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Determination of antioxidant capacity of capsule loaded textiles

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In this study, microcapsules containing α-Tocopherol (α-TP) have been prepared by complex coacervation technique and applied to cotton fabric by padding method. Characterization of the capsules is determined by scanning electron microscopy, thermogravimetric analysis, fourier transform infrared spectroscopy and particle size measurement. Yield of microencapsulation process is found in the range of 41.63 - 62.20%. Antioxidant capacity of capsule loaded textiles has been examined according to DPPH free radical scavenging method, and α-TP existence in ethyl cellulose capsules is found as 65.218 - 330.722 µM. α-TP activity in capsule treated fabric is determined as 61.73 µg. Presence of the capsules on fabric and also α-TP activity has been found to remain effective even after twenty washes at 40°C.

Keywords: α-Tocopherol, Antioxidant, Complex coacervation, Cotton, Microencapsulation

1 Introduction

Vitamin-E, an important human nutrient, is a fat-soluble vitamin[1,2]. Furthermore, it is a powerful antioxidant that can also be used topically. Antioxidants are molecules, which protect cells through preventing chain reactions causing oxidation. Vitamin-E is composed of eight naturally occurring subunits α, β, γ and δ tocopherols and tocotrienols. α-Tocopherol (α-TP) is the most active form of all [3,4]. Various *in-vitro* and *in-vivo* studies have been carried out with α-TP, and its activity against mortal illnesses like heart diseases, Alzheimer's disease, many forms of cancer, including melanoma and also affect to skin by preventing signs of aging have been previously investigated. Numerous positive results have been obtained[3-8]. In order to comprehend better transmission of vitamin E in the body, intestinal absorption, transport from the liver and cellular intake of α-TP was monitored by *in vivo* studies[9]. Therapeutic (Vitamin A and D) and antioxidant (vitamin E and C, and coenzyme Q) vitamins play a major role in skin care. These vitamins are beneficial in the prevention of various skin diseases such as acne and psoriasis[10]. However, that vital material is susceptible against heat and oxygen [11].

Oxidation reactions cause cell damage via creating chain reactions by producing free radicals. Antioxidant molecules protect the cells by preventing the chain reaction. However, especially α-TP is oxidized very quickly. Biological function of vitamin E is based mainly on its antioxidant feature. Therefore, storage conditions of the α-TP compounds should be broadened and must be protected from environmental conditions[10].

Capsules are tiny droplets that conserve the functional core material such as antioxidants, antimicrobials, flame retardants, insecticides, pharmaceuticals, phase change materials, etc. from external factors using a thin film of shell. Thus, these perishable materials can resist those environmental factors, like oxidation, light and vaporization, and retain their effect longer [12]. They are named according to the size of the particles, which are <1 µm as nanocapsules, between 1 µm and 1000 µm as microcapsules and larger than 1000 µm as macrocapsules. However, the process is named as microencapsulation. Textile materials are able to carry capsules with these various features, thereby microencapsulation is employed as an alternative to finishing processes, which have provided functional properties to the textile products. With that technique, utilization of oily substances in direct applications to textiles has become possible.

Cosmetotextiles are textiles carrying durable cosmetic products, mainly for dermatological applications generally via microencapsulation and release of the active agents while in contact with skin[13,14]. In recent

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years, they are popularized in the textile market with the consumer orientation, commonly containing agents promising moistening, slimming, anti-cellulite, anti-aging, and anti stretch mark. Some of the successful commercial products have been Skintex® (Pulcra Chemicals) and Cellecense™. Due to free radicals in the structure, Vitamin E is a natural antioxidant and provides anti-aging effects. In recent studies, importance and preservation possibilities via encapsulation of α-TP are investigated broadly. Yenilmez *et al*.[15], encapsulated α-TP inside chitosan wall. This promising product was found to increase moisture and elasticity of the skin and delayed signs of aging according to *in-vivo* studies.

Coacervation is one of the capsule production methods that is suitable for water-immiscible liquids [13]. Ethyl cellulose (EC), a material that is compatible for this technique, has chosen as shell material. EC is resistant to water, alkali and salt and can provide its strength and flexibility in very wide temperature range [17,18].

In literature, several studies have been reported on antioxidant textiles. Alonso *et al*.[19] used resveratrol and trolox as antioxidants and applied directly to the textile material. Koh and Hong[20] used walnut extract as antimicrobial and antioxidant. Antioxidants are very susceptible against environmental factors such as light, oxygen and heat. When the antioxidants meet the air they vanish quickly and so this desired effect remains limited. On the other hand, in this study, α-Tocopherol is microencapsulated to enhance the antioxidant effect. In addition, washing resistance is expected due to binding of these antioxidant microcapsules.

The aim of this research is to determine the antioxidant effect of the capsule loaded textiles. For that purpose, capsules have been produced using three different shell (EC):core (α-TP) ratios (w/w) at the first step. At the second step, the chosen capsule, according to several characterization methods, is applied to cotton fabric by padding method. At final stage of the study, antioxidant properties of capsules and fabrics are examined. Washing durability of antioxidant effect in fabrics is also investigated.

2 Materials and Methods

2.1 Materials

In this research, desized, mill scoured and bleached plain weave cotton fabric (specific weight 129 g/m^2) was used. The shell material ethyl cellulose (EC, Premium 4) was donated kindly from Dow Chemicals, Istanbul, Turkey. Pure α-TP was employed as core material, Tween 20® was chosen as a surfactant. All of these and organic solvents, [ethanol and ethyl acetate (EA)], were supplied from Merck, Darmstadt, Germany. The acrylic based commercial binding agent of Organik Kimya A.Ş. ORGAL® NA 366 was used. The other auxiliary chemicals used in the study were of technical grade.

2.2 Preparation of Nano and Micro Capsules

In order to obtain EC capsules, coacervation method was employed. In this process, the interactions of water-insoluble polymers with water were utilized to form the capsules [21, 22]. α-TP and EC in a specific ratio were dissolved homogenously in organic solvent. Polymer-rich organic phase was then added to polymer free aqueous phase. Active ingredients were separated into micro droplets with the help of Silverson high shear mixer at 8000 rpm, and every single droplet was coated with a thin film of shell material, simultaneously. Afterwards, the liquid film was solidified by adding water into the system. Water was removed by centrifugal machine to obtain microcapsule slurry. Finally, the slurry was treated in ultrasonic bath and dried under laboratory condition. The spherical shaped capsules are obtained successfully at 2:1, 4:1 and 10:1 (w/w) shell:core ratio and named as A-TP M1, A-TP M2 and A-TP M3 respectively.

2.3 Characterization of Nano and Micro Capsules

Scanning Electron Microscopy

Morphological features of capsules were detected by scanning electron microscopy (SEM) images. SEM analysis was carried out at Quanta 250 FEG. Samples were gold-coated (15 mA, 2 min) to assure electrical conductivity. The measurements were taken at 5 kV accelerating voltage and X20.000 magnification.

Particle Size Measurement

Particle size distribution test was performed by Zetasizer Nano-S. Aqueous solution of all capsule formulations in the study was filled into disposable cuvettes after sonification step separately. With an aid of laser doppler, light was scattered through capsule dispersion. Thus, distribution of particles in solution was discovered.

Production Yield

Yield of capsule production was calculated via percentage of mass obtained to total mass used in an equation, as shown below:

$$\text{Production yield}(\%) = \frac{\text{Actual capsule amount (g)}}{\text{Theoretical capsule amount (g)}} \times 100 \quad \ldots(1)$$

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used for determining the success of encapsulation with changes on the infrared spectrum. In this content, samples were measured at wavelength range of 400-4000 cm^{-1} using Perkin Elmer Frontier.

Thermogravimetric Analysis

Thermogravimetric analysis of the capsule was done in order to understand the physical and chemical state changes depending on thermal alteration. Observation of mass change with a temperature increase was the basis of the analysis. TGA was carried out with 5°C per min in the range of 0°– 600 °C under nitrogen medium with Perkin Elmer Diamond TG/DTA.

Determination of α-TP Content in Capsules

Presence of α-TP was studied by Lambda 35 UV-Vis spectrophotometer. Requirement of this analysis was to release the whole inner ingredient by resolving the capsule shell[11]. For this purpose, absorbance values of capsule solutions against blank were read corresponding to λ_{max} (280 nm). These values were placed in standard calibration line formerly plotted. Linear regression formula of α-TP was:

$$y=0.002519x \quad \ldots(2)$$

where y is the absorbance value (280 nm); x, the concentration (μM=μg/L); and r^2 equals to 0.9977.

2.4 Application and Fixation of Nano and Micro Capsules onto Cotton Fabric

Permanent binding of capsules is essential in order to obtain a durable antioxidant effect on cotton fabric. Therefore, the optimum capsule sample was impregnated in a solution bath containing capsules (40 g/L) and binding agent (50 g/L), and then squeezed between rollers to 89% wet pick-up. Achieving long lasting effect on wearable cosmetic textiles, the fabric was exposed to combined drying and fixation process for 7 min at 120˚C in a laboratory Stenter.

2.5 Evaluation of Treated Fabrics

Scanning Electron Microscopy

SEM images were taken to identify the existence of capsules on the textile surface from both washed and unwashed samples. In order to enhance electron density contrast, samples were coated with gold (15 mA, 2 min). The measurements were taken at 5 kV accelerating voltage, and ×2.500 and ×5.000 magnifications.

Washing Procedure

Capsule treated samples were washed for 1, 10 and 20 cycles with 4 g/L Ece nonphosphate reference detergent (A) at 40°C for 30 min separately, according to ISO 105-C06:2010[23]. The fabrics were rinsed then dried in laboratory conditions.

Determination of α-TP Content in Fabric

The amount of the α-TP in fabric and its antioxidant activity were investigated. Alterations caused from washing cycles were observed. α-TP content inside the fabrics were determined by high performance liquid chromatography (HPLC-HP 1100). With the intention of α-TP amount inside 1 gram A-TP M3 capsule, standard line graph was created. According to data obtained by pre-determined α-TP solutions, following regression equation was used:

$$Y=8541.6X \quad \ldots(3)$$

where Y is the area; X, the concentration (μg/μL); and r^2 equals to 0.9996.

Determination of Antioxidant Capacity of Fabric

Antioxidant activities of the fabrics were detected according to 1,1-Diphenyl-2-picrylhydrazyl (DPPH) free radical scavenging method [24]. The basis of this technique includes reading the asorbance values of treated fabrics against blank at 517 nm by UV-VIS Spectrofotometer (Shimadzu UV 160 A), in which fabrics were kept in standard DPPH solution. DPPH inhibition % graph was plotted to determine antioxidant activity of both washed and unwashed fabrics. Regression equation of DPPH inhibition % was calculated using the following equation:

$$Y=0.9304X \quad \ldots(4)$$

where Y is the DPPH inhibition %; X, the concentration (μg/4 mL); and r^2 equals to 0.999.

DPPH inhibition % was calculated using the following equation:

$$\text{DPPH inhibition}(\%) = \frac{(A-E)}{A} \times 100 \quad \ldots(5)$$

where A is the absorbance value of blank sample; and E, the absorbance value of treated sample's solution at 517 nm.

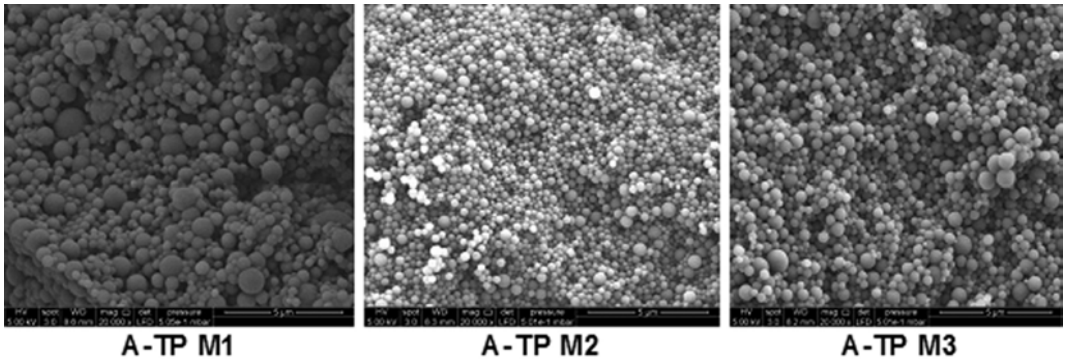

Fig. 1 — SEM images of capsules

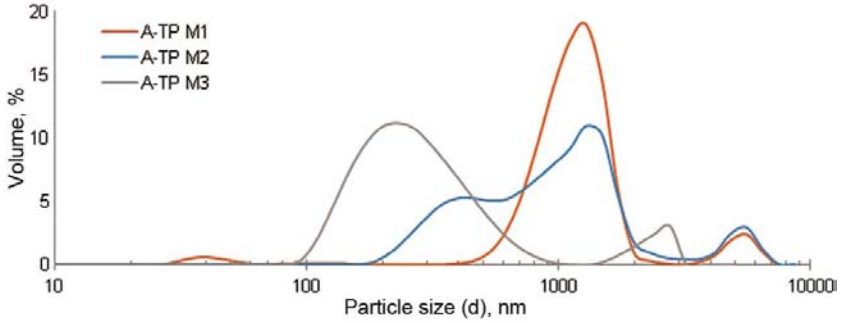

Fig. 2 — Particle size distribution of capsules

3 Results and Discussion

3.1 Morphological Features of Capsules

SEM analysis has been performed to demonstrate the encapsulation success and to determine morphological properties of cosmetic capsules. Magnification of ×20.000 shows that the capsules with spherical shape are prepared successfully, and the images show that A-TP M2 and A-TP M3 capsules are both smaller and possess more homogenous size distribution than A-TP M1 (Fig. 1).

3.2 Particle Size Distribution

The data indicates similar outcomes with the general appearance of the capsules. It is found that all the samples have size range 30 nm - 6µm. According to Fig. 2, 90% volume of A-TP M1 has 1.156 µm average diameters. While 65% of A-TP M2 has 1.141 µm, and 25% of it has 389.2 nm average diameters. On the other hand, A-TP M3 is found to have 282.5 nm diameter of its 90% approximate volume. Particle size distribution is found more homogenous in A-TP M3 (Fig. 1)

3.3 Spectroscopic Studies

FTIR spectra of EC, A-TP and α-TP are shown in Fig. 3. Infrared spectra of EC show characteristics bands for –C–O–C– stretching vibration at 1053 cm^{-1} and C–H stretching bands at 2880 cm^{-1} and 2970 cm^{-1}. The peak at 1354 cm^{-1} belongs to C-H bending bands. Main peaks of α-TP refer C-H out of plane free vibration, –C–O–C– vibration, CH_2 bending and CH stress vibration at 917, 1084, 1458 and 2867 cm^{-1} respectively. It is observed that spectra of capsules synthesized from these materials represent the peaks similar to EC characteristic bands with slight shifts. The missing α-TP bands in the spectrum of capsules are considered as a result of capsulation.

Besides the amount of materials used and eventual capsule output, one of the influencing factors to select ideal capsule is the content of the active substance. Thus, production yields of the different capsule formulations as well as α-TP concentrations are calculated and shown in Table 1. The yield of microcapsules is determined using the following equation:

$$\text{Process yield} = \frac{\text{Recovered mass (g)}}{\text{Mass enterened into the experiment}} \times 100\% \quad \ldots(6)$$

3.4 Thermal Studies

The thermal behavior of ideal capsule and its raw materials are presented in Fig. 4. Weight losses due to moisture of substances are observed at 100ºC. Combustion process of EC is shown to start at 225ºC, and then accelerated at 325ºC. At 440ºC, EC is found

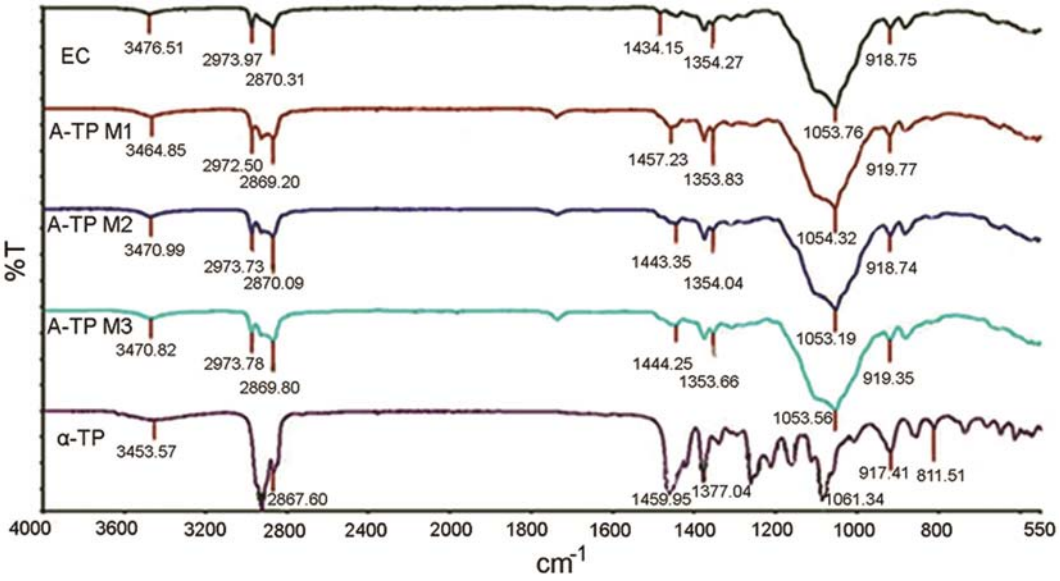

Fig. 3 — FTIR spectra of EC, α-TP and A-TP capsules

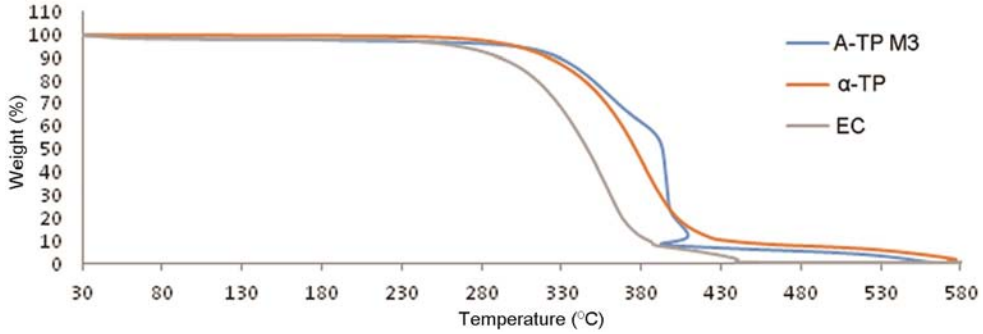

Fig. 4 — TGA diagrams of (a) EC, (b) α-TP and (c) A-TP M3

Table 1– Production yields and α-TP contents of capsules

Capsule	EC: α-TP (w/w)	Production yield , %	Absorbance (280 nm)	Concentration, µM
A-TP M1	2:1	41.63	0.857	330.722
A-TP M2	4:1	57.82	0.398	153.591
A-TP M3	10:1	62.20	0.169	65.218

to lose 99% of its weight. It is found that α-TP starts carbonizing above 150ºC. Decomposition is accelerated at 300ºC and the material is found fully decomposed at 576ºC. When the TGA curve of A-TP M3 is examined, it is found that decomposition has started above 150ºC but accelerated at 390ºC, unlikely the core substance. At 550ºC, major mass of A-TP M3 is combusted.

3.5 Durability of Treated Fabrics

As a result of SEM, FTIR, particle size distribution analysis and yield studies, A-TP M3 is found as the most stable capsule formulation. SEM images of untreated fabric, solely linker applied fabric, treated fabric and fabrics after 1, 10 and 20 washes are given in Fig. 5. Furthermore, both dry and wet rubbing test[25] applied treated fabrics are also analyzed with SEM images (Fig. 5). The images indicate that the fixation is successful. Hence, fabrics preserve the capsule content even after sequential washings. Examination of rubbed samples exhibits that capsules are situated at fibre gaps more than that fabric surface.

3.6 α-TP Content and Antioxidant Activity of Treated Fabrics

With the help of SEM, capsules are detected on the fabrics surface even after sequential washings. However, the α-TP content inside these capsules is unclear. Thus, α-TP content of the samples needs to

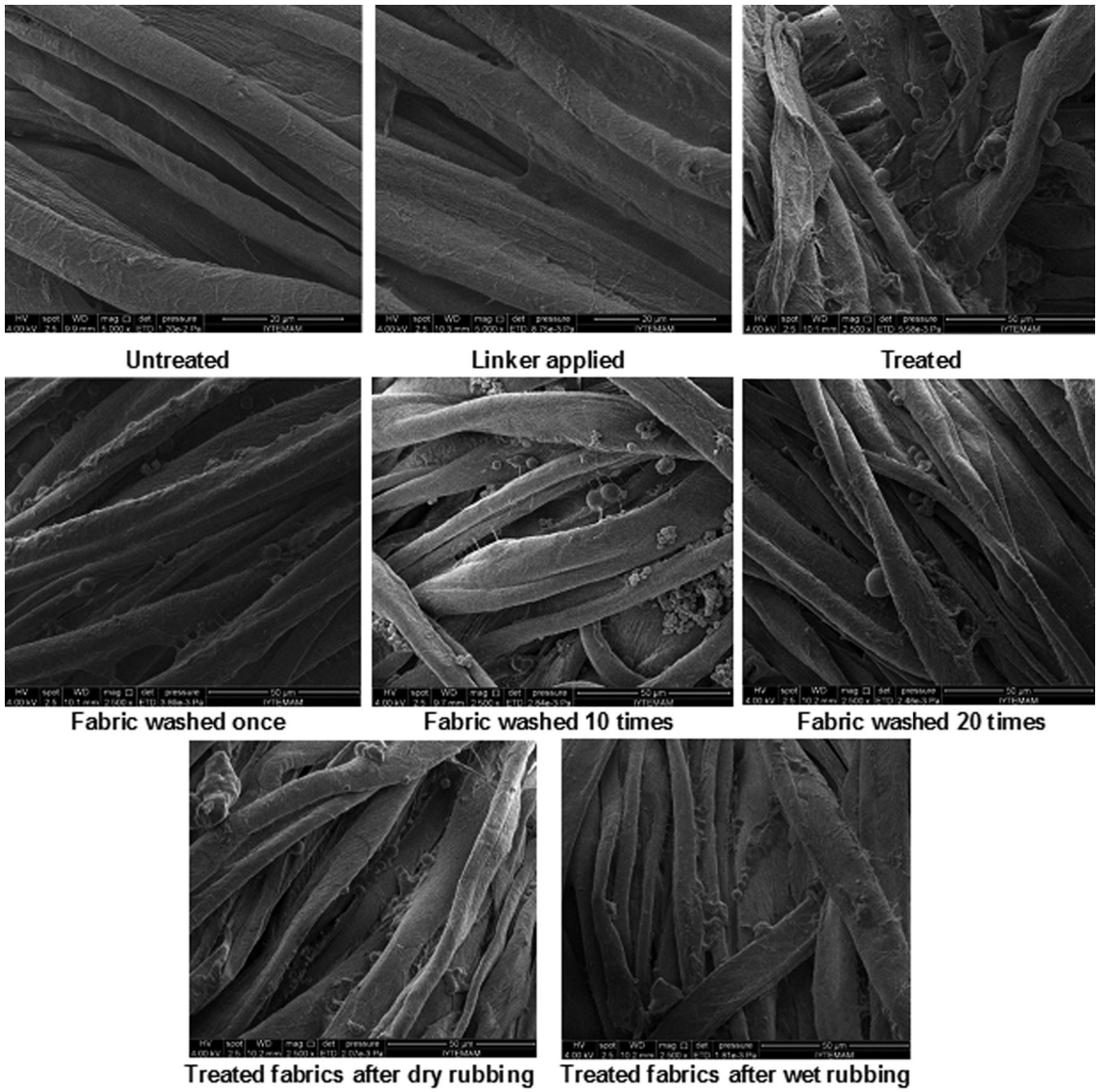

Fig. 5 — Structure and resistance of treated fabrics against washing and rubbing

Table 2 — Production yields and α-TP contents of capsules

Fabric	α-TP (mg)/ A-TP M3 (g)	α-TP loss, %	DPPH inhibition, %	α-TP activity, µg
Treated	0.86148	0	57.4338	61.73
After single wash	0.55364	35.73	32.58655	35.02
After 10 washes	0.384039	55.42	26.78207	28.78
After 20 washes	0.228104	73.52	14.05295	15.10

be examined. Decrease in α-TP amount due to washing is calculated (Eq. 3). After single washing, it is detected that 35.73% of α-TP content has perished. The fabrics after 10 sequential washings, lose its 30.63% α-TP ingredient more, and α-TP content of the 20 times washed fabric is determined 40.60% less than that of 10 times washed sample. In addition, antioxidant activity of fabrics against washing is studied based on DPPH inhibiton method. Antioxidant activity of samples is shown in Table 2.

4 Conclusion

4.1 It is found that A-TP M3 capsules has more consistent structural distribution. Surface of the capsules is found to be smoother and as a particle size, it has the smallest of all. Particle size distribution analysis

is supported by SEM. Production efficiency is qualified and A-TP M3 is found to have the best yield ratio. TGA curves are examined and resemblance in combustion behavior is observed between capsule and its shell material.

4.2 Considering all the data attained from these analyses, it is concluded that A-TP M3 has the ideal capsule formulation. Afterwards selected formulation is applied to fabric, and fabric handle is compared with a blank sample. It is found that the linker has changed the handle tolerably but it is not influenced adversely by addition of capsule.

4.3 It is also observed that capsules have an average diameter of 280 nm. Due to having such a small size, it is easier to get in fibre gaps. After sequential washings, it is discovered that capsules are departed from fabrics. Even after 20 washings major part of the capsules are found to remain especially in the fiber gaps. Several studies have been conducted in order to evaluate the active substance content and antioxidant properties of capsule treated fabrics after sequential washings. Consequently, it is determined that α-TP presence sustains its presence and antioxidant activity.

Acknowledgement

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