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Synthesis, characterization and application of eco-friendly lavender oil microcapsules on cotton

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In this study, lavender oil microcapsules have been synthesized, characterized and then applied on cotton fabric through padding followed by drying and curing. The treated samples are evaluated for wash fastness, tensile strength, stiffness, and the most important, release rate from treated fabric. Most of the synthesized microcapsules are found in the range of 10-30 microns. Cross-linking with DETA shows improvement in the shell morphology with slow release of lavender from treated fabric. Stiffness of the treated fabric increases proportionately with increase in concentration of microcapsules with simultaneous fall in strength.

Keywords: Cotton, Lavender oil, Microencapsulation, Release rate, Wash fastness

1 Introduction

Lavender, apart from possessing relaxing and soothing smell, also inherits the feature of treating anxiety disorders in people caused due to the stress of everyday work life[1]. Its therapeutic and curative treatments ranging from treating parasitic infections, agitation, neurological disorders and burns to insect bites have also been documented[2-5]. Application of lavender on clothing is known as fragrance finishing and has emerged rapidly as aromatic therapy[6], antibacterial[7] and insecticide textiles[8,9]. However, due to the volatile nature of the fragrance, the question of finish longevity has always been a matter of concern in the industries. A durable finish will endure through successive wet or dry cleanings, whereas non-durable finish will be removed through successive washings[10]. Finishing with fragrances through coating fails to survive one or two washing cycles as the fragrance is highly volatile. To make it resistant to washing, microencapsulation is one of the latest technologies available at present, which can encapsulate the volatile fragrance inside polymer membrane[11,12], and in this way the fragrance is prevented from rapid evaporation in the environment, oxidization and contamination along with its controlled release. In recent years, though few, but there are reports on fragrance microencapsulation and their finishing onto textile material[13].

Intensive studies have been carried out on urea-formaldehyde and melamine-formaldehyde microcapsules (MICS), but formaldehyde based systems are not environmentally accepted and are restricted due to their carcinogenic nature[14-16]. There are reports on polyurea-urethane MICS using polyvinyl alcohol as emulsifier but PVA reacts with the NCO groups of isocyanate very quickly at room temperature creating pores in the walls of MICS, leading to permeable MIC wall[17, 18].

There are no reports on robustness of the polyurea MICS to withstand the pressure exerted on fabric during finishing via padding. Cross-linkers' effect has not been studied yet to verify its effect in terms of strength and leaching of oil out of the capsule shell. Continuous diffusion of fragrance occurs, lasting up to very few days, i.e. fragrance as high as 75% get released in first few days of finishing.

In this study, attempts have been made to synthesize lavender oil MICS, that release fragrance only on scratching or rubbing the fabric, thus helping in increasing the durability of finish on fabrics and keeps the MICS economic[19]. Lavender oil MICS are synthesized using polyurea wall which doesn't have adverse effects on environment, having cross-linker for robust and impermeable wall for no leakage or diffusion of the fragrance oil. Detailed characterization of MICS was carried out in the form of particle size distribution (PSD), scanning electron microscopy (SEM) and fourier transform infrared

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spectroscopy (FTIR) analysis. Microencapsulated fabrics were also subjected to SEM analysis. Wash durability along with fabric properties like stiffness and tensile strength was also evaluated. Release study of core material (Lavender oil) from MICS was also carried out under perfect sink conditions by UV spectroscopy which is a qualitative method to have precise measurements and understanding of release[20,21].

2 Materials and Methods

2.1 Materials

Bleached and mercerized cotton fabric was used for the study. Lavender oil (Grade C, procured from Mane India Private Limited), isophorone diisocyanate (98%, IPDI) and 1, 4-Diazobicyclo (2, 2, 2) octane (98%) (DABCO, procured from Sigma Aldrich), hexamethylene diamine (HMDA), ethylene diamine (EDA), diethylene triamine (DETA) and polyvinyl pyrrolidone (PVP, K90, procured from SDFCL, India) were of AR grade. Distilled water was used as the continuous medium.

2.2 General Procedure for Ppreparation of MICS

Polyurea MICS was prepared using interfacial polycondensation technique, keeping the molar ratio of isophorone diisocyanate and ethylene diamine constant as 1:1. A typical procedure for MICS containing lavender oil is described as follows. PVP aqueous solution (5 wt%, 40 g) was taken in 250 ml beaker. To this surfactant solution, the mixture of IPDI and lavender oil was added and stirred at 1000 rpm. Known amount of EDA was diluted in 15 g of PVP K90 solution and added slowly dropwise over a period of 7-8 min; stirring was continued at 1000 rpm and the reaction was continued for 4 h at room temperature (30°C) followed by heating at 50°C for one hour to ensure complete formation of the polyurea membrane.

2.3 Techniques for MICS Characterization

The samples were analyzed through transmitted light mode. The particle size distribution of the produced MICS was determined by Malvern Mastersizer 2000. Field emission gun-scanning electron microscope (FEG-SEM) was used to study the morphology of MICS alone and in the impregnated textiles substrate. Following to the MICS synthesis, cotton fabric samples were coated with a thin layer of sputtered gold prior to examination to avoid charging. FTIR analysis was done specifically to assess the amount of residual IPDI left in the microencapsulated solution using 'Miracle ATR' method. The dried film of sample was placed on Miracle ATR and scanned on FTIR range 4000-600 cm^{-1} respectively. UV-visible spectrophotometer (Hitachi model 220) was used to study the release of the lavender oil from polyurea MICS.

2.4 Release Studies

Diffusion or evaporation of the lavender oil from MICS was studied using an incubator/oven for 50 continuous hours at 50°C. Four dry microcapsule (MICS) samples of 2g each were taken in duplicate ensuring equal concentration of lavender oil in all the samples. Weight of the samples was taken at an interval of 5, 15, 30, 60, 120, 240, 360, 480, 600, 1320, 1440, 1800, 2160, 2400, 2700, 3000 min to record the loss in weight of MICS due to diffusion of core from the microcapsule shell.

2.5 Characterization of Microencapsulated Fabric

Once the characterization of MICS is over, microencapsulated fabric was subjected to characterization to find out the efficacy of the imparted finish and the durability of the microencapsulated finish alongwith the post-effects on mechanical properties of fabric.

2.5.1 Impregnation of MICS on Textile

MICS were applied on the textile at laboratory scale using a laboratory padding mangle (EEC, Mumbai). Lavender oil MICS at 8 different concentrations, viz. 1-8 g/L were taken in 50 mL distilled water and applied on 8 different samples of scoured and bleached cotton via padding for *in situ* development on the fabric succeeded by drying for 5 min at 80°C and curing for 1-2 min at 150°C.

2.5.2 Wash Cycle and Odor Evaluation

Washing cycles were performed on the finished sample in Rota Dyer at 60°C for 30 min using soap (5 g/L) and soda ash (2 g/L) to evaluate the wash durability of the microencapsulated finish as per ISO 3 specification. The washed samples were evaluated within 24 h. The samples were to be hung on, so that they get completely dried. A total number of 10 washes was imparted to evaluate the laundering durability. To judge the fragrance odour, 5 cm × 5 cm cotton swatch was taken and burst effect of capsules was observed just after rubbing of cloth swatch.

2.5.3 Mechanical Properties of Treated Fabric

ASTM D 1388 cantilever test method was used for evaluation of stiffness of the fabric, according to which the fabric specimen was allowed to bend under its own weight. The tensile strength was tested in UTM (Zwick) as per determination of breaking strength and elongation standard ASTM D 5035:1995 – (Strip test method).

3 Results and Discussion

3.1 Emulsion Stability using Different Surfactants

Polymeric surfactants play key role in stabilizing oil and water emulsion forming stable MICS dispersion as well as to ensure least emulsion size[22,23]. Firstly, the emulsion process was studied to optimize the stability of the emulsion preceding the formation of MICS. Different oil-water surfactants were used to stabilize the organic phase comprising lavender oil. An organic solution was prepared with 2.5 g of surfactant dissolved in distilled water (5 wt%, 40 g) along with 4-5 g of lavender oil, making an oil-in-water emulsion under constant stirring at 1000 rpm using a mechanical stirrer. Emulsion stability was observed using optical microscopy at different intervals of time, viz. 10 and 30 min to study the size and stability of the emulsion. The detailed study on stabilization of oil-in-water emulsion with seven different surfactants was carried out with their respective observations as mentioned in the Table 1. Out of all the emulsions prepared, PVP K90 shows most stable emulsion for longer period of time. Reduction in interfacial tension, which occurs on the addition of surfactant, has been reported to increase uptake of core materials. The emulsion stability and droplets' size are found to be different for different kinds of surfactants. Among all the 7 surfactants studied, emulsion prepared using PVP K90 (5%) for 30 min of stirring time shows the least emulsion size (2–40 µ overall range with 5–20 µ majority). This shows ability of PVP K90 to provide better emulsification compared to other stabilizers and hence is used for the preparation of MICS.

3.2 MICS Prepared with IPDI-polyamine Wall

Due to the formaldehyde content present in the urea-formaldehyde and melamine-formaldehyde based MICS, these MICS are proved to be hazardous to the environment, whereas polyurea (IPDI-polyamine) based MICS are more environmental

Table 1 — Emulsion stabilization of lavender oil with different surfactants and stirring time

Stirring time, min	Size range, µ	Majority of particle size, µ	Observation
		Tween 80	
10	3-35	5-10	Some irregular droplets
30	3-100	10-20	Some irregular droplets
		Emulsogen L	
10	1-30	5-10	Less stabilized emulsion
30	1-35	5-15	Matrix type structure emulsion, few irregular droplets
		Brij 35	
10	1-30	5-15	Spherical emulsion initially formed
30	1-30	5-15	Agglomeration occurred
		Easy sperse	
10	3-40	10-20	Spherical droplets
30	1-40	15-25	Stable emulsion with irregular sized droplets
		PVP K90	
10	2-40	5-25	Stable emulsion with spherical droplets
30	2-40	5-20	Spherical droplets and stable emulsion
		IGEPAL CA-630	
10	3-200	20-60	Spherical emulsion, irregular droplets
30	3-150	20-50	Few irregular droplets along with spherical droplets
		Brij S100	
10	3-40	5-15	Very few irregular droplets
30	3-50	5-20	Spherical droplets and stable emulsion

friendly; IPDI of all the isocyanates being a bio-compatible monomer.

MICS are prepared using interfacial polymerization technique which involves polymerization (polycondensation / polyaddition) of two immiscible monomers (m1 and m2). Both the monomers m1 and m2 react at the interface of two immiscible phases forming either oil-in-water (o/w) or water- in-oil (w/o) emulsion. In this case, oil-in-water emulsion has been prepared, viz. lavender oil and IPDI being in the oil phase and amine monomer in water as the continuous phase. A detailed study on the mechanism of interfacial polymerization has been proposed by Reza Arshady[24]. By using IPDI as one of the organic phase wall forming monomers, the study of the effect of polyamine monomers on the yield, shape and size of polyurea MICS is also carried out (Table 2). Lavender oil MICS with 70% core loading is prepared with different wall forming polyamine monomers, namely EDA, HMDA and DETA. Out of these, IPDI-HMDA(IH) MICS shows maximum yield but in case of HMDA and DETA when the MICS dispersion is kept for 1 week, leaching of lavender oil could be seen forming two layers of solution. This is attributed to the fact that HMDA and DETA, having comparatively longer spacer arms and long length of alkyl chain, results in higher polymer mesh and thus the MICS prepared with IH and (IPDI-DETA) IT wall material are not studied further, but the study is done with (IPDI-EDA)IE wall[25]. Ethylene diamine, possessing high diffusivity in organic phase, diffuse quickly into organic phase forming polymeric membrane, and due to shorter chain length of soft segments, shows less flexibility of polyurea chains[26].

3.3 Effect of Cross-linker on Morphology of MICS

Influence of cross-linker DETA was also studied to confirm the yield and size of MICS. Four different compositions of wall material were prepared altering the DETA concentration with respect to EDA and have been coded as EI-1, EI-4, EI-5 and EI-6. Table 3 shows varying concentration of cross-linker, viz. 0, 20, 50 and 100% with respect to EDA (w/w) and its subsequent effect on yield (%) and size of MICS. DETA (0%) was used in the EI-1. DETA, at 20% and 50% concentration with respect to EDA, was used in EI-4 and EI-5 respectively. 100% DETA was used in EI-6, i.e. the composition of capsule wall consists of IPDI and DETA only.

SEM images of MICS of EI-1 and EI-5 are compared to see the morphology of MICS with and without cross-linker and it can be seen that the addition of cross-linker has helped the MICS wall to become more robust as compared to IPDI-EDA MICS wall, which shows strains on it (Fig. 1). It should be noted that EDA walls itself are not strong enough to withstand the force that is exerted by the padding machines while finishing of fabrics, so it is desirable

Table 2 — Yield, shape and size analysis of MICS with different amines

MICS (70% loading)	Yield, %	Shape	Size range, μ
IPDI-EDA	80.5	Spherical	10-20
IPDI-HMDA	82	Spherical	10-30
IPDI-DETA	78	Spherical	5-35

Table 3 — Cross-linker concentration, yield and size analysis of MICS

MICS, %	Cross-linker (DETA, w% of EDA)	Yield, %	Size, μ
EI-1 (70)	0	80.64	1-20
EI-4 (70)	20	84.52	1-30
EI-5 (70)	50	88.58	1-30
EI-6 (70)	100	78.30	1-30

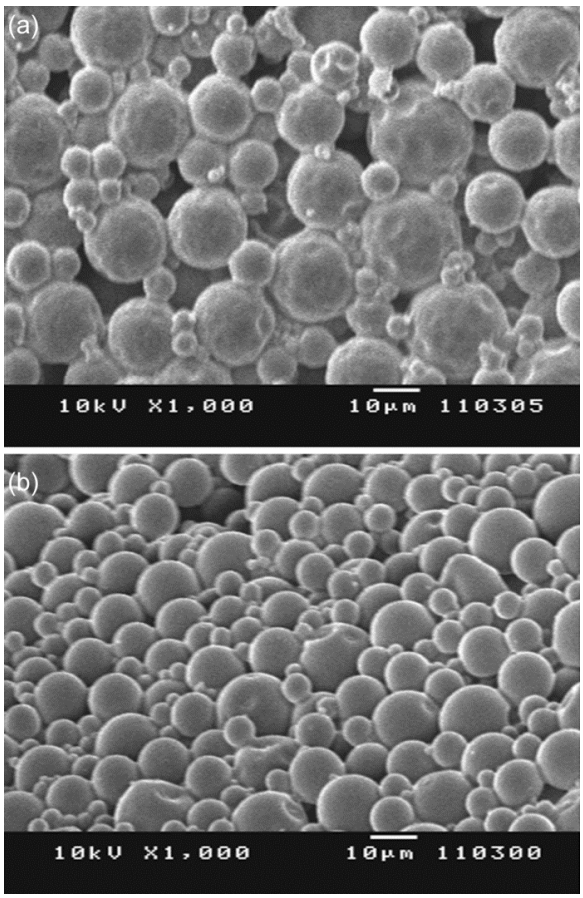

Fig. 1 — SEM images of MICS (a) without and (b) with cross-linker DETA (50%)

in the textile industry for MICS to have pressure resistant walls. A comparative release study of lavender oil from polyurea MICS is carried out in water under perfect sink conditions. Figure 2 shows representative percentage release (%) *vs.* time plots of EI-1, EI-4, EI-5 and EI-6 with 0, 20, 50 and 100% cross-linker w.r.t. ethylene diamine respectively. A sharp decrease in diffusion of core material is observed with increase in concentration of the cross-linker. EI-5 shows the release of core as minimum as 10% even after 3000 min, whereas in EI-6, the release is highest i.e. upto 80%. The high diffusion of the core material pertains to the bigger polymer mesh formed by DETA reaction with IPDI, forming more porous wall[25]. However, in case of EI-5 almost 90% of the perfume oil remains intact in the microcapsules due to high cross-linking of linear polymer chains, resulting in robust shell. This type of shell is required in the textile processes like padding to bear the pressure exerted by rollers of padding mangle.

3.4 Particle Size Distribution of MICS

The particle size distribution curve shows a steep bell curve and also confirms the MIC particle size in the range of 1-30 microns, while majority of the MICS lying in the range of 10-20 microns (Fig. 3). MICS having size bigger than 30 micron is liable to be crushed during padding process and also the ones with varied distribution. Smaller particles tend to have better adhesion property and corrosion resistivity over the bigger ones[25,27,28]. The consumption of isocyanate in the produced MICS is evaluated by FTIR in transmittance mode.

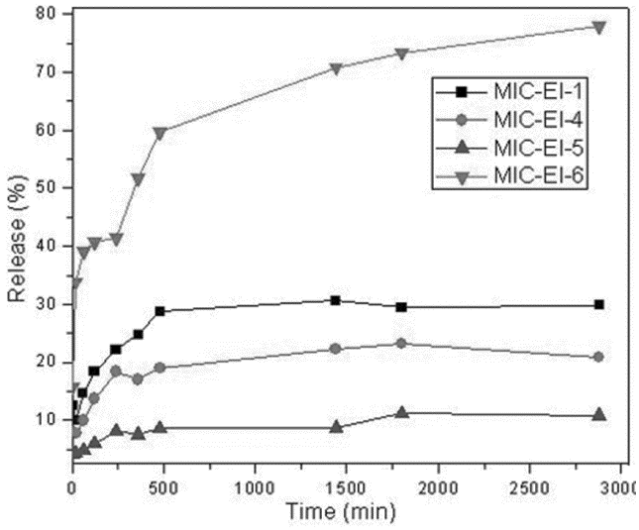

Fig. 2 — Percentage release *vs.* time plots of EI-1, EI-4, EI-5 and EI-6 samples

3.5 FTIR Analysis

The FTIR spectrum of the produced polyurea MICS, confirms the complete utilization of IPDI during the reaction[29]. The peak at around 2270 cm^{-1} remains absent validating the same. Other peaks can also be observed, viz. N-H stretching peak at 3323 cm^{-1}, C-H peak at 2952 cm^{-1} and urea carbonyl peak at 1635 cm^{-1}.

3.6 Wash Durability and Odor Release Evaluation of Microencapsulated Fabric

Cotton fabric is padded with fragrance MICS at a concentration of 20 g/L at 80% pick up followed by drying at 80°C. Wash durability and odour release evaluations were carried out by a panel of judges.

As the SEM images show (Fig. 4), MICS are adhered into the fibre interstices but with increase in wash cycles, MICS tend to get washed-off and broken by the external physical forces. After the impregnated textile is subjected to 10th wash, there is only a hint of fragrance found and very few MICS remain on the textile material. No binder is used for the finishing purpose as polyurea is likely to react with cellulosic part of cotton fibre as per the reaction given below, resulting in curing of capsules onto textile material:

$$\text{Cell-OH} + NH_2\text{- CO- } NH_2 \rightarrow \text{Cell-O-CO-}NH_2 + NH_3$$

With progressive wash cycles, resistance to washing decreases which leads to removal of MICS from the fabric interstices.

3.7 Mechanical Properties of Treated Fabric

Application of microcapsules might restrict the flexibility of the fibre, developing stiffness, which, in

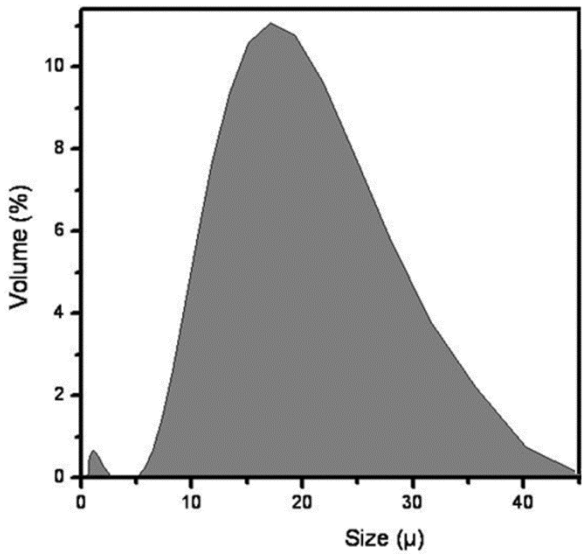

Fig. 3 — Particle size and particle size distribution

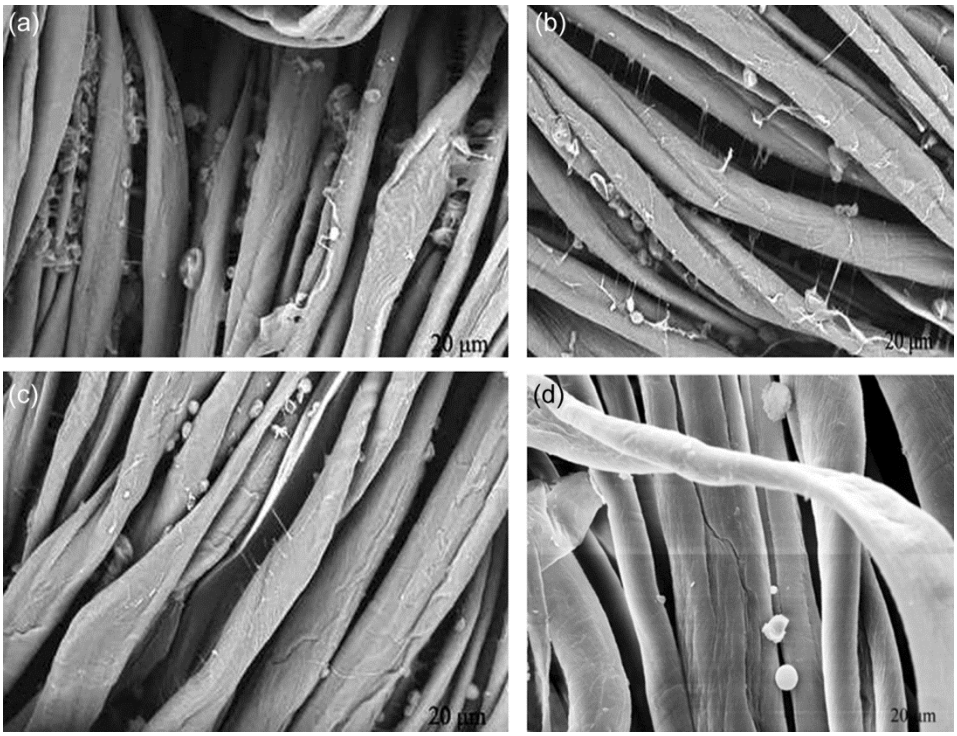

Fig. 4 — SEM images of treated cotton after different wash cycles (a) 0, (b) 5, (c) 8 and (d) 10

Table 4 — Mechanical properties of MICS finished fabric

Lavender oil MICS, g/L	Bending length, cm	Flexural rigidity, g.cm	Breaking strength, N	Extension %
0	3.2	19.66	611.3	10.67
1	3.3	21.56	285.6	11.28
2	3.5	25.73	276.8	13.52
3	3.6	27.99	274.0	14.26
4	3.9	35.59	235.8	15.73
5	4.1	41.35	189.6	16.96
6	4.4	51.11	183.0	13.09
7	4.8	66.36	177.0	13.30
8	5.2	84.36	159.0	15.33

turn, reduces tensile strength of cotton. Because of this, it is essential to evaluate stiffness and tensile strength of finished cotton.

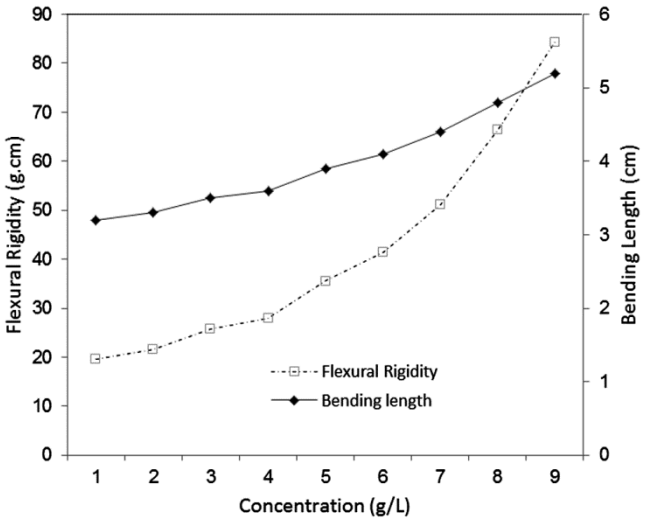

Fig. 5 — Concentration *vs.* flexural rigidity and bending length

3.7.1 Stiffness

It is observed that with the increase in concentration of MICS, stiffness increases alongwith the bending length and flexural rigidity of fabric (Table 4 and Fig. 5). Bending length and flexural rigidity are calculated as per the equations given below:

$$G = ML^3\left[\frac{\cos\theta/2}{8\tan\theta}\right]$$

$$C = L\left(\frac{\cos\theta/2}{8\tan\theta}\right)^{1/3}$$

where M is the mass per unit area (g/cm^2); G, the flexural rigidity; C, the bending length (cm); θ, the fabric bending angle; and L, the length of fabric projecting.

3.7.2 Tensile Strength

The increase in concentration of lavender oil MICS decreases the breaking strength of treated cotton fabric. With the minimum concentration of lavender oil (1 g/L), the corresponding tensile strength is found

to be 285.6 N, whereas the specimen with 8 g/L lavender oil shows a breaking strength of 159.0 N (Table 4).

4 Conclusion

In this work, polyurea microcapsules containing lavender have been synthesised and applied on cotton fabric for fragrance finishing without a binder, as the capsule reacts with cotton. Cross-linking with DETA has shown some definite improvement in the shell morphology as observed in SEM images along with the reduction in release of lavender oil from the polymer shell. Particle size distribution analysis shows that the majority of the microcapsules are in the range of 10-30 microns. FTIR analysis confirms the full consumption of IPDI in the reaction, leading to isocyanate free microcapsules. Synthesized microcapsules are applied on cotton fabric by padding and covalently bonded to cotton at high temperature. High wash durability of microcapsules is observed due to the covalent bonding of amine groups of microcapsules with hydroxyl groups of cotton fabric. High number of wash cycles at low concentration of finish is advantageous for the textile industry. Stiffness of the fabric is observed to be increased with high concentration of microcapsules along with simultaneous fall in strength.

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