30 ℃ to 600 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere. Differential scanning calorimetry (DSC 4000, Netzsch, Germany) was used to record the heat storage/releasing capacities of MPCMs and treated fabrics. Measurements were done by varying the temperature in the range from 0 ℃ to 70 ℃ with a heating rate of 10 ℃/min.

The encapsulation efficiency (E_{en}) of MPCMs was calculated from the DSC results by the following equation (1)(Gao et al. 2017)

$$E_{en} = \frac{\Delta H_{m,core}}{\Delta H_{m,PCM}} \times 100\% \quad (1)$$

where $\Delta H_{m,core}$ and $\Delta H_{m,PCM}$ are the melting enthalpies of pure n-octadecane and the MPCM, respectively.

The thermo-regulating performance of pristine and treated fabrics was recorded by an infrared thermal camera (Fluke TiX450, USA). The samples were set in a heating plate (40 ℃) and the infrared thermal camera was used to capture changes in temperature of the samples. To test washfastness of the treated fabrics, the samples were soaked in a solution of standard soap (2.0 g/L) at a liquor ratio of 1:50, and washed for 30 min at 45 ℃ in a SBW-12 laundry machine. This operation was repeated for 30 times and the sample was coded as Wash-30.

Results And Discussion

Characterization of MPCMs

Due to the superior emulsifying ability of RCh, Pickering emulsions stabilized by as little as 0.10 wt % RCh have been be successfully. Fig. 2a shows the optical microscopic image of such a Pickering emulsion of n-octadecane in water stabilized by 0.15 wt % RCh, which shows droplets sized between 10-30 μm. Morphology of the corresponding MPCMs generated from the emulsion is shown in Fig. 2b and Fig. 2c. It can be seen from the images that the microcapsules are well separated and no agglomeration is noticed. The diameter of the spherical MPCMs corresponds well with that of the droplets, ranging from 10 μm to 30 μm. The surfaces of the microcapsules appear to be wrinkled with protrusions and indentations likely caused by the voluminal shrinkage of n-octadecane during liquid to solid transition(Qiu et al. 2018).

Thermal stability of octadecanethe MPCMs was evaluated and compared to that of pure n-octadecane by TG (Fig. 2d and Table S2). Results show that pure n-octadecane exhibited a typical one-step weight loss curve spanning from 133 ℃ to 230 ℃, with a T_{max} (temperature at which the maximum weight loss rate occurs) at 230.9 ℃ due to evaporation and left almost no residue (Li et al. 2019a; Xu and Yang 2019). An obvious thermal stability enhancement was achieved for the MPCM as indicated by the increment in T_{max} by about 45 ℃ compared with pure n-octadecane. The three distinct stages observed in the decomposition curve of MPCMs can be attributed to gasification of n-octadecane and decomposition of the PU shell(Ma et al. 2015b), respectively. The final char residue was also low at 0.09%.

Melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) are two important indexes representing the thermal storage/release capability of MPCMs. Fig. 2(e) displayed the DSC curves of MPCMs as compared with that of pure n-octadecane. Form Fig. 2(e), the melting and crystallization temperature of MPCM were slightly lower than that of pure n-octadecane. It is because that motion of the n-octadecane molecules was limited by the confined internal spaces of microcapsules, resulting in the crystallization

defects(Li et al. 2020). Based on the ΔH_m of pure n-octadecane (246.0 J/g) and MPCMs (190.8 J/g), the encapsulation rate of the microcapsules was calculated to be 77.3% according to equation (1).

Characterization of the treated cotton fabrics

Chemical compositions of the microcapsules and treated fabrics

The changes in chemical composition during the preparation process were studied by FT-IR. As shown in Fig. 3(a), the IR spectrum of MPCMs shows a peak at 2260 cm^{-1} , characteristic of -NCO stretching(Shi et al. 2019). MPCMs also show a broad peak at about 3330 cm^{-1} corresponding to stretching vibrations of -NHs and -OHs. The existence of the stretching vibrations of -NH and -C=O at 1560 cm^{-1} and 1637 cm^{-1} illustrated that the PU shell was successfully formed by the isocyanate-amidogen reaction(Qian et al. 2020; Wu et al. 2015). These peaks also appear in the spectrum of treated cotton fabrics, which also show additional peaks at 1069 cm^{-1} and 1240 cm^{-1} , due to the presence of P-O and P=O moieties(Peng et al. 2020; Ullah et al.) compared with pristine cotton. These results suggest that the LBL treatment yielded a physical composite of MPCM, APP and cotton.

Surface Morphology

The morphology of pristine and treated fabrics were examined by SEM (Fig. 4). As shown by the SEM images, the pristine cotton fabric displayed a typical morphology of woven fabrics with smooth fiber surface. After 5 cycles of repeated LBL treatment (MPCM/APP-5), the cellulose fibers were clearly covered by discrete films but remained distinguishable. Surface of MPCM/APP-10 was clearly covered by continuous thin films and MPCMs. When the number of bilayers increased to 15 (MPCM/APP-15) and 20 (MPCM/APP-20), the cellulose fibers became completely undistinguishable. Moreover, the thickness of the samples increased from 0.25 mm (pristine cotton) to 0.26 mm, 0.27 mm, 0.28 mm and 0.29 mm, respectively with 5, 10, 15, and 20 cycles of LBL treatment (Fig. S2) These results confirmed that APP and MPCMs were successfully deposited on the surface of the cotton fabrics.

Thermal stability

Fig. 5a shows the TG curves of the pristine and treated cotton fabrics heated up to 700 ℃. The corresponding thermal degradation data are listed in Table 1. The pristine cotton exhibited a one-step weight loss curve due to the depolymerization of glycosyl units and left about 6.78% residue. In contrast, all treated fabrics displayed a two-staged weight loss pattern. The first weight loss occurred at around 150 ℃, which was significantly lower than the T_{onset} of pristine cotton (261.2 ℃) and could be attributed to evaporation of n-octadecane as observed in the TG curve of the MPCMs. The resulting polyphosphoric

acid promoted carbonize of cotton cellulose to formation of an intumescent char layer(Xue et al. 2020) that prevent further decomposition of cellulose and MPCMs(Fang et al. 2015; Horrocks 2011). As a result, although T_{max2} values of MPCM/APP-5, MPCM/APP-10, MPCM/APP-15 and MPCM/APP-20 were all lower than that of the pristine cotton, their yields of charwere significantly higher. It is well known that flame retardancy of materials is reflected by their yield of char in pyrolysis(Wang et al. 2015). Therefore, the APP treatment was effective in enhancing the flame retardancy of the cotton fabrics by promoting charring to suppress thermal oxidation degradation(Shi et al. 2018).

Thermal storage capacity and thermo-regulating performance

The MPCMs possess high phase change enthalpy measured to be 190.8 J/g, which is expected to endow the cotton fabrics with active thermo-regulating function. The heat storage capacities of treated fabrics were measured by DSC and the corresponding curves and melting and crystallization parameters are shown in Fig. 4c and Table 2. As expected, the latent heat of treated fabrics gradually increased from 13.01 J/g to 30.16 J/g with increasing number of deposited layers from 5 to 20. The melting and crystallization temperature of all treated fabrics are about 30 ℃ and 22 ℃, respectively, showing distinct difference than the MPCMs. Thus, it can be considered that the Layer-by-Layer coating process had little effect on the melting and crystallization performance of the microcapsules.

Garments made from MPCM-containing textiles can provide superior protection to the wearer in extreme environmental conditions, for they are endowed, by the MPCMs, the ability to store and release energy in a certain temperature range. Herein, temperature-regulating performance of MPCM/APP-20 was evaluated and compared to that of pristine cotton and using a hot plate set at about 40 °C. An infrared thermal camera was used to capture changes in temperature of these samples. As seen in Fig. 5c, there was a significant temperature difference between MPCM/APP-20 and pristine cotton during the heating process. Pristine cotton was quickly heated to 40.9 °C within 10 s, by which time the surface of MPCM/APP-20 was measured to be 34.5 °C, 6.4 °C lower than the set temperature of the hot plate. By 40 s, the surface temperature of MPCM/APP-20 was still 3.8 °C lower than the set value. These results confirmed that efficient thermo-regulating ability could be imparted to cotton fabrics by this LBL strategy.

Table 1 Thermal degradation data of MPCM, treated fabrics and after being washed

Sample	T_{onest}(°C)	T_{max1}(°C)	T_{max2}(°C)	Char residues at 700°C(wt%)
Cotton	261.2	369.2	-	6.78
MPCM/APP-5	118.2	148.5	318.9	26.31
MPCM/APP-10	116.6	168.3	312.9	30.25
MPCM/APP-15	118.2	166.9	309.9	32.49
MPCM/APP-20	115.0	166.9	308.3	34.24
Wash-30	119.6	168.3	325.1	19.82

Table 2 The corresponding DSC data of n-octadecane, MPCM, treated fabrics and after being washed

Sample	Melting		Crystalling	
	T_m	ΔH_m (J/g)	T_c	ΔH_c (J/g)
n-octadecane	34.13	246.6	19.11	245.1
MPCM	34.04	190.8	25.19	190.4
MCPM/APP-5	30.10	13.01	22.53	11.65
MCPM/APP-10	31.20	20.59	22.16	19.33
MCPM/APP-15	30.37	24.46	22.31	23.52
MCPM/APP-20	31.54	30.16	21.67	29.15
Wash-30	27.64	17.14	19.42	15.64

Flame retardancy of the treated fabric

LOI is used to evaluate the fire resistance of treated fabrics and the results are shown in Fig. 6. LOI of the cotton fabrics increased from 17.9% to over 24% after 15 cycles of LBL treatments, suggesting the incorporated APP was effective in improving the flame retardancy of the fabrics. However, further increase of the deposited layers from 15 to 20 didn't lead to appreciable improvement in LOI. Considering the handle and wearability of the fabrics are negatively affected by the number of deposited layers, MPCM/APP-15 seems to be the optimum choice.

The treated fabrics were burned and their surface morphology analyzed by SEM (Fig. 7). Surprisingly, not only the fibers in the burnt fabrics remained distinguishable, some of the MPCMs were also intact, indicating the presence of APP also protected the microcapsules from being destroyed by burning.

Durablility test

Washfastness of MPCM/APP-20 was evaluated using by repeatedly wash the sample using a SBW-12 laundry machine. Fig. 8a shows the SEM image of MPCM/APP-20 after being washed for 30 times. The film and MPCMs covering the surface of fabric were still present, while some of the underlying fibers were also revealed, indicating that MPCM and APP were partially lost after repeated laundering. Results from the TG analysis (Fig. 8b) showed the TG curve of the washed sample was very similar to the unwashed one, but with markedly reduced amount of residue char (decreased by 42%).The results indicated that although washing had no significant impact on the thermal stability of the treated fabric, the flame-retardancy were moderately impaired.

The DSC curves and data of MPCM/APP-20 after being washed is presented in Fig 6c. The melting and crystallization enthalpies of the washed samples were calculated to be 24.89 J/g and 25.39 J/g, respectively, representing a 43.1% drop compared with pre-wash values. These results collectively showed that both the thermo-regulating property and flame retardancy imparted to the cotton fabric by the LbL technology were moderately durable against repeated washing.

Conclusions

In this paper, Layer-by-Layer assembly technology was used to coat cotton fabric with a thermo-regulating and flame retardant fishing. The morphology and the distribution of elements of treated fabrics were examined by SEM and EDX, illustrating MPCMs and APP were successfully deposited on the fabrics. The fabric with 20 deposited multilayers, MPCM/APP-20, displayed a latent heat of 30.16 J/g and reasonable thermo-regulating performance. It also showed enhanced flame retardancy with LOI of 24.4% and residual char of 34.24%. After being washed 30 times, MPCM/APP-20 was able to maintain 57.9% of its original enthalpy and still showed moderated flame retardancy, demonstrating the LbL technology as a facile and eco-friendly strategy for imparting durable thermo-regulating ability and flame retardancy to cotton fabrics.

Declarations

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Figures

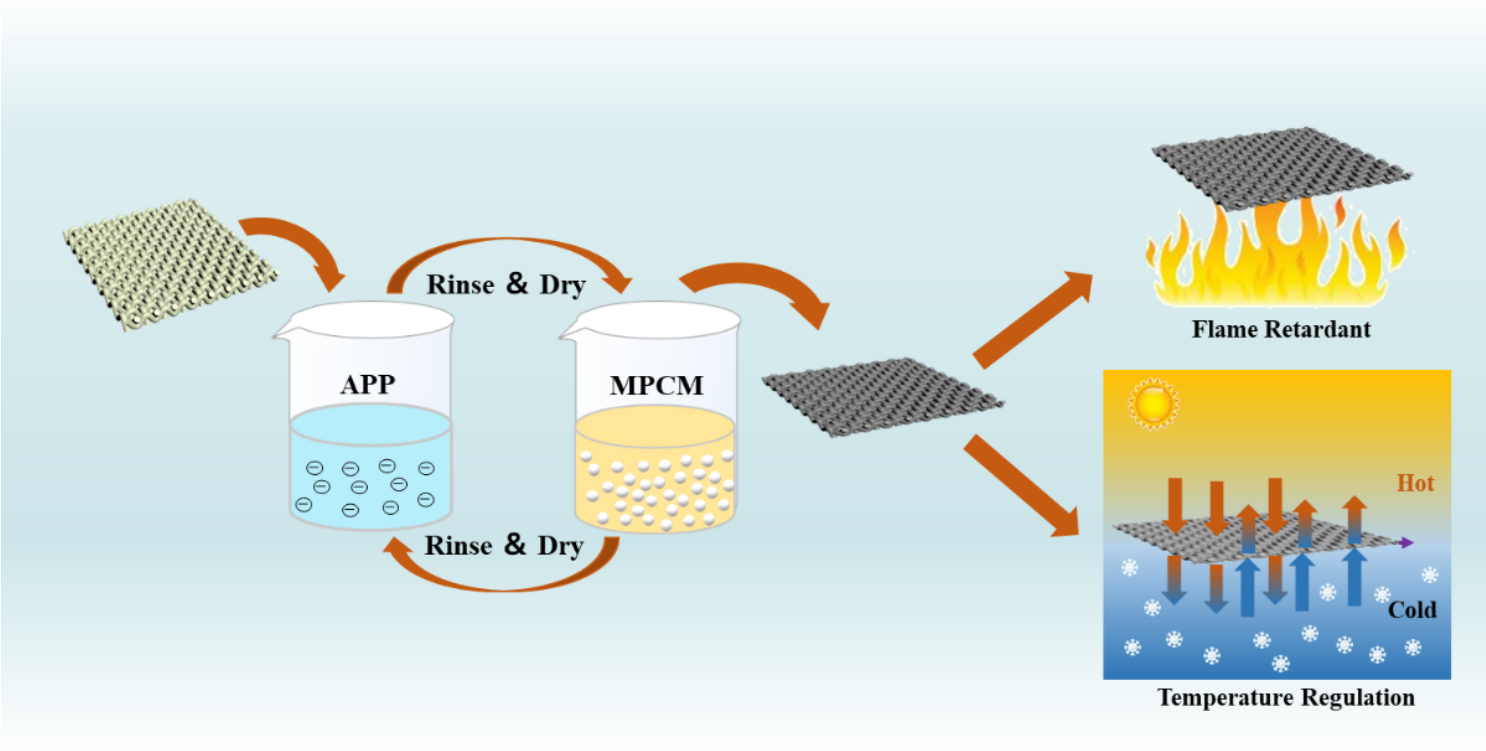

Figure 1

Schematic illustration of thermo-regulating and flame retardant cotton fabric using layer-by-layer assembly

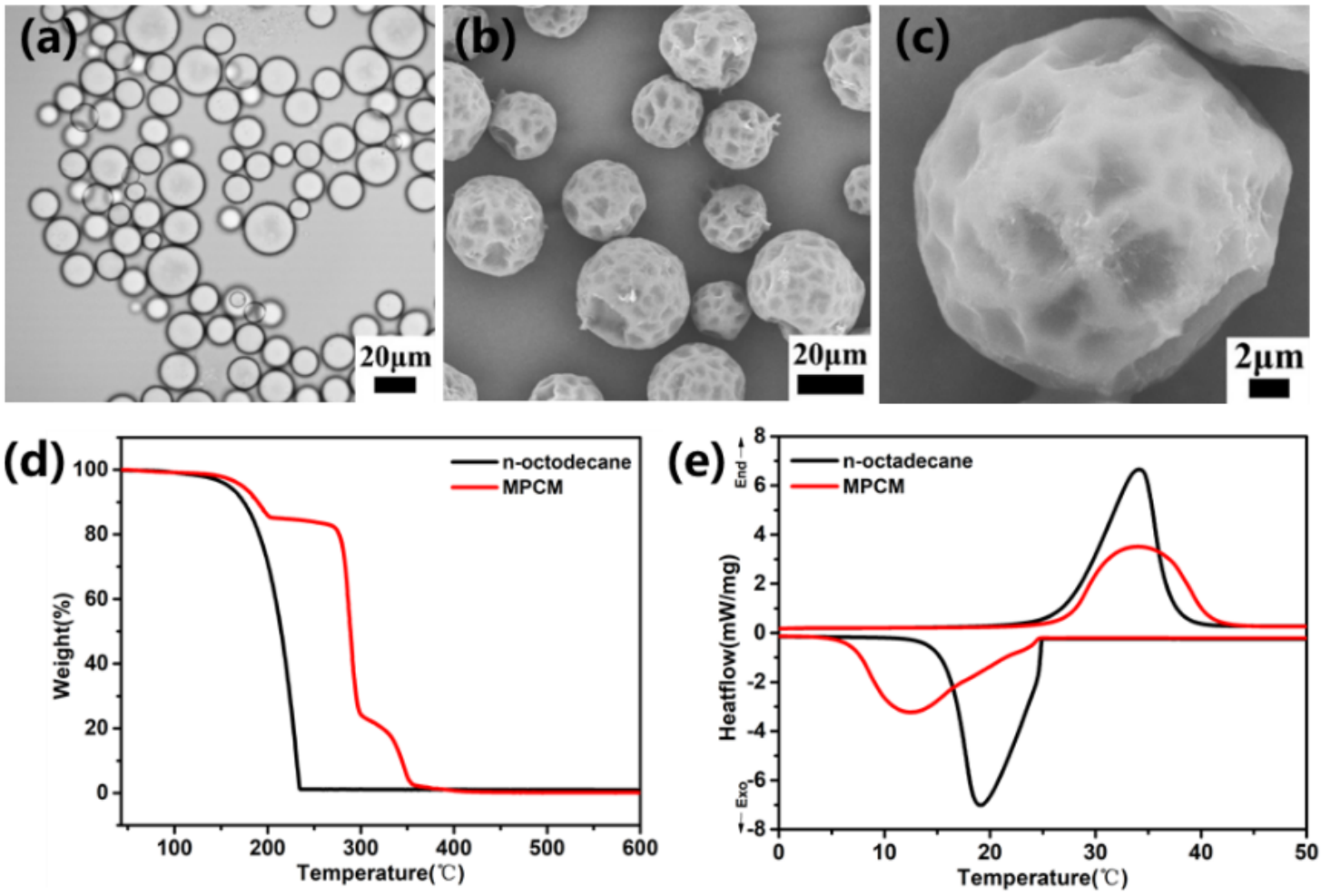

Figure 2

(a) Optical microscopic image of O/W Pickering emulsion stabilized by RCh suspension; (b, c) SEM images of MPCMs at different distinguishability; (d) TG curves of n-octadecane and MPCM; and (e) DSC curves of n-octadecane and MPCM

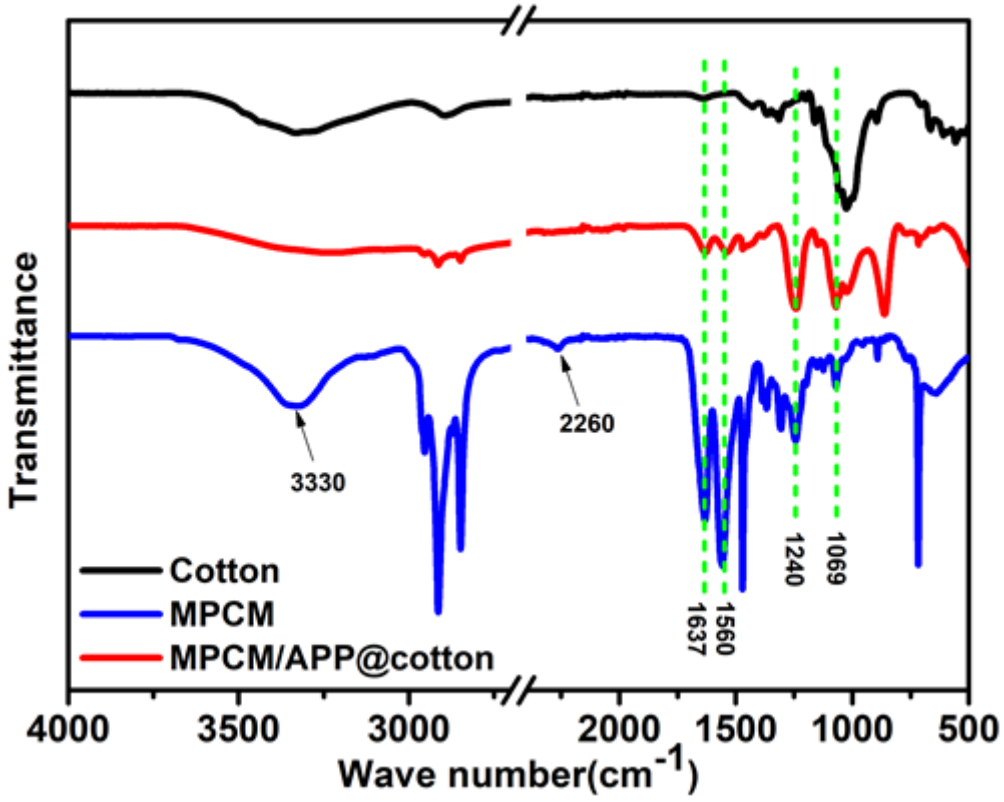

Figure 3

FT-IR spectra of pristine cotton, MPCMs and the treated fabric (MPCM/APP@cotton)

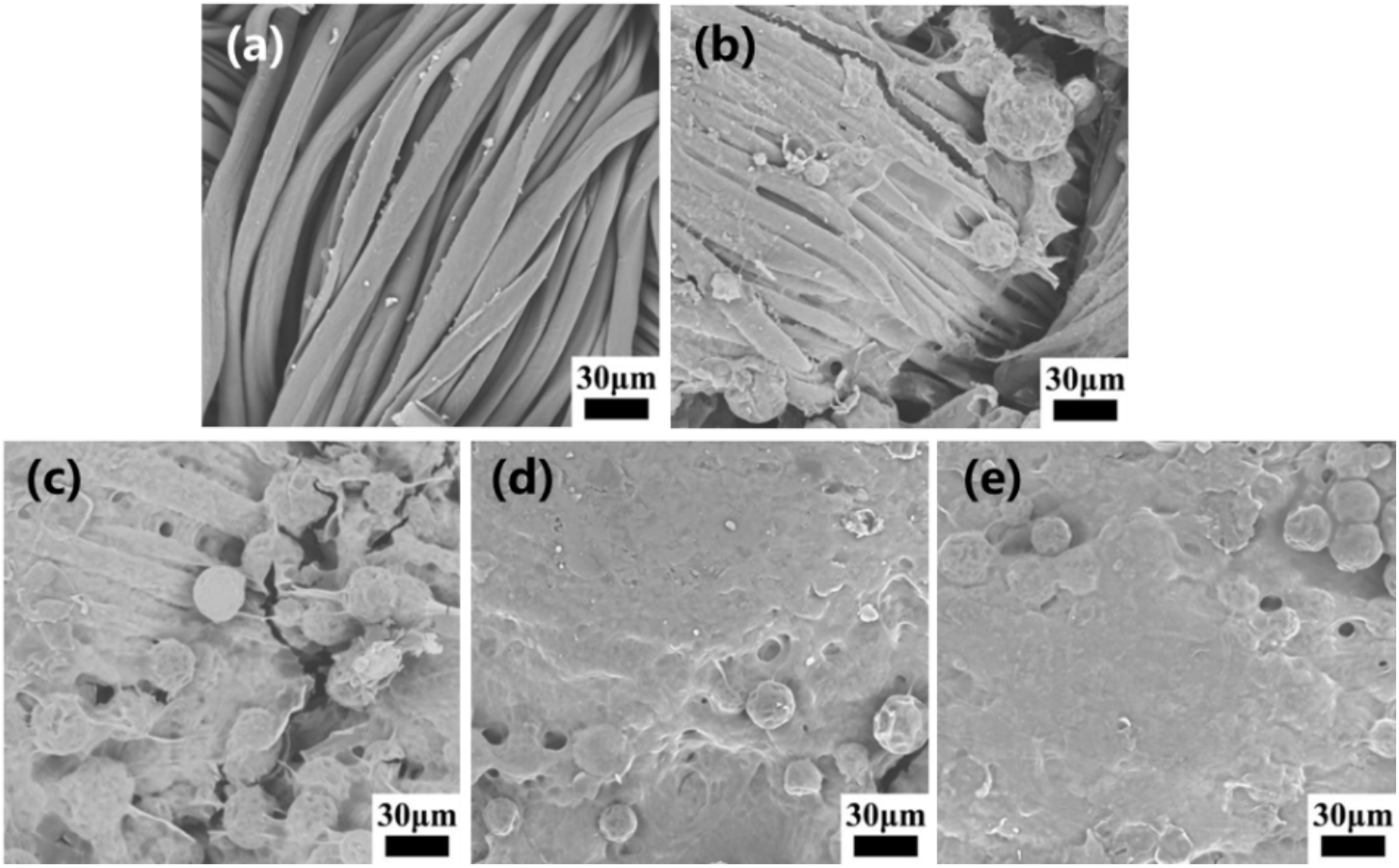

Figure 4

Surface morphology of pristine cotton and treated cotton fabrics. (a) SEM of pristine cotton; (b) SEM of MPCM/APP-5; (c) MPCM/APP-10; (d) MPCM/APP-15; (e) MPCM/APP-20

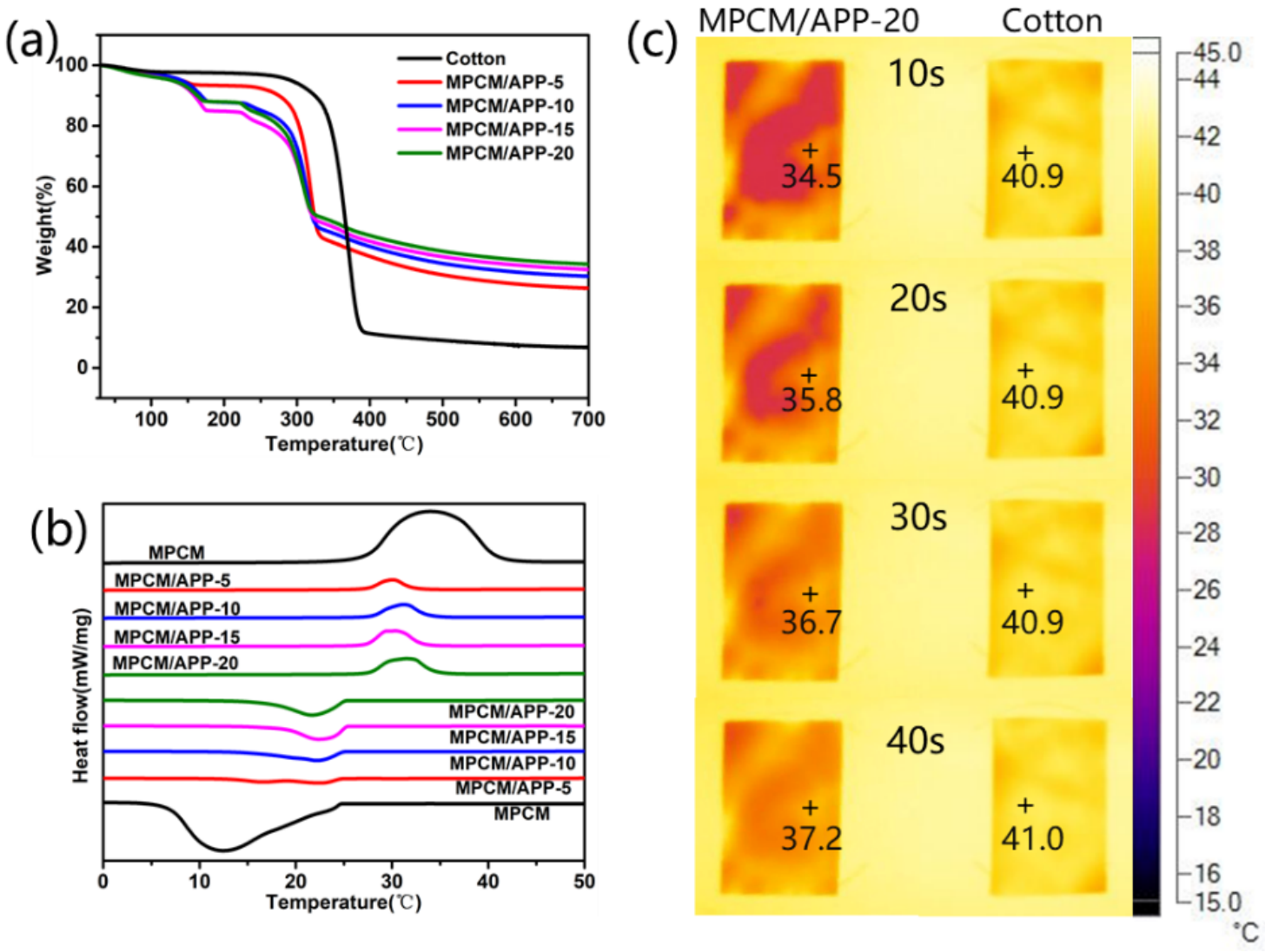

Figure 5

(a) Thermal stability and thermal storage capacity of cotton and treated cotton. TG curves of cotton and treated cotton; (b) DSC curves of MPCM and treated cotton; (c) Infrared thermal imaging monitored the heating process of the fabric at a heating plate (≈40 °C)

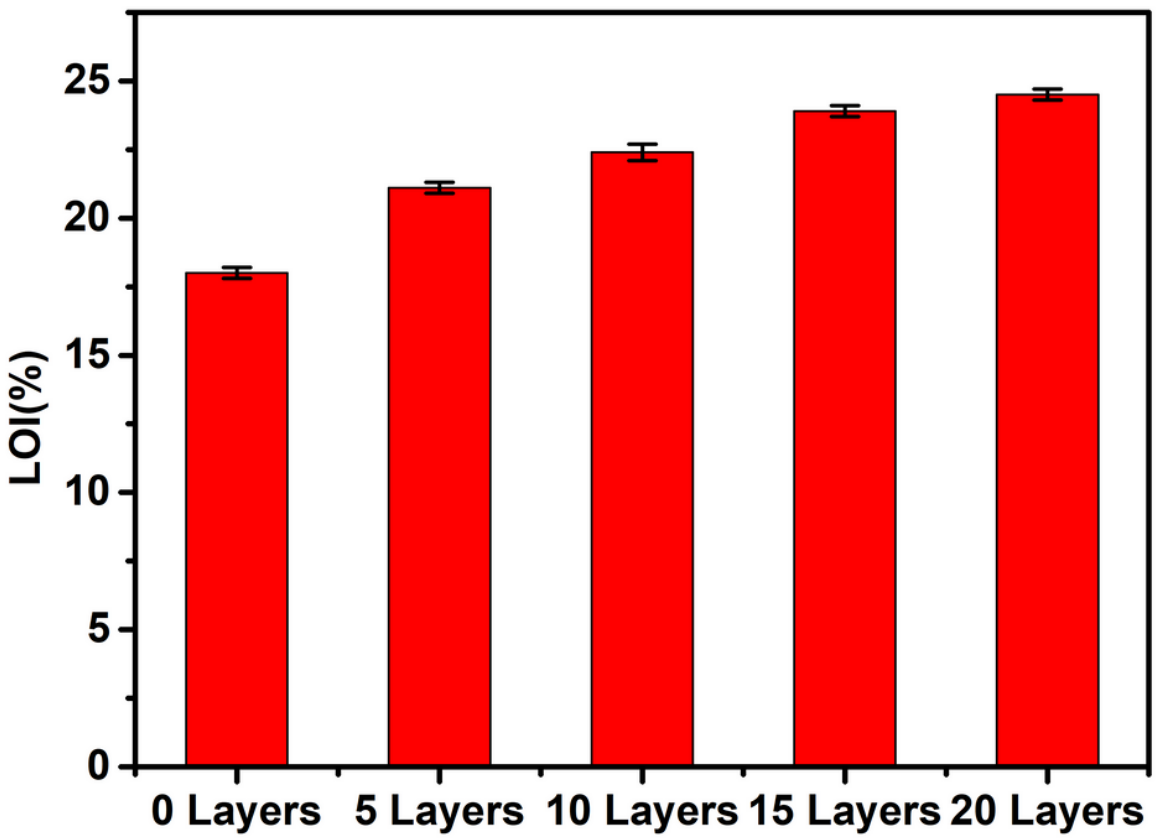

Figure 6

LOI of treated fabric with different layers

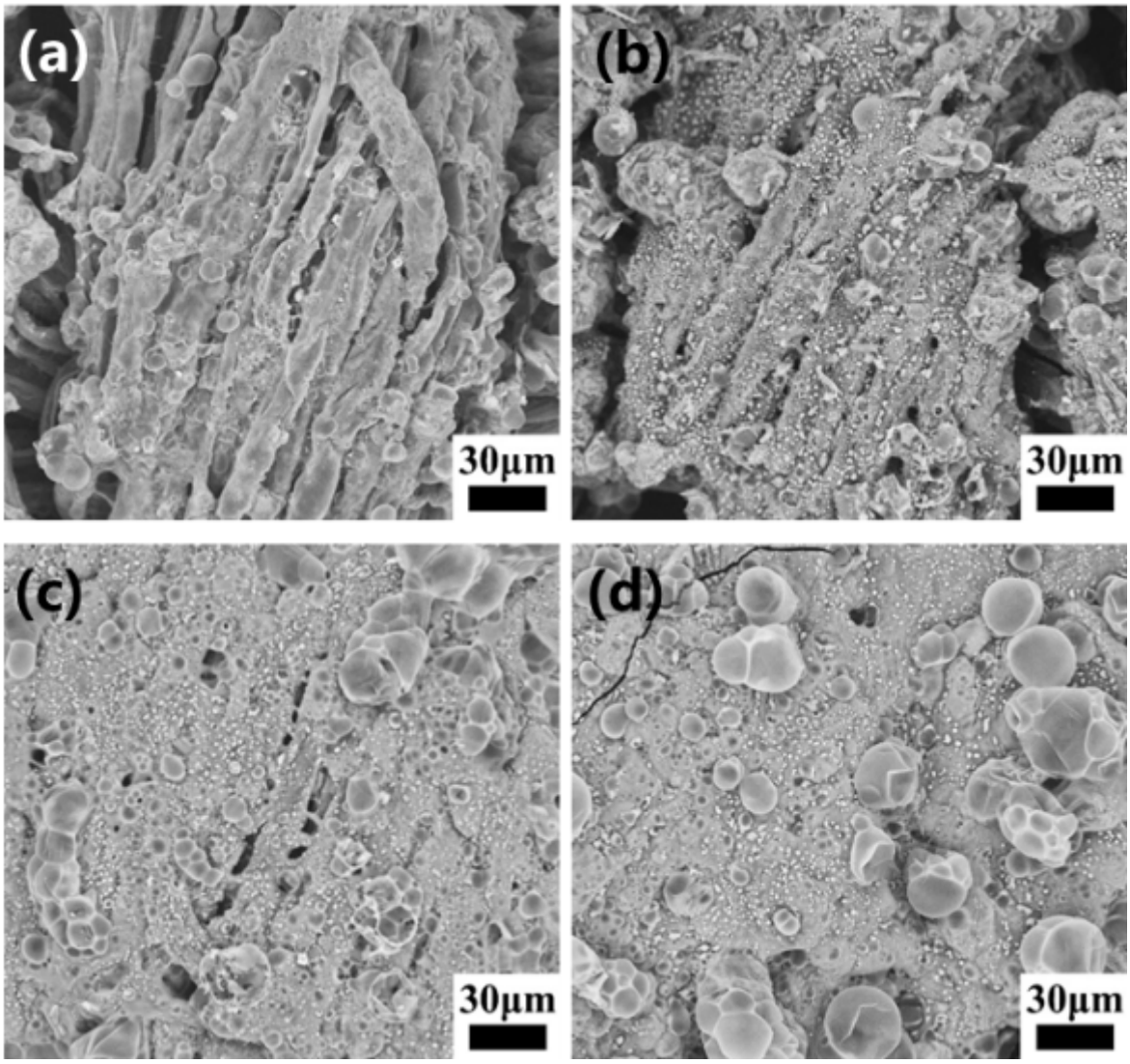

Figure 7

Surface morphology of treated cotton fabrics after burning. (a) SEM of MPCM/APP-5 after burning, (b) MPCM/APP-10 after burning, (c) MPCM/APP-15 after burning, (d) MPCM/APP-20 after burning

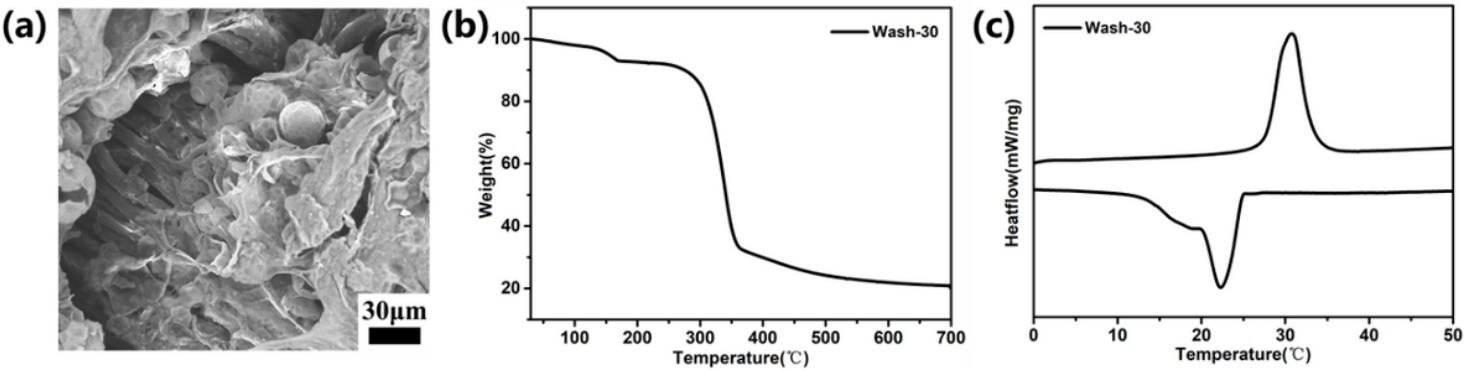

Figure 8

Durability of MPCM/APP-20. (a) SEM image of MPCM/APP-20 after being washed for 30 times; (b) TG curves of curves MPCM/APP-20 after being washed for 30 times; (c) DSC curves of MPCM/APP-20 after

being washed for 30 times

Supplementary Files

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