Supporting Information

Preparation of Waste Incorporated Bio-Smart Shape-Stable Phase Change Material (FSSPCM) with Smart Fluorescent Properties

Shilpa K K, [a] *Ramya Padmanaban,* [a] Satishkumar M,[a] *Jit Sarkar,* *[a,b]

[a]Polymer Science & Technology Unit, Advanced Materials Laboratory, CSIR-Central Leather Research Institute (CSIR-CLRI) Sardar Patel Road, Adyar, Chennai 600 020, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

1. Experimental section

1.1 Materials

Leather Waste (LW, vegetable-tanned leather waste was collected from CSIR-Central Leather Research Institute (CLRI) tannery and utilized without purification.), polyethylene Glycol-6000 (PEG 6000 LR, M_w = 5000 to 7000 g/mol from Laboratory Rasayan, India), glycidyl methacrylate (GMA, ≥97% from Sigma-Aldrich), 2,2'-Azobisisobutyronitrile (AIBN, 98%, Sisco Research Laboratories Pvt. Ltd.) were used as received to prepare the composite. Dyes such as Rhodamine-B (≥95%, Sigma-Aldrich) and Fluorescein (Fluka analytical) were used to impart fluorescence to the composite material. Metal salts $CuSO_4$, $5H_2O$ (Merck), anhydrous $FeCl_3$ (S D Fine Chem Ltd.), anhydrous $MgSO_4$ (Laboratory Rasayan), $Pb(OAC)_2$, $3H_2O$ (Merck) were purchased and utilized.

1.2 Preparation of Leather waste incorporated PGL composite.

PEG6000 (2.33 g, 70 wt%) and LW (0.33 g, 10 wt%) were blended in a double-neck Schlenk tube using an overhead at 70 ºC for one hour. Subsequently, a mixture of GMA (0.66 g, 20

wt%) and AIBN (50 mg, 1.5 wt%) was added. Mixture was stirred at 70 ºC for 2 h under N_2 gas. The resulting blend was then cast in between the steel mold and subjected to compression with a 5 kg load at 70 ºC for 2 hours. Thus, PGL721 was prepared. Similarly, all composites were prepared using different ratios of LW, PEG, and GMA, as represented in Table 1.

1.3 Preparation of Fluorescent SSPCM (FSSPCM).

FSSPCMs were prepared using the following procedure (Figure 1a). PEG6000 (2.33 g, 70 wt%) and LW (0.33 g, 10 wt%) were blended in a double-neck Schlenk tube using an overhead at 70 ºC for one hour. Subsequently, a mixture of GMA (0.66 g, 20 wt%), Rhodamine-B (Rh-B, 0.0033 g, 0.1 wt%), and AIBN (50 mg, 1.5 wt%) was added. Mixture was stirred at 70 ºC for 2 h under N_2 gas. The resulting blend was then cast in between the steel mold and subjected to compression with a 5 kg load at 70 ºC for 2 h. Thus, FSSPCM2 was Prepared. Similarly, FSSPCM1 was prepared by using Fluorescein (0.033 g, 1 wt%) instead of Rh-B.

1.4 Shape memory experiment

The bending test was employed to evaluate the shape memory properties of the composites. Samples were cut into pieces maintaining the dimensions approximately 2.5 cm × 0.5 cm × 0.1 cm (length × width × height). The pieces were heated at 70 ºC for 1 to 2 min, bent into a 'U' shape, cooled at -15 ºC for 2 min in a fridge, and measured the fixed angle (Θ_f). Subsequently, the bent sample was heated to 70 ºC in a vacuum oven until complete recovery. Recovery time and angle (Θ_r) were recorded. Similarly, shape recovery experiments were performed in water at 37 ºC and Θ_r was recorded. The experiments were repeated for three times per composite, taken mean as a value of representation and standard deviation as an error bar.

The shape fixity ratio (R_f) and shape recovery ratio (R_r) were determined using the following equations;

Shape fixity ratio (%) = $\frac{\Theta_f}{180} \times 100$ ……(1)

Shape recovery ratio (%) = $\frac{\Theta_f - \Theta_r}{\Theta_f} \times 100$ ……...(2)

1.5 Shape stability experiment

The composites were cut into small pieces, about 1 cm × 1 cm × 0.1 cm (length × width × height), to evaluate thermal form stability. The composites were heated at 70, 90, and 110 °C, and pictures of every composite specimen were taken at predetermined intervals of 0.5, 1, and 2 h. The goal was to assess the thermal form stability of the composites at different heat levels.

1.6. Quantitative Leakage Study.

The quantitative leakage study was analyzed by gravimetric analysis as reported by Tejashree et al.[1] A piece (about 1 cm × 1 cm × 0.1 cm (length × width × height)) of sample (PEG and PGL721) was taken. The sample was kept on filter paper and heated at different temperatures for the prescribed time. The weight of the filter paper was recorded before and after heating and leakage was calculated.

1.7. Self-healing study

PGL721 was cut into the dimensions approximately 2.5 cm × 0.5 cm × 0.1 cm (length × width × height). The composite was broken by bending. Subsequently, the cracked

composite was placed in an oven at 70 ℃ for 1.5 h. After cracking and healing process, images were captured using both a mobile camera and a microscope.

1.8 Thermo-responsive fluorescence sensing study.

FSSPCM1 was cut into small pieces, about 1 cm × 1 cm × 0.1 cm (length × width × height), to evaluate the thermo-responsive fluorescence properties. The samples were subjected to thermal treatment for 30 min at 50 and 70 ℃. Images of the composite before and after the heating process, were captured using a mobile camera under a UV lamp, as depicted in **Figure S10**. Before and after heating at 70 ℃ and cooling to room temperature for 30 min, the sample was analyzed with fluorescence microscope and spectroscopy.

1.9 Metal-Ion analyte sensing study

FSSPCM2 was cut into small pieces, about 1 cm × 1 cm × 0.1 cm (length × width × height), to evaluate the metal-ion sensing property of the composite. The composite (LPCM 14) was immersed in 0.7 M solutions of various metal ions such as $FeCl_3$, $MgSO_4$, $CuSO_4$, and $Pb(OAc)_2$ for 5 minutes. The images (before and after immersion in metal-ion solution) of the composite were captured using a mobile camera under a UV lamp as shown in **Figure S10**. The composite which was immersed in $FeCl_3$ was also analyzed with fluorescence microscope as well as fluorescence spectroscopy.

1.10. Mechanical Property Analysis

A piece (l × w × h = 7.5 cm × 1.5 cm × 0.1 cm) of PGL721 was cut and mechanical properties such as elongation at break, tensile strength were analyzed using a Universal Testing Machine (UTM- Instron-3369). The experiments were repeated for three pieces, taken mean as a value of representation and standard deviation as an error bar. Similarly, mechanical properties of FSSPCMs were evaluated.

1.11. Water contact angle analysis

The water contact angle of the composites was measured by placing sufficiently sized samples on the glass slide. Water contact angle measurements were conducted for all composites. The experiments were repeated for three pieces, taken mean as a value of representation.

1.12. Fluorescence analysis

The fluorescent emission of composites was analyzed using a CARY ECLIPSE FLUORESCENCE SPECTROPHOTOMETER. The emission spectra of FSSPCM2 were obtained for the pure sample and the quenched sample (which was immersed in 0.7 M $FeCl_3$ for 5 minutes and dried). The emission spectra for FSSPCM1 were recorded before heating (at 70 °C), after heating, and after cooling at r.t.

2. Characterization

The functional groups in the composites were assessed using the Bruker Alpha II Platinum ATR instrument at a wavenumber ranging from 4000 to 400 cm^{-1}.

T_c, T_m, *and* T_g were recorded in the TA DSC 25 instrument from -90 ^oC to 150 ^oC at the heating and cooling of 10 ^oC/min. ΔH_m, and ΔH_c were calculated using the software in the NETZSCH Polyma DSC 214 from -60 °C to 150 °C instruments under the heating and cooling rate of 10 ^oC/min. The thermal stability of composites was analyzed using a TA TGA 55 instrument using a heating rate of 10 ^oC/min. TGA and DSC analysis were performed using 8-10 mg of sample in the aluminium pan.

Morphological characteristics of composites were investigated using a CLARA GMU Field Emission Scanning Electron Microscope (FE-SEM).

Microscopic images of fluorescent composites were captured using a LEICA fluorescence microscope.

The surface wettability of the composites was evaluated using Holmark Opto Mechatronics Contact Angle equipment.

The fluorescence emission of composites was analyzed using a CARY ECLIPSE FLUORESCENCE SPECTROPHOTOMETER.

Mechanical Properties were analyzed using the Universal Testing Machine (UTM- Instron-3369).

3. Supplementary Figures.

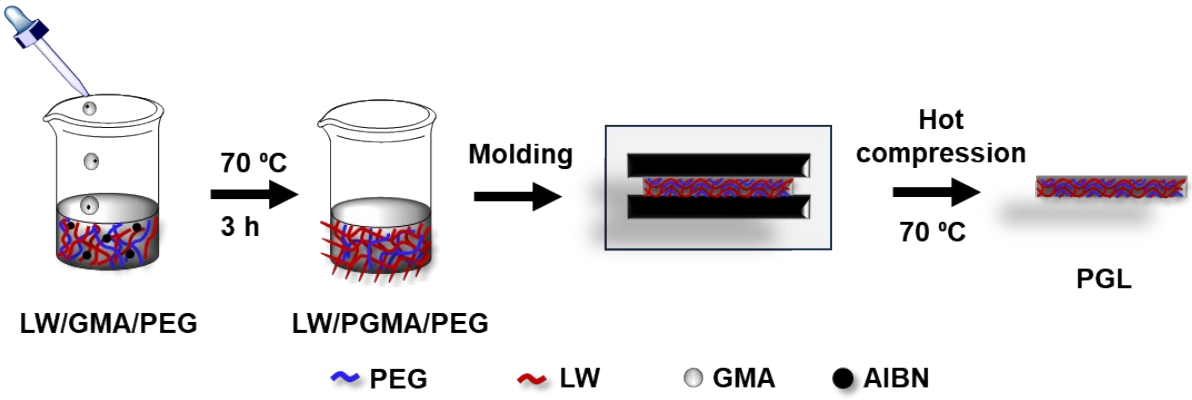

Figure S1. Preparation of PGL composites.

Figure S2. Shape memory of composites in water.

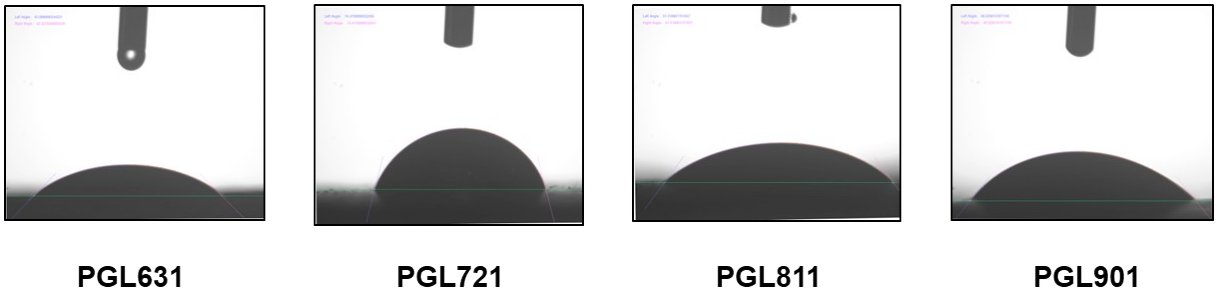

Figure S3. Water contact angle images of composites.

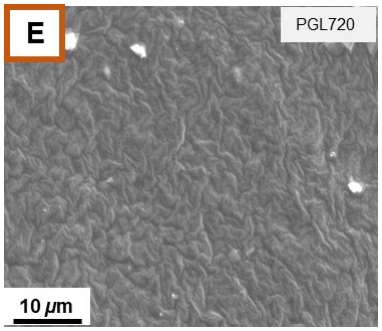

Figure S4. FESEM image of PGL720.

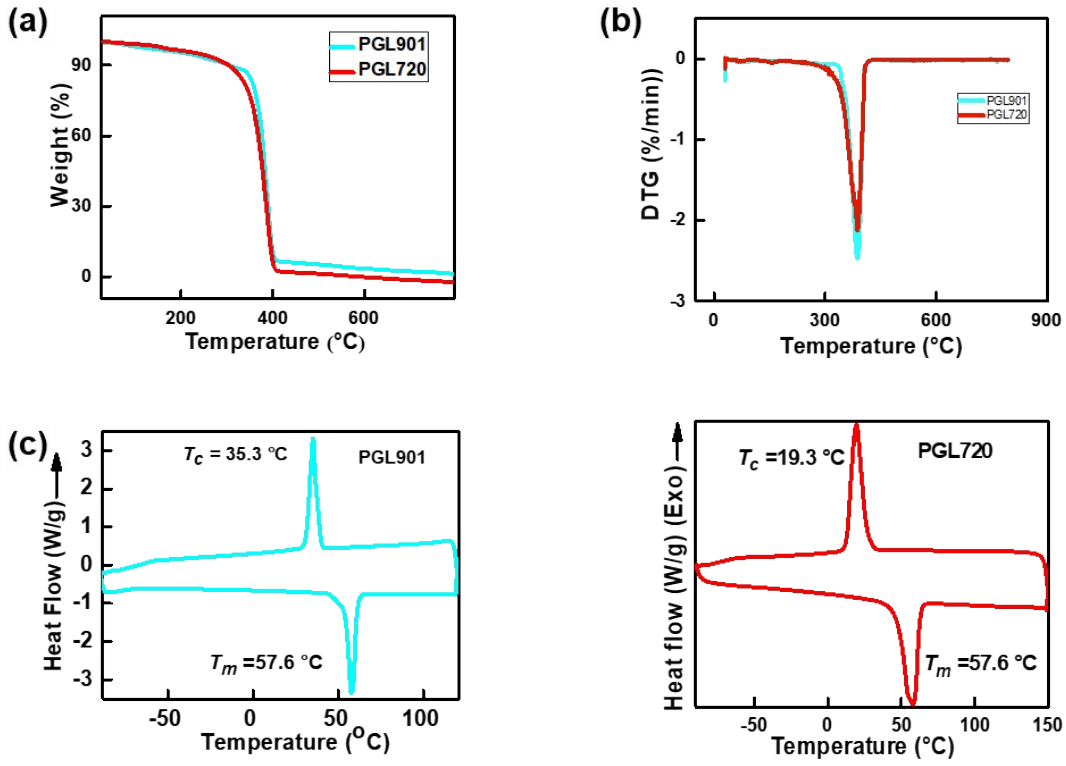

Figure S5. TGA (a), DTG (b), and DSC plots of PGL901 (cyan line) and PGL720 (red line).

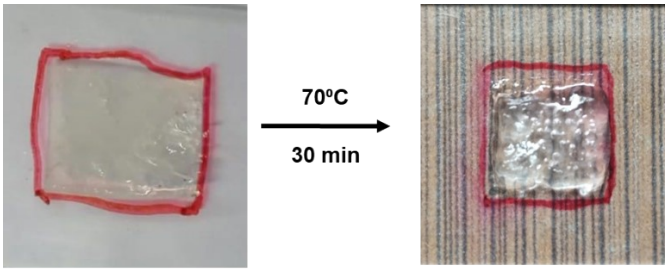

Figure S6. Images of PGL720 before and after heating at 70 °C after 30 min.

Time (h)	PEG	PGL631	PGL901	PGL721	PGL811
0					
0.5					
1					
2					

Figure S7. Images of the composites at different times (before and after heating) at 90 °C.

Time (h)	PEG	PGL631	PGL901	PGL721	PGL811
0					
0.5					
1					
2					

Figure S8. Images of the composites at different times (before and after heating) at 110 °C.

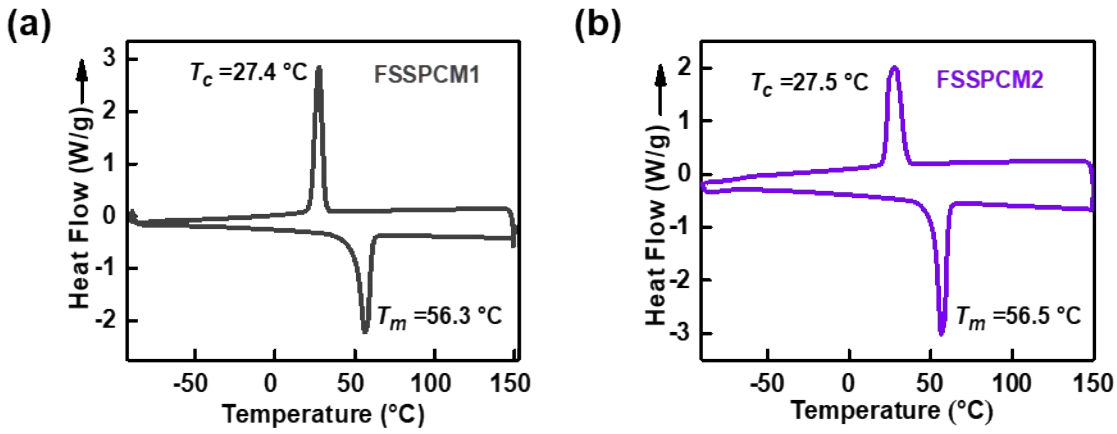

Figure S9. DSC plots of FSSPCM1 and FSSPCM2.

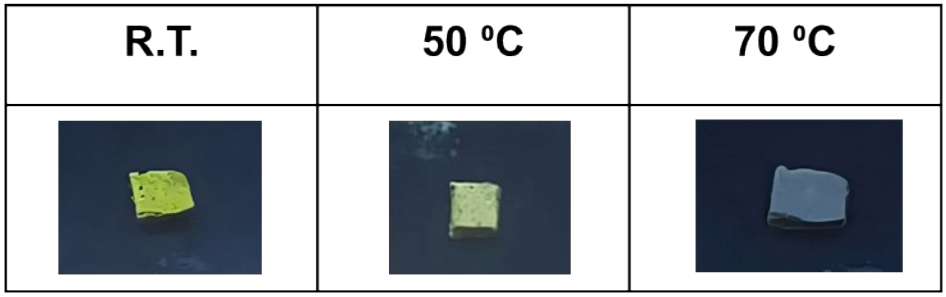

Figure S10. Images of FSSPCM1 at r.t., 50, and 70 °C.

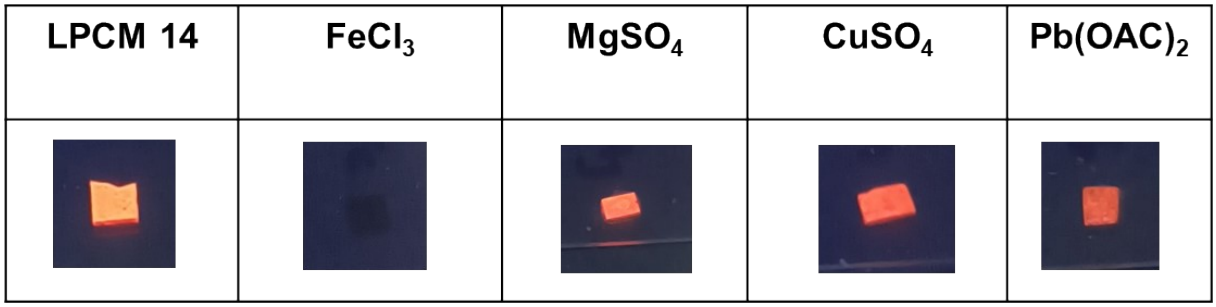

Figure S11. Fluorescent image of metal ion detection using 0.7 M of $FeCl_3$ solution.

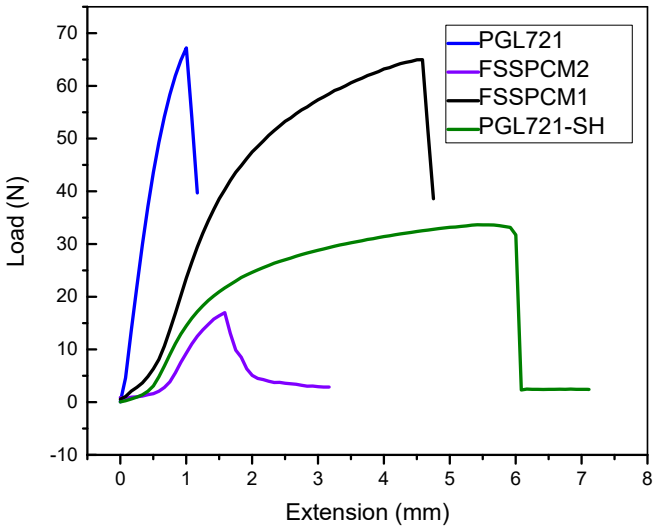

Figure S12. Load vs Extension Curve for the PGL721, FSSPCM1, FSSPCM 2.

4. Supplementary Videos.

Video S1. Shape Memory Experiment in Air for PGL 721.

https://drive.google.com/file/d/1GIfwb_picr8olPfe31AAohWIz9Fq_8YQ/view

Video S2. Shape Memory Experiment in Water for PGL 721.

https://drive.google.com/file/d/1GCDs-ufLtbrjGI_NkN4MROOBEbEYbCkM/view

Reference.

1. T. Amberkar and P. Mahanwar, Study and Characterization of Phase Change Material-Recycled Paperboard Composite for Thermoregulated Packaging Applications.*Journal*, 2021, **7**.