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Electronic Supplementary Information

New Composite Thixotropic Hydrogel Composed of a Low-Molecular-Weight Hydrogelater and a Nanosheet

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Materials and Methods

Palmitoyl-glycine-histidine hydrogelator (PalGH) was provided by Nissan Chemical Industries, Ltd. and used as received. Laponite® XLG (Rockwood Additives Limited) was provided by Wilbur-Ellis Co., (JAPAN) LTD. and used as received. Water was deionised with an Elix UV 3 Milli-Q integral water purification system (Nihon Millipore K.K).

The gelation tests were performed using vial inversion method in a vial with a rubber seal (mighty vial, no. 01; Maruemu Corporation). White crystalline PalGH was placed in a vial containing a 1 wt% aqueous Laponite solution at a specific concentration (wt%), and the vial was capped. The vial was then heated in a dry bath at 110 °C until the PalGH crystal was dissolved, at which point the PalGH solution was left to stand for 1 h at room temperature, and gelation was determined by visual observation after inversion of the vial.

Thixotropic behaviour was evaluated using the vial inversion method. The prepared hydrogel in the vial was shaken and mechanically collapsed using a vortex genie (Scientific Industries, Inc). The obtained sol was then allowed to set for a given time at room temperature, and the recovery of the gel state from the sol state was determined by visual observation after inversion of the vial.

Scanning electron microscopy (SEM) images were recorded using an SU-8000 scanning electron microscope (Hitachi High-Technologies Corporation) at 1.0 kV; the SEM sample (xerogel of hydrogel) was freeze-dried and placed on a conductive tape on the SEM sample stage. Pt, as a conductive material, was used as a coating (10nm-thick) on the sample.

Thermal analysis was performed using an EXSTAR6000 differential scanning calorimeter (DSC, Seiko Instruments Inc.) with a Ag closable sample pan. The transition temperatures of the hydrogels ($T_{gel\rightarrow sol}$ and $T_{sol\rightarrow gel}$) were determined as the extrapolated onset temperatures from the DSC curves.

Rheological measurements of the frequency sweep were performed at 25 °C using an MCR-301 rheometer (Anton Paar Japan K.K.) with a parallel plate (8 mm diameter) at a gap of 0.50 mm and γ of 0.01 %. Rheological measurements of the strain sweep were performed at 25 °C using an MCR-301 rheometer with a parallel plate (8 mm diameter) at a gap of 0.50 mm and a constant angular frequency of 1 rad s^{-1}. For the rheological measurements, the organogel sample was applied onto the parallel plate and sample stage and then any overflow gel was swept away. Step-shear measurements were carried out by repeatedly applying a normal strain (strain amplitude 0.01% and frequency 1 Hz) and a large strain (shear rate 3000 s^{-1} for 0.1 s).

Infrared spectroscopy was performed using an FT/IR-620 (JASCO Corporation) and the ATR method (ZnSe prism).

Small angle x-ray scattering (SAXS) data were recorded on a D8 Discover X-ray diffractometer (Bruker AXS K.K.) using CuKα at 26 °C (the sample was placed in a 2 mm-diameter quartz glass capillary tube).

Figs. S1 and S2

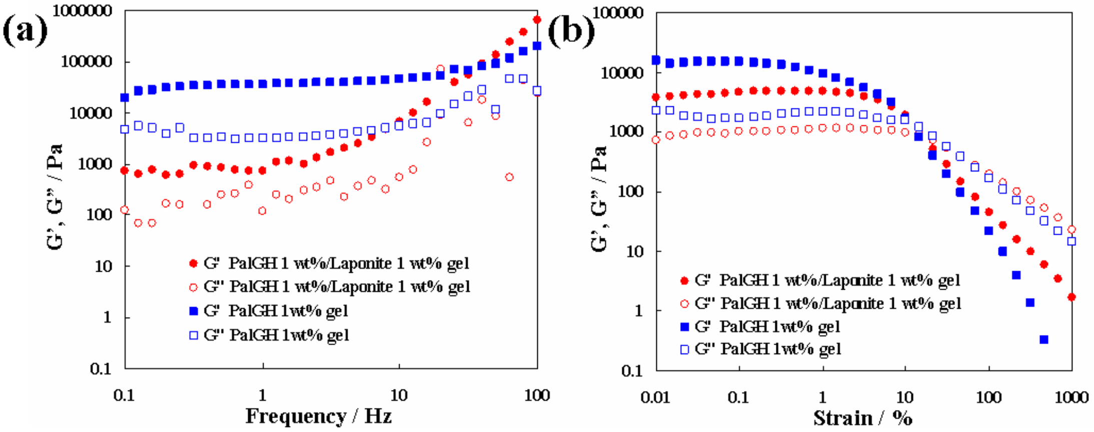

Fig. S1 Dynamic rheological properties of the PalGH 1 wt% and PalGH 1 wt%/Laponite 1 wt% hydrogels: (a) Frequency sweep and (b) strain sweep. These results confirmed the existence of gel state (G′ > G″) in the composite hydrogel composed of PalGH and Laponite, and also indicated that the composite hydrogel possessed a lower G value (softer material) compared to that of PalGH of the same concentration.

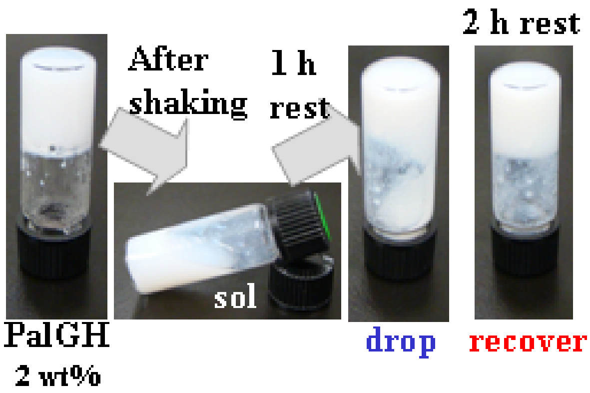

Fig. S2 Photographs of the thixotropic test of the PalGH 2 wt% hydrogel.

Table S1 and Fig. S3

Table S1 Transition temperatures of the Laponite aqueous solution, PalGH hydrogel and PalGH/Laponite composite hydrogel obtained from differential scanning calorimetry (DSC) measurements (heating and cooling rates of 2 °C/min)

Sample	$T_{gel\rightarrow sol}$ /°C (ΔH/mJ mg^{-1})	$T_{sol\rightarrow gel}$ /°C (ΔH/mJ mg^{-1})
Laponite 1 wt% aqueous solution	ND*	ND*
Laponite 3 wt% aqueous solution (gel state)	ND*	ND*
PalGH 1 wt% hydrogel	62 (0.85)	50 (0.90)
PalGH 2 wt% hydrogel	59 (5.11)	55 (5.05)
PalGH /Laponite 1 wt%/1 wt% hydrogel	46 (0.58)	37 (0.58)

* ND: no detection

Fig. S3

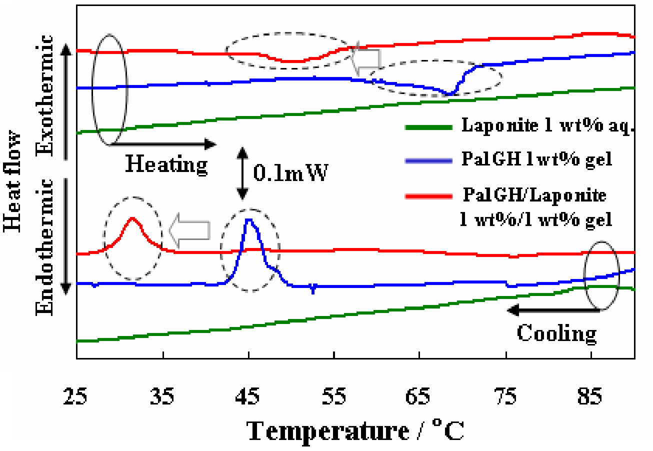

Fig. S3 DSC curves of the Laponite 1 wt% aqueous solution, PalGH 1 wt% hydrogel and PalGH 1 wt%/Laponite 1 wt% hydrogel (heating and cooling rates of 2 °C/min).

Figs. S4 and S5

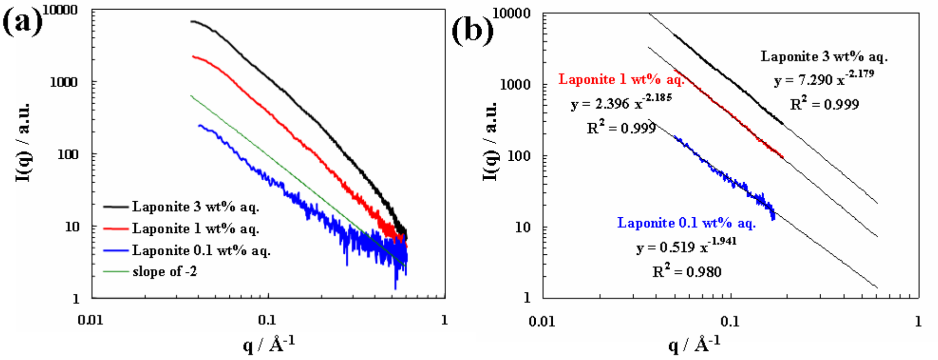

Fig. S4 SAXS data for Laponite aqueous solutions: (a) 0.1 wt%, 1 wt% and 3 wt% aqueous solutions and (b) exponential approximations for Laponite 0.1 wt% ($0.05 < q < 0.17$), 1 wt% ($0.05 < q < 0.19$) and 3 wt% ($0.05 < q < 0.19$) aqueous solutions. From Fig. S4 (a), it appears that the Laponite aqueous solutions have a slope of ca. –2. From Fig. S4(b), within $0.05 < q < 0.17$, the SAXS results showed better exponential fitting of the exponential curve (with a slope of–2 in the double logarithmic graph), indicating the existence of flat particles.[1]

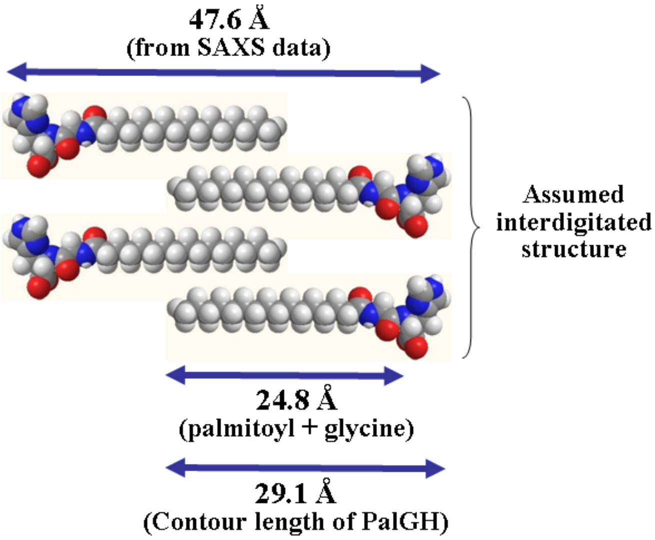

Fig. S5 Schematic of the possible interdigitated lamellar packing structure of PalGH. The molecular lengths of PalGH were obtained from MM2 calculation performed in ChemDraw.

Acknowledgements

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Reference

1 Eds. O. Glatter and O. Kratky, *Small Angle X-ray Scattering,* Academic Press, 1982.