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Urea phosphate/β-cyclodextrin inclusion complex to enhance thermal behavior of cotton fabric

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ABSTRACT

Inclusion complex of urea phosphate (UP) and β-cyclodextrin (βCD) was prepared under different reaction times and UP concentrations. The inclusion complex of UP and βCD (βCD–UP-IC) was characterized by measuring nitrogen percentage, FTIR and thermal gravimetric analysis (TGA). The optimum conditions used for the preparation of βCD–UP-IC were used to prepare an inclusion complex of UP and monochlorotriazinyl β-cyclodextrin onto cotton fabric in presence and absence of epichlorohydrin to enhance the thermal stability of cotton fabric. The treated cotton fabric was monitored by measuring nitrogen percentage, before and after washing, and TGA. The results obtained indicate that the loss of weight of the treated fabrics is lower than that of untreated fabric.

1. Introduction

Cyclodextrins are bio-synthetic cyclic oligomers formed from 6(α), 7(β) and 8(γ)-glycopyranosyl units, linked by α-1–4 linkages (Szejtli, 1982). They are produced in nature by the enzyme cyclodextrin glycosyltransferase from starch (Schmid, 1991). Cyclodextrins are water-soluble, since all the free hydroxyl groups are on the outer surface of the ring; the inner hydrophobic cavity can form inclusion complexes with guest molecules. Usually these inclusion complexes can be crystallized, purified and are successfully exploited in different fields such as food manufacturing, cosmetics, pharmaceuticals, analytical & organic chemistry (Chisvert, Pascual-Martí, & Salvador, 2001; Connors, 1997; Huang, Gerber, Lu, & Tonelli, 2001; Junquera, Romero, & Aicart, 2001; Lee, Yoon, & Ko, 2000; Lee, Yoon, & Ko, 2001; Loftsson & Brewster, 1996; Lo Nostro, Lopes, & Cardelli, 2001; Savarino, Viscardi, Quagliotto, Montoneri, & Barni, 1999; Szejtli & Osa, 1996). Several papers and patents report relevant applications of cyclodextrins for antibacterial, insect-free aroma finishing and textile dyeing (Lee et al., 2000, 2001; Le Thuaut et al., 2000; Savarino et al., 1999).

Cotton is the most important textile fiber and there is a great demand all over the world for cotton fabrics that exhibit improved functional characteristics. Flame retardant cotton fabric can be prepared by resin finishing with organophosphorus compounds (LeBlank, 1989; Nakanishi & Aoki, 1991; Nakanishi & Ohkouchi, 1992), but such treatment causes a drop in tensile strength, deterioration of fabric hand and sometimes skin irritation. Low cost treatments, such as those using ammonium phosphates with urea, are excellent flame retardants for some specific applications. However, they may not be suitable for particular end-uses because of fiber strength loss, discoloration of the substrate upon heat fixation and insufficient durability.

The aim of the present study is to investigate the possibility of formation of an inclusion complex between urea phosphate (UP) and β-cyclodextrin (βCD). The effect of this inclusion complex on the thermal behavior of cotton fabric will also be studied.

2. Experimental

2.1. Materials

β-Cyclodextrin (βCD) and monochlorotriazinyl β-cyclodextrin (MCT-βCD) were kindly supplied by Wacker Chemie (Germany). Urea phosphate, epichlorohydrin, Na_2CO_3 and NaOH are of laboratory grade chemicals. Bleached 100% cotton fabric was kindly supplied by Misr Company for spinning and weaving, Mehalla El Kobra, Egypt.

2.2. Preparation of urea phosphate and βCD inclusion complex (βCD–UP-IC)

6 g of βCD was dissolved in 60 ml of distilled H_2O; the temperature was raised to 70 °C until complete dissolution of βCD. Solutions of UP (2–6%, w/v) in distilled H_2O were added drop wise

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Table 1
Effect of UP concentration on the N% of βCD–UP inclusion complex.

UP concn (g)	N%
2	0.57
4	0.74
6	0.83

3 g βCD, 30 H_2O, UP in 20 ml H_2O, 70 °C for 3 h. Cooling overnight, filtration, washing, and drying at 40 °C under vacuum.

Table 2
Effect of inclusion time on the N% of βCD–UP inclusion complex.

Time (h)	N%
0.5	0.513
1	0.560
2	0.690
3	0.8299

3 g βCD, 30 H_2O, 6 g UP in 20 ml H_2O, 70 °C, cooling overnight, filtration, washing, and drying at 40 °C under vacuum.

to βCD solution; the temperature was maintained at 70 °C with stirring for a definite time. The solution was kept at room temperature overnight. The inclusion complex crystals were filtered off and washed thoroughly with water and dried at 40 °C in vacuum oven.

2.3. Treatment of cotton fabric with MCT-βCD–UP

Cotton fabric was immersed in a solution containing different concentrations of MCT-βCD (2–20%, w/v), 2% Na_2CO_3, padded to pick up 100%, dried at 100 °C for 3 min and cured at 120 °C for 10 min. The treated cotton fabric with MCT-βCD was transferred to a solution containing 10% UP at 70 °C for 3 h.

2.4. Treatment of cotton fabric with MCT-βCD–UP in presence of epichlorohydrin as crosslinking agent

Cotton fabric was treated with a solution containing a definite concentration of MCT-βCD (15%, w/v), different concentrations of epichlorohydrin (0–3%) in presence of 1% NaOH, padded to pick up 100%, dried at 100 °C for 3 min and cured at 140 °C for 3 min. The so treated cotton fabric was then treated with 10% UP at 70 °C for 3 h.

2.5. Characterization

- Nitrogen percentage (N%) was measured using micro Kjeldhal method.
- FTIR spectroscopy was measured using FTIR Raman model Nexus 670 (Nicollet-Madison, WI).
- Thermal gravimetric analysis (TGA) was carried out using Perkin Elmer 7DX Thermo Gravimetric Analyzer, USA.
- The % fixation of N% related to UP was calculated using Eq. (1):

$$\%\,\text{Fixed} = \frac{(\text{N\% UP} + \text{MCT-}\beta\text{CD})_a - (\text{N\% MCT-}\beta\text{CD})_a}{(\text{N\% UP} + \text{MCT-}\beta\text{CD})_b - (\text{N\% MCT-}\beta\text{CD})_b} \times 100 \qquad (1)$$

where a and b are after and before washing, respectively.

3. Results and discussion

3.1. Preparation of βCD–UP-IC

3.1.1. Effect of concentration of UP

Table 1 shows the effect of concentration of UP on the N% of the βCD–UP-IC. N% was found to increase from 0.57 to 0.83 by increasing the concentration of UP from 2% to 6% (w/v). These results indicate that βCD has the ability to form inclusion complex with UP and also the quantity of UP in the inclusion complex increases with increasing the concentration of UP in the solution.

3.1.2. Effect of inclusion time

It is clear from Table 2 that up to 1 h, the reaction time has no serious effect on the N% of the βCD–UP-IC (N% = 0.513 at 0.5 h and 0.560 at 1 h). By increasing the reaction time above 1 h the N% increased from 0.560 to 0.690 by increasing the reaction time to 2 h and to 0.829 by increasing the reaction time 3 h.

3.1.3. FTIR spectroscopy

Fig. 1 shows FTIR spectra of (a) βCD, (b) UP and (c) βCD–UP-IC. FTIR spectrum of βCD–UP-IC shows only shifts of the peak at 1649.8 cm^{-1} of βCD (Fig. 1a) to a longer wave length 1654.1 cm^{-1} (Fig. 1c) otherwise FTIR spectra have no important differences.

3.1.4. TGA

TGA of βCD and βCD–UP-IC is presented in Fig. 2. It is clear from Fig. 2 that the presence of UP in the cavity of βCD has a very important effect on the thermal behavior of βCD. Fig. 2a shows that the maximum decomposition temperature of βCD is 303 °C and the maximum weight loss is 60%, while the maximum decomposition temperature of βCD–UP-IC is 257 °C and the maximum weight loss is 36% (Fig. 2b). These results emphasize that the presence of UP in the cavity of βCD leads to the decrease of the maximum weight loss from 60% to 36%. Also Fig. 2b shows that the βCD–UP-IC is not a simple physical mixture of the UP and βCD, because of the absence of discontinuous weight loss in the sample at around 305 °C.

3.2. Effect of treatment of cotton fabric with MCT-βCD followed by inclusion with UP on the N% and TGA of the treated fabric

3.2.1. Effect of MCT-βCD concentration on N% and TGA of cotton fabric

It is obvious from Table 3 that the N% increases with increasing the concentration of MCT-βCD before and after washing in presence and absence of UP. These results indicate that MCT-βCD was not completely fixed onto the fabric which is very clear from the results of N% of the treated fabric with MCT-βCD before and after washing. This holds true for the fabric treated with MCT-βCD followed by UP before and after washing. In all cases the N% before washing was higher than after washing. The N% fixed on the fabric related to UP is calculated using Eq. (1). Table 3 shows that the fixed N% on cotton fabric after washing increases from 22% to 59.5% by increasing MCT-βCD concentration from 0% to 20%, which may be attributed to the increasing of quantity of UP in MCT-βCD's cavity.

3.2.2. Effect of the concentration of epichlorohydrin on the % fixed N% of the treated fabric

The treatment was carried out by immersion of the fabric in 15% MCT-βCD in presence of 1% NaOH and different concentrations of epichlorohydrin (0–3%), padded to 100% pick up and cured at 140 °C for 3 min followed by inclusion with 10% UP at 70 °C for 3 h. The N% fixed on the fabric increases by increasing the epichlorohydrin concentration from 0 to 3%. Table 4 shows that the fixed amount of N% increases from 56.7% to 70% by increasing epichlorohydrin from 0% to 3%. The results obtained indicate that the presence of epichlorohydrin leads to the increasing amount of MCT-βCD fixed on the fabric through crosslinking between cellulose chains and MCT-βCD.

3.2.3. TGA of cotton fabric treated with MCT-βCD followed by inclusion with UP in presence and absence of epichlorohydrin

Fig. 3 shows TGA of (a) cotton fabric, (b) cotton fabric treated with MCT-βCD, (c) cotton fabric treated with UP, (d) cotton fabric

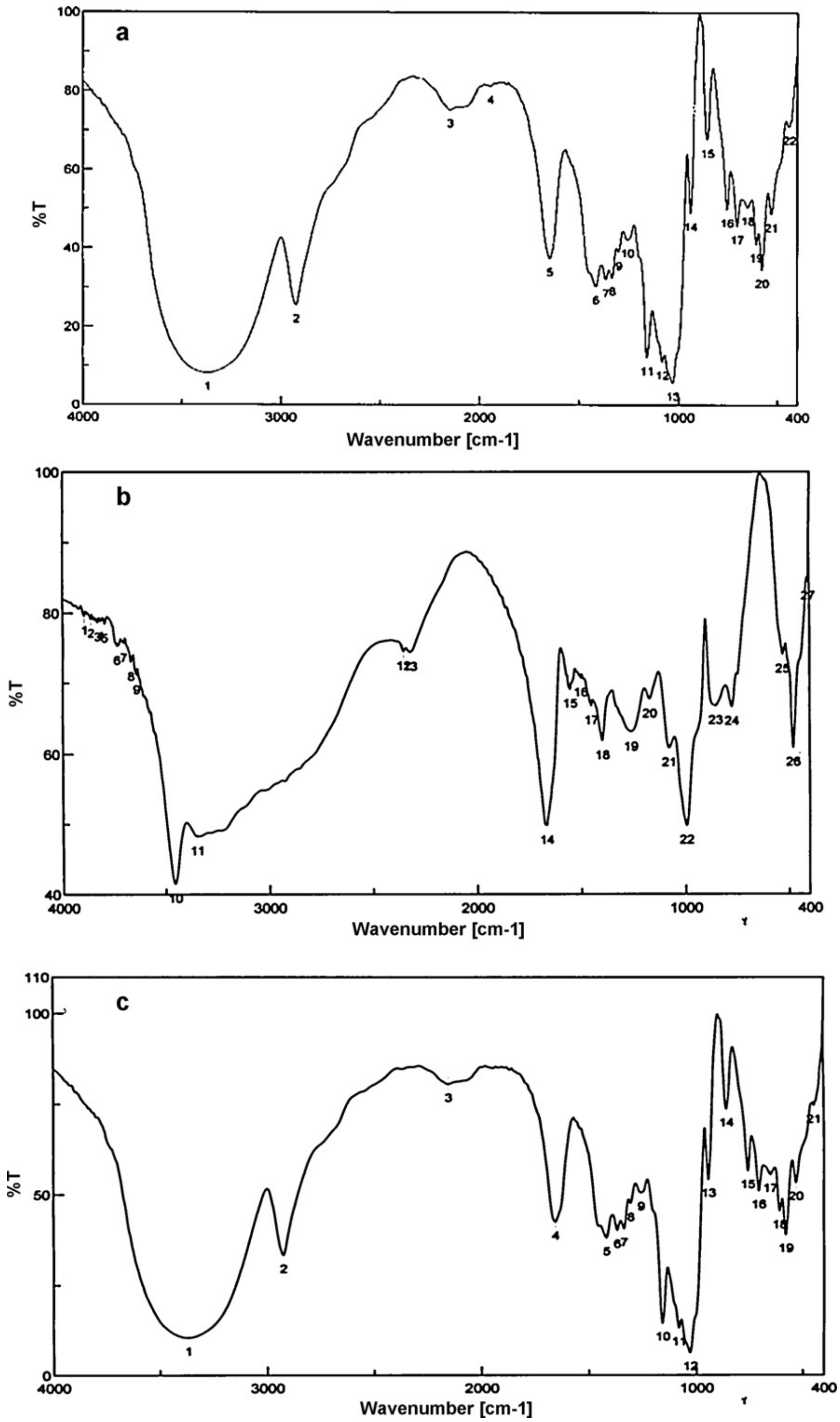

Fig. 1. FTIR spectra of (a) β-cyclodextrin, (b) urea phosphate and (c) urea phosphate–β-cyclodextrin inclusion complex.

treated with MCT-βCD followed by treatment with UP (e) cotton fabric treated with MCT-βCD in presence of epichlorohydrin followed by treatment with UP. The decomposition temperature and weight loss% are shown in Table 5. The results reveal that the decomposition temperature of cotton fabric alone is 310 °C, this is against 270 °C, 285 °C, 289 °C and 290 °C for cotton fabric treated with MCT-βCD, cotton fabric treated with UP, cotton fabric treated with MCT-βCD followed by treatment with UP, and cotton fabric treated with MCT-βCD in presence of epichlorohydrin followed by treatment with UP respectively. It is obvious that the treatment of cotton fabric leads to the decrease of decomposition temperature by 40 °C for MCT-βCD and only by 20–25 °C for UP, MCT-βCD followed by treatment with UP and MCT-βCD presence of epichlorohydrin followed by treatment with UP. Also the weight loss decreases from 66% for cotton fabric only to 40.2%, 40.3%, 20% and 6.34% at the decomposition temperature for cotton fabric treated with MCT-βCD, cotton fabric treated with UP, cotton fabric treated with MCT-βCD followed by treatment with UP,

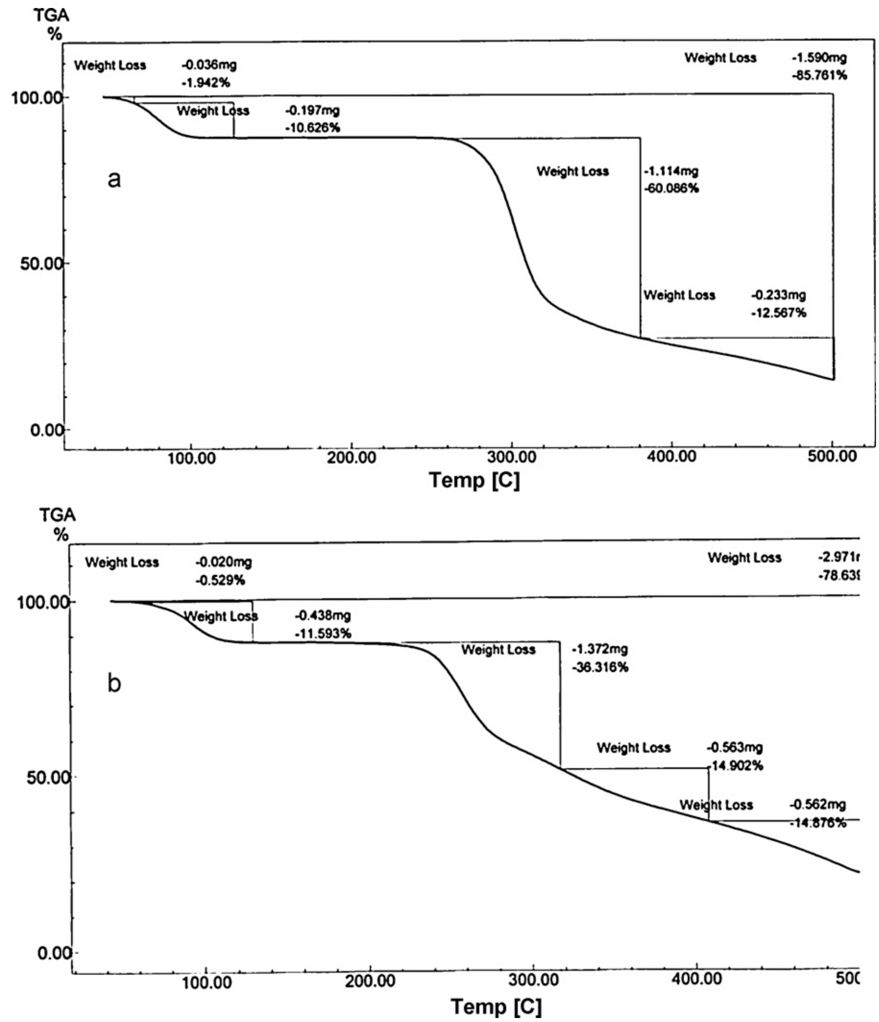

Fig. 2. TGA of (a) βCD and (b) βCD–UP-IC.

Table 3
Effect of MCT-βCD on the nitrogen content of the treated fabric.

MCT-βCD conc. %	N% (MCT-βCD)[b]	N% (MCT-βCD)[a]	N% (MCT-βCD–UP)[b]	N% (MCT-βCD–UP)[a]
0	0	0	1.23	0.289
5	0.56	0.1	1.6	0.51
10	0.72	0.189	1.81	0.688
15	1.02	0.25	1.83	0.71
20	1.05	0.25	1.93	0.772

βCD + 2% Na_2CO_3, dried at 100 °C for 3 min and cured at 120 °C 10 min. Up alone 10% exhaustion 3 h, drying at 50 °C.
[a] After washing.
[b] Before washing.

Table 4
Effect of of epichlorohydrin on the nitrogen content of the treated fabric.

Epichlorohydrin concn. (%)	N% (MCT-βCD)[b]	N% (MCT-βCD)[a]	N% (MCT-βCD–UP)[b]	N% (MCT-βCD–UP)[a]
0	1.02	0.25	1.83	0.71
1	1.02	0.21	1.83	0.73
2	1.015	0.23	1.81	0.79
3	1.02	0.27	1.81	0.85

15% MCT-βCD + 1% NaOH, dried at 100 °C for 3 min and cured at 140 °C 3 min followed by exhaustion with 10% UP, 3 h.
[a] After washing.
[b] Before washing.

Table 5
Decomposition temperature and % weight loss of treated cotton fabric.

Sample	Decomposition temperature (°C)	Weight loss (%)
Cotton	310	66.6
Cotton + MCT-βCD	270	40.2
Cotton + UP	285	40.3
Cotton + MCT-βCD + UP	289	20.6
Cotton + MCT-βCD + UP + epichlorohydrin	290	6.34

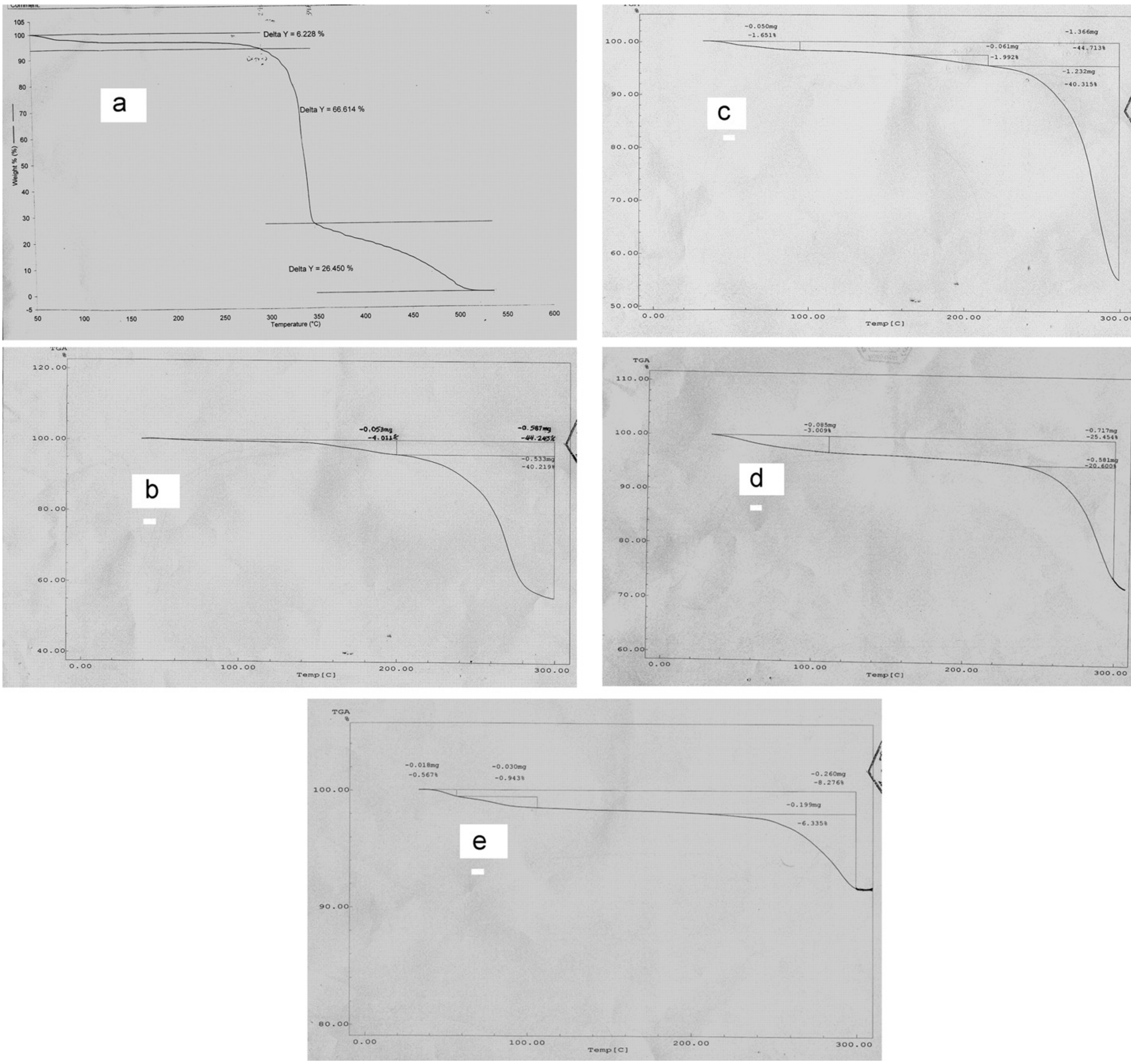

Fig. 3. TGA scan of (a) cotton fabric, (b) cotton fabric treated with MCT-βCD, (c) cotton fabric treated with UP, (d) cotton fabric treated with MCT-βCD followed by UP only, and (e) cotton fabric treated with MCT-βCD followed by UP in presence of epichlorohydrin.

and cotton fabric treated with MCT-βCD in presence of epichlorohydrin followed by treatment with UP respectively (Fig. 3). These results could be explained by the synergistic effect of nitrogen and phosphorus present in the UP structure which give the cotton fabric the ability to liberate less volatile components than in absence of UP.

4. Conclusion

From the results obtained we can conclude that UP can form an inclusion complex with βCD and MCT-βCD. The formation of this complex increases by increasing of the time of reaction and the concentration of UP which is confirmed by N%, FTIR and TGA.

Cotton fabric treated with MCT-βCD followed by inclusion with UP exhibits a good thermal stability. Presence of epichlorohydrin leads to good fixation of MCT-βCD and enhances the thermal behavior of cotton fabric which is confirmed by N% and TGA.

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