Microencapsulation of the as-Synthesized and off-the-Shelf Thermochromic Dyes by Nanosized SiO₂ for Thermal Energy Savings Applications

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Abstract: This study is mainly focused on the fabrication of nano-SiO₂ as an inorganic shell material encapsulated an organic thermochromic (TC) core material comprising of either the (i) three-component assynthesized blue dyes [BDTCM@SiO₂] or (ii) off-the-shelf (commercial) black dyes [CDTCM@SiO₂]. Both the SiO₂ encapsulated thermochromic systems have successfully demonstrated the color transition at around 31 °C. For the three-component thermochromic microcapsules, we have used the crystal violet lactone (CVL) as a leuco dye, bisphenol-A (BPA) as a color developer, and 1-tetradecanol (TD) as a solvent. Different wt% ratios of the thermochromic dye and the metal oxide were prepared to examine the effect of the core@shell ratio on the microstructural and thermal properties of the encapsulated microcapsules. The mean particles sizes of the BDTCM@SiO₂ are below 100 nm, whereas, the CDTCM@SiO₂ samples exhibited the mean particle sizes varied in the range of 100-1000 nm. The endothermic phase transition due to melting and in general, the thermal stabilities of these SiO₂ encapsulated TCMs have been explored for the purpose of deploying these systems for thermal energy savings or storage applications.

Key words: Thermochromic materials, nanoparticles, chromaticity, transition temperature, enthalpy, BDTCM@SiO₂, CDTCM@SiO₂.

1. Introduction

The technology of Chromaticity in device can be used to vary the throughput of visible light and solar energy for windows and buildings surfaces applications. The technologies can make use of a range of chromic materials either by themselves or in combinations with other encapsulants [1]. The rapid development of smart materials has encouraged researchers to explore new possibilities. The market for chromic materials is growing rapidly because of their optical, storage and color changing properties under different stimuli. Examples of such materials are thermochromic inks [2], electrochromic windows [3], and photochromic fibers [4]. Eventhough different chromic materials change color by different stimuli, the mechanism for such changes is similar, that is, a reversible electron or ion transfer. Generally, electrons need energy to overcome a potential barrier (ΔE) to complete the transfer and this can be provided by photons, heat, or electric potential. The TC chemicals also need to be metastable for the process to be reversible [5]. Leuco dye systems

contain three components: dye, developer, and long-chain solvent. Briefly, the dye interacts with the developer to form one color when the solvent is in the solid form, while upon heating and melting of the solvent, this interaction is lost, forming an alternate color. Thus, the color change of the leuco dye system is controlled by the melting or crystallization of the long-chain solvent [6].

According to Nassau, a dye can undergo photodegradation under sunlight when its ultraviolet light interacts with the chemical bonds and destroys the chromophores in the dye [7]. Wan Zhang reported that the encapsulation of a thermochromic material (TCM) by amorphous silica could protect it from UVB light (290-320 nm) [8]. Therefore, it is important to encapsulate the TC material with an inorganic metal oxide. A variety of nanoparticles (NP's) such as SiO₂, Al₂O₃, Fe₃O₄, ZrO₂ and TiO₂ [9]-[13] have been used for surface modifications and coating. Among them, the addition of nano sized SiO₂ had received the greatest attention because of its physical and chemical stability, and wide availability. However, addition of nanosized silica with the nanosized titania gives rise to additional effect, photocatalytic properties due to the presence of titania [14]. For this the Korean workers have developed nano hollow-spheres of the combined silica-titania systems which may be a potential approach for encapsulation of TCM by silica-titania system. However, in our present work, we are mainly focusing on the encapsulation of TCM by the one component nanosized silica spheres. We have prepared two different TCMs separately, one of them is commercial dye encapsulated with SiO₂ nanoparticles [BDTCM@SiO₂]. Extensive characterizations and color changing behavior have been systematically carried out for these two different TCMs@SiO₂.

2. Materials and Methods

2.1. Materials

The commercial Leuco dye that changes color at about 30° C was bought from Amazon Company. The blue dye changes color at about 30° C and contains 1-tetradecanol, crystal violet lactone (CVL) and bisphenol A (BPA), the surfactant sodium dodecyl benzene sulfonate (SDBS), the precursor tetraethyl orthosilicate (TEOS) and encapsulation precursor catalyst, ammonia which are procured from Sigma-Aldrich and used without further purification.

2.2. Microencapsulation of Commercial dye by SiO₂ Nanoparticles

For the preparation of commercial dye encapsulated by SiO₂ NPs [CDTCM@SiO₂], 80ml of DI water is measured and taken in a beaker. It is kept for stirring on hot plate at 400 rpm and at 70 °C. Then 0.5 g of commercial Leuco dye is added to the beaker. After 5 minutes, sodium dodecyl benzenesulfonate (SDBS) and Tetraethyl orthosilicate (TEOS) are added to the solution and stirred until an emulsion is formed. Then ammonia is added as a catalyst and kept for an additional stirring for 2 hours. Finally, the sample is washed thoroughly with ethanol and kept for drying in an incubator at 150 °C for 24 hours. The [CDTCM@SiO₂] powder sample is stored in a glass tube for further characterization and property measurements.

2.3. Microencapsulation of As-synthesized Dye by SiO₂ Nanoparticles

The blue dye solution [BDTCM] is prepared with 1-tetradecanol, CVL and BPA in the ratio 1:4:70. The mixture is taken in a beaker and it is stirred at 400 rpm for about an hour at 70 °C. At the same time, 100ml DI water is taken in another beaker kept for stirring at thermostatic temperature. Then, 4.5 ml of blue dye and ~1g of SDBS are added into the hot DI water solution and stirred at 800 rpm. After an hour, 3ml of the SiO₂ precursor (i.e. TEOS) solution is added. Finally, 2 ml ammonia is added, and the solution is turned off after 3 hours. The final product was kept for cool down to room temperature and then it is filtered to obtain a powder sample. After washing it with ethanol, the sample was placed in an incubator at 150° C for 24 hours to dry. Finally, the [BDTCM@SiO₂] powder sample is stored in a glass tube for further characterization and

property measurements.

3. Analytical Characterizations

The Hitachi SU3500 is used to obtain a higher resolution scanning electron microscopy (SEM) image. The elemental analyses of both commercial dyes based, and blue dye samples are characterized by energy dispersive x-ray spectroscopy using Oxford Instrument's EDAX detector attached to SU3500 SEM, with a working distance of 10 mm, a take of angle of 35° and an accelerating voltage of 15 kV. The Hitachi's HT7800 series is a HRTEM instrument used to determine if the encapsulation is successful or not because it can offer a higher resolution to allow the delineation of the sample's surface morphology. Dynamic Light Scattering (DLS) was run on samples to see the extent that the reaction schemes can break down large aggregates of the TCM samples using the Zetasizer Nano Series (ZS, Model: ZEN3600) which is designed to measure particle size, molecular weight and zeta potential. Fourier transform infrared spectroscopy (Nicolet iS50 FTIR) was utilized to determine the chemical and bonding environment. For the FTIR experiments, an ATR cell was used for the plain dye and core@shell powder samples placed on the diamond window and applied a pressure using a screw gauge. The transmission mode was chosen to collect IR signals between 400 to 4000 cm⁻¹ wavenumbers. The thermal properties of these SiO_2 encapsulated TCMs were analyzed by differential scanning calorimetry (TA Instruments, DSC 2500) and thermo-gravimetric analysis (Mettler Toledo, TGA/DSC 1 STAR^e Systems). For the TGA studies, the TCM@SiO₂ sample size of <10 mg was treated from room temperature to 600 ° C with ramping rate of 10 ° C/min under nitrogen flow of 50 mL/min. To determine the visual color change, TCM@SiO₂ was placed on white filter paper on top of a hot plate. The hot plate's temperature was adjusted in increments of 5 °C while the actual temperature of the fibers was determined by infrared thermometer.

4. Results and Discussion

4.1. Thermochromic (Color Change) Characteristics

Table 1 and Table 2 contain all the design of experiments carried out in the encapsulation process but with different parameters for both [CDTCM@SiO₂] and [BDTCM@SiO₂] respectively. In all the experiments, a thermal (hot) plate was used to heat each sample to see if it shows the thermochromic (color change) property. Samples showing color change are stored for further tests. For the [BDTCM@SiO₂], the blue dyes consisting of three components such as, CVL, Bisphenol A and 1-tetradecanol are in liquid form during the encapsulation process, due to the high temperature (70 °C) in an incubator, however, it turns to solid after encapsulation when the temperature cooled down to room temperature. Based on this phenomenon, emulsion end samples may not have been fully encapsulated and, therefore, not suitable for this thermal characterization tests. Samples S1 and S2 of [CDTCM@SiO₂] have different surfactant and yet both change color at 31 °C. However, the SEM images show sample 2 having a non-uniform particle formation in the microscale.

Table 1. Design of Experiments of [CDTCM@SiO ₂] Samples with Different Surfactants							
Sample	Solvent	Surfactant	Dye	Precursor	Catalysts	Color change	Final
#			-		-	point	solution
S1	DI water	SDBS 1g	black	TEOS 3ml	Ammonia	31 °C	Suspension
	80ml		dye 0.5g		2ml		
S2	DI water	Poly (sodium 4-	black	TEOS 3ml	Ammonia	31 °C	Suspension
	80ml	styrenesulfonat) 1g	dye 0.5 g		2ml		

Table 1. Design of Experiments of [CDTCM@SiO₂] Samples with Different Surfactant

From samples S3 to S6 for [BDTCM@SiO₂], all experiments ended with an emulsion form which means the concentration difference of the dye did not cause failure of encapsulation. In addition, samples S6 and S7 indicate that the surfactant has not caused the encapsulation failure. Therefore, the new experimental

process carried out by adjusting the order of adding chemicals and reaction time, to obtain the sample S8 with blue dye of 10 ml could yield a suspension form. The pictures are taken to show the color change of sample S8, [BDTCM@SiO₂]; it changes color from, blue to white when temperature goes through from 25 °C to 35 °C and they are shown in Fig. 1.

Different Surfactants (Samples S6 and S7) and a New Experiment Sample S8							
Sample	Solvent	Surfactant	Dye	Precursor	Catalysts	Color change	Final
#						point	solution
S 3	DI water	SDBS 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Emulsion
	80ml		2.7ml		2ml		
S4	DI water	SDBS 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Emulsion
	80ml		5.4ml		2ml		
S5	DI water	SDBS 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Emulsion
	80ml		8.2 ml		2ml		
S 6	DI water	SDBS 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Emulsion
	80ml		20ml		2ml		
S 7	DI water	CTAB 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Emulsion
	80ml		20ml		2ml		
S 8	DI water	SDBS 1g	Blue dye	TEOS 3ml	Ammonia	31 °C	Suspension
	80ml		10ml		2ml		

Table 2. Design of Experiments of [BDTCM@SiO₂] with Different Dye Concentrations (Samples S3-S7) and Different Surfactants (Samples S6 and S7) and a New Experiment Sample S8



Fig. 1. Color change of [BDTCM@SiO₂] at different temperature.



Fig. 2. Scanning electron micrographs of [CDTCM@SiO₂] at different magnifications.

4.2. Scanning Electron Microscopy & Energy Dispersive X-Ray Spectroscopy

The scanning electron micrograph of the commercial dye encapsulated with SiO₂ nanoparticles, it is observed that all microcapsules are in spherical shape and smooth surfaces with particle sizes ranging from 100 nm to 1000 nm, as shown in Fig. 2. The particles sizes are not uniformly distributed and agglomerated as well, because it is significantly influenced by the stirring speed and surfactant concentration, which was mentioned by Geng *et al.* [15]. The energy dispersive x-ray spectroscopic (EDS) results of the plain commercial dye [CDTCM] as shown in Table 3, exhibit the presence of various elements including carbon, oxygen, sodium, and chlorine. It is easy to see that carbon and oxygen are the main components because the

commercial leuco dye which we used for the synthesis is organic and coated with an organic polymer. Small traces of sodium and chlorine is found, it may be due to the surfactant residues after processing. As far the encapsulated [CDTCM@SiO₂] sample, Table 3 reveals the presence of silicon with 0.4 wt%. The lower concentration of Si could be due to aforementioned non-uniformity and agglomeration effects.

	[CDTCM]		[CDTCM@SiO ₂]		
Element	Atomic%	Conc, wt%	Atomic%	Conc, wt%	
С	81.78	76.75	79.98	74.75	
0	17.74	22.19	19.67	24.49	
Na	0.32	0.57			
Cl	0.16	0.46			
Si			0.19	0.41	
Al			0.16	0.34	
Total	100.00	100.00	100.00	100.00	

Table 3. EDS Results for the Commercial Dve and	[CDTCM@SiO ₂]
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Fig. 3. Scanning electron micrographs of [CDTCM@SiO₂] at different magnifications.



Fig. 4. Energy dispersive x-ray mapping and spectrum of [BDTCM@SiO₂] (inset) with the SEM image at corresponding sample zone.

Fig. 3 shows the SEM results obtained for [BDTCM@SiO₂]. SEM images reveal that the size of the particles is not uniform, and it shows some smaller particles are embedded on the organic substrate. We may consider those smaller particles as SiO₂ nanoparticles adsorbed on theromochromic core material. This feature of core@shell morphology is visible in the HRTEM images as discussed in the next section. Based on the EDS x-ray mapping and spectrum results as demonstrated in Fig. 4, the concentration (in wt.%) of carbon, oxygen, sodium, and sulphur are 66.95%, 20.22%, 4.1%, and 4.7%, respectively. The sodium is attributed by SDBS that we used as surfactant. The percentage of silicon present in the synthesized product is ~3.4 wt% which

is not high as we expected but it confirms the existance of SiO_2 in the prepared sample.

4.3. High Resolution Transmission Electron Microscopy

Fig. 5 shows the high resolution TEM images of two specific particles of the commercial dye encapsulated with silicon dioxide [CDTCM@SiO₂]. Since the main core material [CDTCM] was already coated with a polymer, it is hard to encapsulate it with another metal oxide like reactive species unless we create some cleavages on the surface of the TCM material which would generate some active sites for stable bond formation with the inner surface of the shell formed by the nanosized silica. The HRTEM image confirms the spherical core-shell structure of [CDTCM@SiO₂] where nanosized SiO₂ particles are embedded onto the TCM core structure. The prepared sample does not have greater amount of silicon dioxide in it, because the presence of SiO₂ concentration is low (0.41wt %), as we discussed previously in the EDS results. From the analysis of SEM and HRTEM results, we can conclude that the encapsulation process is successful and that silicon dioxide particles are adsorbed on the surface of the commercial dye coupled with the existing polymer. It is unambiguously clear that to increase the percentage of SiO₂ nanoparticles in encapsulation layer, higher concentrations of the silicon dioxide precursor (TEOS) are needed.



Fig. 5. HRTEM images of the [CDTCM@SiO₂] at two different magnifications.



Fig. 6. HRTEM Microstructure of [BDTCM@SiO₂] at different magnifications.

Fig. 6 shows that the average particle size of the [BDTCM@SiO₂] is much smaller than that of the [CDTCM@SiO₂], because in [BDTCM@SiO₂], the core and the shell material are prepared in the laboratory, so we can control the particle size and it is not pre-encapsulated by any polymer. We can also see the particle size has a wide range because it is significantly influenced by the physical and chemical parameters of preparative conditions such as stirring speed and surfactant concentration [15]. When a single particle is

magnified as shown in Fig. 6, we can clearly observe two types of encapsulated particles. All the particles are in perfect spherical shapes having diameter less than 100 nm.

Some of the core-shell structure have many small particles around it. Whereas some of them show relatively smoother and more uniform ring shaped which may be considered as a perfect encapsulation. This could also be the result of surfactant concentration and stirring speed. The inner ring can be considered as the three-component system with diameter of ~90 nm encapsulated by an outer layer consisting of SiO₂ nanoparticles of diameter ~13 nm. The wall thickness of hollow SiO₂ spheres strongly depends on the amount of TEOS in the system. This is because almost all SiO₂ nanoparticles generated by the hydrolysis of TEOS can easily diffuse onto the surface of core material due to electrostatic interaction initially which would interact with the available hydroxyl or carboxyl group of the core in the next step to form a silica coating. Therefore, it is easy to control the wall thickness by adjusting the amount of TEOS in the system.



Fig. 7. FTIR spectra for [CDTCM] and [CDTCM@SiO₂].

4.4. Dynamic Light Scattering – Particle Size Analysis

The dynamic light scattering (DLS) provides the information for the average particle sizes and range for the plain (as procured) and SiO₂ encapsulated TCM. At least 20 μ g of [TCM@SiO₂] either the commercial black dye or the three-component blue dye is dissolved in 1 ml DI water and mixed by ultrasonic vibration for 2 min. The DLS measurements have been carried out at three different temperatures, say 20, 30 and 40 °C and the particle size distribution histograms are allowed to get the particle size ranges. The average particle size for the commercial dye [CDTCM] is 2,032 nm, after encapsulation, [CDTCM@SiO₂] it is 2,518 nm. On the other hand, for the three-component based blue dye system, [BDTCM@SiO₂] it is 373 nm. The particle size increased roughly 486 nm from that of plain commercial dye due to encapsulation with SiO₂ which would lead to the core@shell configuration. For the [BDTCM@SiO₂], the lower particle size is due to the dye preparations from the three-component systems followed by the SiO₂ encapsulation via TEOS admixing. Overall, the DLS results support the SEM particle size analysis mentioned in the previous section.

4.5. Fourier Transform Infrared Spectroscopy – Chemical Bonding Environment

Fig. 7 represents the FTIR Spectra of both [CDTCM] and [CDTCM@SiO₂] samples at room temperature. Based on the overlay spectra, both the pristine commercial dye and the SiO₂ encapsulated dye have almost similar chemical bonding stretches and bending modes due to similar spectral pattern as shown in Fig. 7. The bonding stretches for the O-H, C=O, C-O, O-CH₃ vibrations appear at wavenumbers 3389, 1470, 1347, 1175 cm⁻¹ respectively, however the bending modes for CH₂, O-CH₃, C-H correspond to the wavenumbers 2915, 1009, 719 cm⁻¹ respectively. However, the [CDTCM@SiO₂] exhibits a week inflection like absorption at 798 cm⁻¹ due to the stretching vibration of Si-O-Si of microencapsulated SiO₂ [16], [17] in addition to the all vibrations of the plain dye's functional groups such as O-H, CH₂, C=O, O-CH₃, C-O, and C-H. Since the EDS results as demonstrated in Table 3, revealed the low concentration of the encapsulant Si which is less than 0.5 wt%, therefore an appreciable intensity of the Si-O-Si stretching band [16], [17] at around 800 cm⁻¹ is missing in our [CDTCM@SiO₂] samples . Overall, this FTIR investigation of both pristine and SiO₂ encapsulated commercial dye shows well matched functional groups and identical feature with no outliers. The FTIR for the three-component system [BDTCM] and its SiO₂ encapsulated counterpart [BDTCM@SiO₂] was not performed due to the lower melting nature of the dye itself.



Fig. 8. DSC spectra for the heating and cooling cycle of (a) [CDTCM] and (b) [CDTCM@SiO₂].

Table 4. DSC Results of [CDTCM] and [CDTCM@SiO ₂]					
Samples	Endo-peak temp. (Heating) (°C) Exo-peak temp. Enthalpy				
		(Cooling) (°C)	(heating cooling) (J/g)		
[CDTCM]	33.03 ~29.72	26.4 23 14.6	95.021 87.442		
[CDTCM@SiO ₂]	~32.6 29.72	26.4 22.5	97.558 91.749		

4.6. Heat Flow Characteristics via Differential Scanning Calorimetry

About 5 mg size samples of pristine commercial TCM and [CDTCM@SiO₂] are suitable for differential scanning calorimetry (DSC) testing at temperature ramp rate of 5° C per minute to allow greater details near the critical point (color change point). The range is set from 0 to 60° C to save testing time and energy, because we know the critical point is about 31° C. The cool down process is set at the same ramp rate with the results also recorded for endothermic or exothermic transitions. The DSC results for both the [CDTCM] and the [CDTCM@SiO₂] are plotted and shown in Fig. 8 (a and b) and the data are tabulated in Table 4. For the commercial dye, the over layered two peaks, which are possibly because of the two different organic crystal morphologies. It could also suggest that the commercial dye may contain an irregular nucleated structure and sphere structure where all the crystallites are roughly symmetric. So, either one of these is not a perfect crystal structure with a lot of defects that means it is going to melt more easily and shows up as the lower melting peak.

In contrast, the other structure is highly ordered and close to perfect, that means they will melt at a higher temperature and will show as the peak at a higher temperature. The enthalpy of heating and cooling values from Table 4 shows the high degree of reversibility at which the endothermic and exothermic transitions occurs. About 2-4 J/g enthalpy for [CDTCM@SiO₂] is greater than the plain [CDTCM], and this may be due to SiO₂ encapsulation. In addition, there is an inflection at around 24°C in the cooling stage of DSC curve for the encapsulated TCM while there is sharp cooling at this point for the non-encapsulated TCM. This would possibly imply about the phenomenon of coming back of shell structure in ordered form. As the two materials, core and shell are of different materials, the cooling would dissipate different heat energy if it is compared with that of non-encapsulated TCM. The DSC of both [BDTCM] and [BDTCM@SiO₂] was not performed due to

the melting nature of the core three component dye and also the lower concentration of SiO_2 nanoparticle shell material.

4.7. Thermal Stability via Thermogravimetric Analysis

Samples for the TGA test were about 3-4 mg for the commercial dye, as-developed dye and their SiO_2 encapsulated counterparts. The temperature range was set from room temperature to 600° C with a ramp rate of 10 °C per minute. The nitrogen flow rate was set at 5.0 ml per min during the entire testing process. The results are organized in Table 5 to show the detail of the two significant weight loss steps. The TGA results are also plotted and shown in Fig. 9 (a and b).

Table 5. For Results for the commercial by calle the object at 5102						
Step one T (onset	Step one loss (weight	Step two T (onset	Step two loss (weight			
end set)	%)	end set)	%)			
206 º C 324 º C	0.3627 mg 10.10%	330 º C 496 º C	2.6544 mg 73.94%			
226 º C 32 2º C	0.2522 mg 8.40%	328 º C 496 º C	2.0638 mg 68.77%			
100 °C 225 °C	3.4478 mg 98.51%	NA	NA			
100 °C 225 °C	4.0724 mg 75.79%	400 °C 485 °C	0.404 mg 7.52%			
	Step one T (onset end set) 206 ° C 324 ° C 226 ° C 32 2° C 100 °C 225 °C 100 °C 225 °C	Step one T (onset end set) Step one loss (weight %) 206 ° C 324 ° C 0.3627 mg 10.10% 226 ° C 32 2° C 0.2522 mg 8.40% 100 ° C 225 ° C 3.4478 mg 98.51% 100 ° C 225 ° C 4.0724 mg 75.79%	Step one T (onset end set) Step one loss (weight %) Step two T (onset end set) 206 ° C 324 ° C 0.3627 mg 10.10% 330 ° C 496 ° C 226 ° C 32 2 ° C 0.2522 mg 8.40% 328 ° C 496 ° C 100 ° C 225 ° C 3.4478 mg 98.51% NA 100 ° C 225 ° C 4.0724 mg 75.79% 400 ° C 485 ° C			

Table 5. TGA Results for the Commercial Dye and the CDTCM at SiO₂



Fig. 9. TGA profiles for the (a) [CDTCM] and [CDTCM@SiO₂] and (b) [BDTCM] and [BDTCM@SiO₂].

The first weight reduction step is due to polymer weight loss and the second due to the dye weight loss. It is noticeable that the weight loss of CDTCM at SiO₂ is less than the commercial dye, which means the SiO₂ shell on the polymer surface may store some energy that retards the polymer degradation. Furthermore, the CDTCM at SiO₂ starts losing weight 20° C higher than the commercial dye, which also confirms that the SiO₂ shell could store high latent heat. For step two, CDTCM at SiO₂ also shows less weight reduction (5.2%) which may benefit from the protection of SiO₂ shell. The reason why the protection is not significant is the low concentration of SiO₂ which just partially encapsulated on the dye surface. The TG curve of Blue dye [BDTCM] had two degradation steps in Fig. 8b (black color). It is interesting to note that there is almost sharp decomposition pattern of the dye which contained three entities of different melting points (35-39°C for 1-tetradecanol; 158-159°C for BPA, 180-183°C for CVL) as if there is a formation of a congruent blue dye medium. It is true the blue dye is a reaction product, but there must be contamination of the component systems which must exhibit their presence in the decomposition pattern. On the contrary the blue dye product exhibits a single component like as evident from the TGA.

The onset temperature is about 100°C, which was attributed to the decomposition of tetradecanol, the following weight reduction from 190 to 225°C is considered as the decomposition of BPA and CVL [18]. Therefore, the blue dye degrades about 98% in total. Meanwhile, the thermal stabilities of BDTCM at SiO₂ was also analyzed by TGA experiments. As shown in Fig. 8b (red color), a similar weight loss (75.79%) occurs from 100 to 225 °C which is the dye decomposition. And a 7.5212% weight loss from 400 to 485° C is the decomposition of silica-bonded groups such as -OH group [16], [17]. And the final residual weight is 16.68%.

for the first step, the weight loss of BDTCM at SiO2 is 22.8% less than that of plain blue dye. If we compare the results from SEM, we know the Si weight percentage is 3.4% and for SiO₂ is about 7.28%. therefore, weight residual cannot all being the SiO₂ because 16.68% is 9.4% bigger than 7.28%. One reason can be that the weight remaining is for both blue dye and SiO₂ which implies that blue dye is inside the SiO₂, so it did not degrade at the first step.

5. Conclusion

In this work, the thermochromic dye either in its commercial black powder [CDTCM] form or threecomponent emulsion form [BDTCM] can be successfully encapsulated with nanosized SiO₂ particles as shell form of the core@shell structure. The HRTEM results reveal the core@shell structure which is predominant in the case of [BDTCM@SiO₂]. The thermogravimetric analysis of [BDTCM] clearly indicate the formation of a congruent blue dye system starting with three components of different melting points-a new approach of synthesis of TCM. The thermal behavior results as obtained by the DSC may also indicate that these encapsulated TCMs could be deployed as a potential thermal energy storage material due to their large enthalpy values. The DLS particle size analysis is in support of SEM observations in terms of particle size distribution. The FTIR spectral profiles of [CDTCM@SiO₂] is very similar to the commercial dye [CDTCM], except a minor inflection band stretch of Si-O-Si at 798 cm⁻¹ appeared due to the lower concentration of SiO₂ encapsulation, Overall, we have successfully developed a metal oxide encapsulated TCMs for thermal energy saving in prospective building applications.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Authors, AH, SI, MH have conducted the experimental research in synthesis of microencapsulated TCMs. SS and KS did the characterization. AK and SS wrote the paper. PKB and ES proofread the paper. All authors had taken part in group discussions to improve the quality of the manuscript and finally approved the final version of the manuscript.

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