

Reversible Thermochromic and Phase Change Composites Based on Dicarboxylic Acid

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Abstract: Reversible thermochromic and phase change dual functional composites were synthesized with crystal violet lactone as the leuco dye, the mixture of stearic acid and decanoic acid as the developer and phase change materials, and cetyl alcohol as the solvent by a process of grinding, mixing, stirring and heating. The samples have a well reversible thermochromic and phase change properties. The enthalpies reached up to about 200 J/g. The phase change temperatures and color change temperatures are about 40°C – 50°C. The absolute differences between the phase change temperatures and color change temperatures of the optimum samples were $\leq 1.92^\circ\text{C}$, meaning that to visualise phase change phenomena with a colour indicator is feasible. The samples also exhibited an excellent ultraviolet absorption property, meaning they could be used in ultraviolet protection aspect besides using as the phase change materials and colour indicators.

1 INTRODUCTION

Recently, reversible thermochromic and phase change dual functional composites have been reported by some authors (Li et al., 2018). On the one hand, due to the significant changes in their absorption and fluorescent properties in response to external stimulation, giving them numerous potential applications such as thermal indicators, optical storage devices and other luminescent switches (Seyfour and Buddhi, 2017; Kumar et al., 2017; Jin et al., 2017; Carmona et al., 2010; Berdahl et al., 2008; Raditoiu et al., 2016; Oswald et al., 2014; Jeong et al., 2018; Oh et al., 2016; Ma et al., 2001; Ma et al., 2002; Mapazi et al., 2017; Liu et al., 2017; Pospíšil and Nešpurek, 2000; Malherbe et al., 2010; Wu et al., 2014; Shobo and Mawire, 2017; Yu et al., 2017). On the other hand, phase change materials based on the heat absorption or release exhibited some outstanding advantages in some areas, for example, solar heat storage or industrial waste heat recovery (Zalba et al., 2003; Sharma and Buddhi, 2005; Amin et al., 2016). Most good results about phase change materials, focused on building energy efficiency, solar heating systems, air-conditioning systems, photovoltaic systems, temperature adaptable greenhouse, thermo-

regulating fibers, smart textile materials, and so on, have been reported (Sharma et al., 2009; Sharma et al., 2014; Sari, 2005; Kant et al., 2016; Sari et al., 2015; Sari et al., 2004; Costa et al., 2009; Gandolfo et al., 2003; Kim et al., 2017; Hasl and Jiricek, 2014; Dimaano et al., 2002). There are many studies on phase change materials or thermochromic materials, but the materials having the reversible thermochromic and phase change properties at the same time have been less studied (Li et al., 2018; Wu et al., 2014). The phase change materials in Li et al. (Li et al., 2018) or Wu et al. (Wu et al., 2014) studies, were single fatty alcohol, which led to definitive and nonadjustable phase change temperatures, and this would narrow their application. The phase change temperatures could be adjusted by binary fatty acid in some ratio (Sari, 2006; Keleş et al., 2005; Wang and Meng, 2010; Ding et al., 2017). The focus in this study is to prepare reversible thermochromic and phase change materials with adjustable phase change temperatures by binary fatty acid, and to visualise phase change phenomena with a colour indicator. The samples were prepared by using crystal violet lactone (CVL) as a leuco dye, the mixture of stearic acid (SA) and decanoic acid (DA) as the developer, and cetyl alcohol (CA) as the solvent. The similar study has not been reported till now. The as-synthesized samples

could be applied in energy storage, colour indicators, memory materials, and so on.

2 EXPERIMENTAL SECTION

2.1 Materials

SA with a mass fraction purity of 98.0% and CA with a mass fraction purity of 98.0% were supplied by Xilong Chemical Co. Ltd (China). DA with a mass fraction purity of 98.5% was supplied by Sinopharm Chemical Reagent Co., Ltd (China) and CVL with a mass fraction purity of 95.0% was supplied by Tokyo Chemical Industry Co. Ltd (China). All the reagents were used without further purification as received.

2.2 Sample Preparation

Mixtures of CVL, stearic acid, decanoic acid and cetyl alcohol in the mass ratio area 1: (5 – 8): (2 – 5): (10 – 50) (Table 1) were firstly ground in a mortar for 15 min, and then transferred into a beaker. The solid mixtures were heated to become the transparent solutions, and then cooled automatically in the air to form the solid samples. All the experiments were repeated at least three times, and the experimental data were given in average.

2.3 Characterization

Thermochromic properties tests were done as follows. The samples were heated and cooled in air between 20°C and 70°C to check the colour change and the respective temperatures during the sample melting and solidifying. The sample colour was recorded by a digital photo. The colour change temperatures were detected by an electronic thermometer. To further test the thermochromic properties of the samples, absorption bands were analyzed by a UV-VIS-NIR Spectrometer (UV3600PLUS, Japan) in the wave length area 200 nm – 850 nm. The scanning rate was medium, and scanning step was 1 nm.

The sample thermal stability was determined using a thermal gravimetric analyzer (American STA Q5000 IR, TGA) at a scan rate of 10°C/min from 25°C to 500°C under a nitrogen atmosphere. A typical mass of the samples used in the TGA analysis was 2.5 mg – 4.2 mg.

The enthalpies, phase change temperatures and thermal cycle stability of the samples were measured using differential scanning calorimetry (American Q2000, DSC). All experiments were carried out in

heating and cooling rates of 5°C/min in the temperature area of –20°C – 80°C under a constant flow of dry nitrogen (100 ml/min). DSC calibration was done with certified Indium standard reference material. The phase change temperatures were taken at the intersection of an extrapolated base line and tangent to the heat flow curve drawn at the inflection point of the appropriate side of the peak. Enthalpies of the samples were obtained by a numerical integration of the area between the heat flow curve and the extrapolated base line. The reproducibility error of the calorimeter was within ±1%, and the temperature ±0.01°C.

3 RESULTS AND DISCUSSION

3.1 Thermochromic Properties

To synthesize the samples which have both high latent heats in their phase change processes and obvious color change phenomena, and the same temperature area in their phase change processes and thermochromic processes, a series of the raw material ratios were used in preparing the samples. After some preliminary experiments and found that the solvent amount affects the sample color obviously. The sample showed weak color and led to the thermochromic phenomena were not easy to be observed when the excessive solvent was used. But the thermochromic phenomena did not occur when the less solvent was used. The effect of the raw material ratios to the thermochromic temperatures was listed in Table 1, and the thermochromic phenomena were recorded by the digital photos (Figure 1). Thermochromic temperatures are usually related with the melting or solidifying temperatures, but they are not the same. The initial color change temperatures in the melting processes and the temperatures when the samples restored their initial colors in the solidifying processes are in the temperature areas of 40.90°C–48.90°C and 39.60°C–46.00°C, and the melting and solidifying temperatures are in the areas of 40.00°C–48.00°C and 34.20°C–39.60°C, respectively, when the raw material (CVL, (SA+DA) and CA) mass ratio changed from 1: (8+2): 10 to 1: (5+5): 50. No obvious relationship was observed between the thermochromic temperatures with the raw material mass ratio. The samples SDC8210, SDC8220, SDC6420 and SDC5520 could not restore their initial colors in their solidifying processes when the CA mass percentage ≤64.5%. The sample melting and solidifying temperatures, normally related with

the phase change temperatures and they could be tuned by changing the mass ratio of SA and DA which were well studied in the previous study (Wu, 2016), showed a decrease tendency with the SA and DA mass ratio decreasing, this is in agreement with the results reported before (Sarı, 2006; Keleş et al., 2005; Wang and Meng, 2010; Ding et al., 2017), and reasonable because DA melting temperature (31.5°C) was lower than SA (60°C). The thermochromic phenomena could be observed in the raw material (CVL, (SA+DA) and CA) mass ratio area 1: 10: 30 – 1: 10: 70, and the mass ratio corresponding to the most obvious color change was 1:10:50. All the thermochromic phenomena showed a good repeat

ability, suggesting that the samples, except those of the CA mass percentage $\leq 64.5\%$, could be applied as color indicators of phase change phenomena if the thermochromic temperatures and phase change temperatures were much the same by selecting the appropriate raw material ratios. For further explaining the ideal thermochromic phenomena, a sketch about sample color shown after many thermal cycles was shown in Figure 2. When a sample is in a liquid state, the CVL ring closes, and the sample is colorless. When a sample is in a solid state, the CVL ring opens, and the sample color is blue.

Table 1: Effect of raw material ratios to sample melting-solidifying temperatures and color change temperatures.

Sample	R ^a	T _m ^b (°C)	T _s ^b (°C)	T _{cm} ^c (°C)	T _{cs} ^c (°C)
SDC8210	1: (8+2): 10	43.40	34.20	–	–
SDC8220	1: (8+2): 20	48.00	35.33	–	–
SDC8230	1: (8+2): 30	45.30	37.51	48.90	40.81
SDC8240	1: (8+2): 40	43.00	35.72	43.30	41.53
SDC8250	1: (8+2): 50	48.00	36.90	48.21	46.00
SDC6420	1: (6+4): 20	45.70	34.51	–	–
SDC5520	1: (5+5): 20	43.31	35.54	–	–
SDC8260	1: (8+2): 60	43.22	37.21	48.70	43.00
SDC8270	1: (8+2): 70	43.01	39.60	45.02	39.60
SDC6450	1: (6+4): 50	40.00	35.91	40.90	40.50
SDC5550	1: (5+5): 50	42.20	35.53	44.53	41.04

^a Mass ratio of CVL: (xSA+yDA): zCA.

^b Sample melting temperatures and solidifying temperatures.

^c Sample initial color change temperatures in melting processes and temperatures when samples restored their initial colors in solidifying processes.

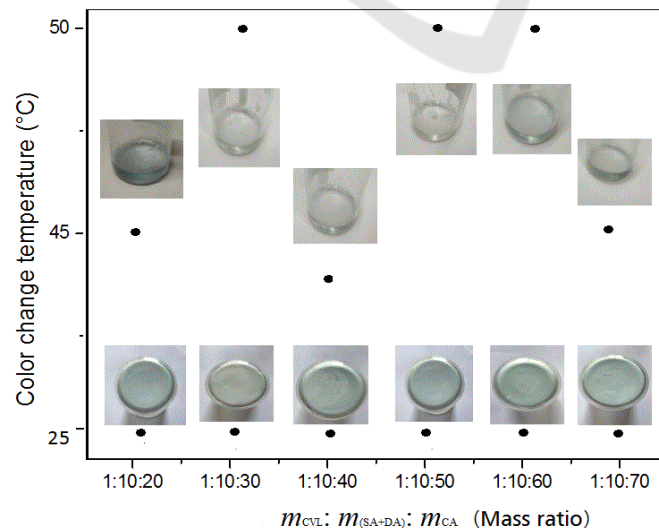


Figure 1: Digital photos of samples in heating and cooling processes.

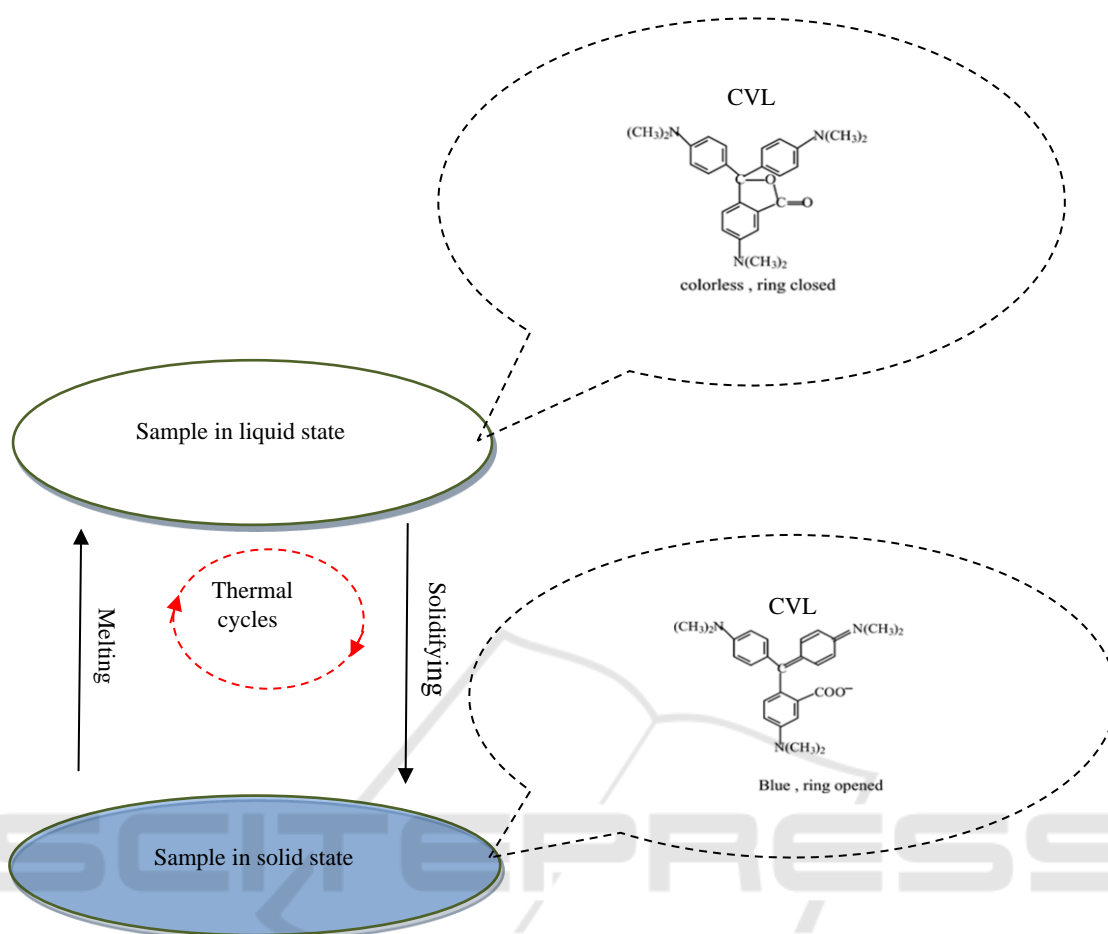


Figure 2: Sketch of sample color shown after many thermal cycles.

3.2 Phase Change Properties

The phase change parameters of all the samples, except SDC8210, SDC8220, SDC6420 and SDC5520 for the undetected thermochromic phenomena or bad thermochromic repeatability, were listed in Table 2, and the DSC curves were shown in Figure 3. The melting and solidifying enthalpies are in the areas of 190.3 J/g – 208.6 J/g, and 184.4 J/g – 214.2 J/g, respectively. The enthalpies increased and then showed a decrease tendency when the mass percentage of CA increased from 73.17% to 86.42%, with a turn point at 81.97%. The phase change temperatures are in the areas of 40.25°C – 47.96°C and 41.67°C – 44.31°C, respectively, in the melting and solidifying processes, and showed an increase tendency in the melting process with the CA mass percentage increasing from 73.17% to 86.42% when the mass ratio of SA and DA was 8: 2. The reason

about the increase tendency is that the CA as both of an solvent and phase change material has a relatively higher phase change temperature (49.6°C) compared with that of the mixture of SA and DA. When the mass ratio of SA and DA decreased from 8: 2 to 5: 5, the phase change temperatures are in the areas of 40.25 °C – 47.75 °C, and 42.33 °C – 44.08 °C, respectively, in the melting and solidifying processes. But no obvious changing tendency in the phase change temperatures was found related with the mass ratio of SA and DA. The optimum mass ratio of CVL, DA, SA and CA, evaluated by the enthalpies, the phase change temperatures and the thermochromic temperatures, are 1: 6: 4: 50 and 1: 8: 2: 50, corresponding to the samples SDC6450 and SDC8250. The phase change parameters of these two samples are as follows.

Table 2: Sample phase change properties.

Sample	T_{pm}^a (°C)	$\Delta T_m = T_{cm} - T_{pm}$ (°C)	T_{ps}^b (°C)	$\Delta T_s = T_{cs} - T_{ps}$ (°C)	ΔH_m^a (J/g)	ΔH_s^b (J/g)
SDC8230	44.63	+4.27	41.67	-0.87	191.7	184.4
SDC8240	45.17	-1.87	44.31	-2.81	203.7	194.3
SDC8250	47.75	+0.45	44.08	+1.92	207.7	214.2
SDC6420	42.38	+2.22	37.44	-	197.1	184.8
SDC5520	41.84	+2.66	37.86	-	196.4	185.4
SDC6450	40.25	+0.65	42.33	-1.83	208.6	202.1
SDC5550	41.09	+3.41	43.15	-2.15	205.2	196.8
SDC8260	46.87	+1.83	43.04	-0.04	190.3	194.1
SDC8270	47.96	-2.96	43.64	-4.04	198.6	193.6

^a Phase change temperature and enthalpy in melting process.

^b Phase change temperature and enthalpy in solidifying process.

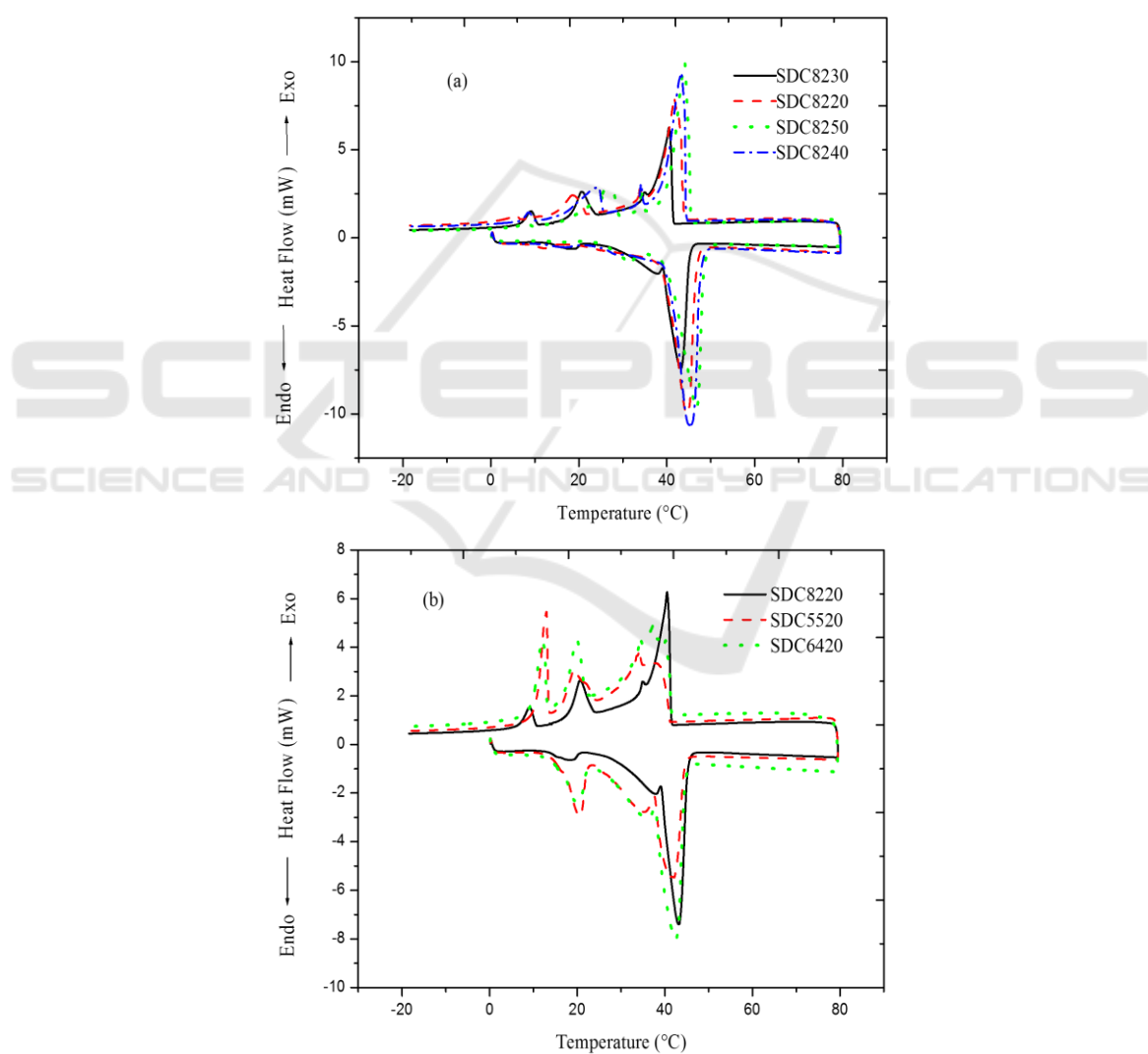


Figure 3: DSC curves of samples.

The Phase change temperatures and latent heats in melting and solidifying processes: 40.25°C and 42.33°C, 208.6 J/g and 202.1 J/g of SDC6450, 47.75°C and 44.08°C, 207.7 J/g and 214.2 J/g of SDC8250. The absolute differences between the phase change temperatures and color change temperatures were $\leq 1.92^\circ\text{C}$, meaning that the original experimental goal was achieved, and visualising phase change phenomena with a colour indicator is feasible. The extra relative weak peaks existing in Figure 3 caused by the phase separation, and this could be weakened by prolonging the mixing time our mixing method (Li et al., 2018; Wu, 2016).

3.3 Thermal Stability

The thermal stability of the samples were evaluated by the thermogravimetric analysis and the parameters of the sample thermochromism and phase change processes after some thermal runs. The thermogravimetric curves of the samples were presented in Figure 4. The curves of the samples were horizontal when the temperatures were $\leq 130^\circ\text{C}$ and $\geq 280^\circ\text{C}$, with a sharp weight loss in the temperature area of $130^\circ\text{C} - 225^\circ\text{C}$, indicating that the samples are thermal stable at $\leq 130^\circ\text{C}$, or in their phase change processes.

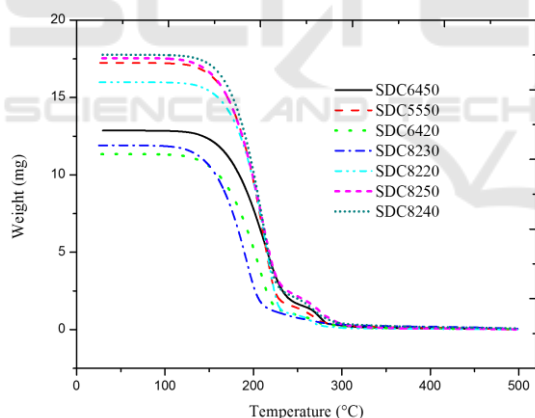


Figure 4: TGA curves of samples.

To evaluate the sample thermal durability, SDC6450 was chosen as a representative. The DSC curves of SDC6450 from the 1st to 20th runs were presented in Figure 5. No obvious changes in the enthalpies and the phase change temperatures were detected from the 1st to 20th runs.

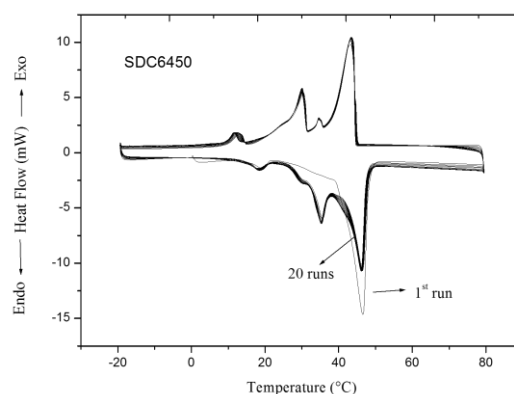


Figure 5: DSC curves of SDC6450 from 1st run to 20th run.

3.4 UV-VIS-NIR Spectrometer Analysis

Figure 6 showed the absorption spectra of the samples at 25°C . In the visible region, a steamed bun peak at $550\text{ nm} - 650\text{ nm}$ could be seen, corresponding to yellow and orange light regions. This was consistent with the sample color (light blue) appeared in the thermochromic experiments. In the ultraviolet region, there was a wide and strong absorption peak in the area $230\text{ nm} - 380\text{ nm}$, indicating other potential application related with this property, such as ultraviolet protection equipment.

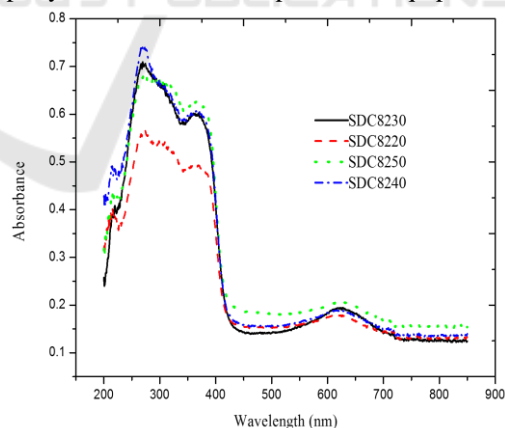


Figure 6: UV-VIS-NIR spectral curves of samples.

4 CONCLUSIONS

Reversible thermochromic and phase change dual functional materials were prepared with the raw materials CVL, DA, SA and CA by mixing, heating and cooling processes. The adequate mass ratio of CVL, (SA+DA) and CA are in the area 1: 10: 30 – 1: 10: 70. The melting and solidifying enthalpies of the samples reached up to 208.6 J/g and 202.1 J/g corresponding to the mass ratio of CVL, (SA+DA) and CA 1: (6+4): 50. The phase change temperatures of the samples (40.25°C – 47.96°C) were well matched with the thermochromic temperatures (39.60°C – 48.90°C). The samples have good thermal stability in their phase change processes. The absolute differences between the phase change temperatures and color change temperatures of the optimum samples were $\leq 1.92^\circ\text{C}$. In addition, the samples also exhibited an excellent ultraviolet absorption property, meaning they could be used in ultraviolet protection aspect.

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