

## **Experimental Section**

### **Materials**

Shellac wax, SSB<sup>®</sup> Cera 2 (Acid value: 2-25 mgKOH/g and Saponification value: 40-60 mgKOH/g) was received as a generous gift sample from SSB Stroever GmbH & Co. KG., Germany. Rapeseed oil was received as a gift sample from Vandemoortele Lipids N.V., Belgium. Nile red was purchased from Sigma Aldrich Inc., USA. Water purified by the MilliQ system was used for all the experiments.

### **Preparation of liquid oil-based soft matter system**

Accurately weighed samples of shellac were dispersed in rapeseed oil to achieve a concentration range of 0 - 6 % wt. The dispersions were heated at 90 °C under a mild agitation (200 rpm) using magnetic stirrer (Model EM3300T, Labotech Inc, Germany). The clear oily dispersions were then cooled to room temperature resulting in the formation of oleogels.

Water-in-oil emulsions were prepared by first mixing the heated oleogel samples and water at 90 °C under continuous stirring (1000 rpm) using a magnetic stirrer followed by cooling the mixture to room temperature.

### **Microstructure studies**

The microstructure of oleogels was studied using Leitz diaphan microscope (Leitz Wetzlar Germany) equipped with a thermo-electric stage (PE94, Linkam Scientific Instruments Ltd., UK). In all the cases, the imaging was carried out by first melting the oleogels at 90 °C followed by cooling at controlled rate. The real time analysis of crystallization done by capturing images under optical and polarized light at predetermined temperatures over a certain duration.

For confocal microscopy, Nile red was first dissolved in rapeseed oil and this oil was then used for preparing the oleogel and emulsion samples. Samples were imaged using a Nikon A1R confocal microscope (Nikon Instruments Inc., USA). Excitation was performed by means of a 488nm Ar laser and fluorescence was detected through a 525/50 bandpass filter. Images were acquired and processed with Nikon NIS Elements software.

### **Thermal analysis**

The thermal parameters were studied using a Q1000 Differential scanning calorimeter (TA Instruments, USA) on samples weighing 10 mg in flat-bottomed aluminium pans. The samples were subjected to heating and cooling cycles from 5 to 100 °C and back at cooling rates of 1 and 10 °C/min. The thermal parameters were obtained from the heat flow curves with the help of TA Universal Analysis software.

### **Rheological measurements**

The rheological measurements were carried out on advanced rheometer AR 2000ex (TA Instruments, USA) using a parallel plate geometry of diameter 40mm. The viscoelastic parameters such as storage ( $G'$ ) and loss ( $G''$ ) moduli were measured as a function of time at a constant frequency of 0.25 Hz, 0.01 % strain and two different temperatures of 5 and 37 °C; and as a function of angular frequency ( $\omega$ ) from 0.1 to 600 rad/sec at 0.01 % strain and a constant temperature of 25 °C.

## Figures

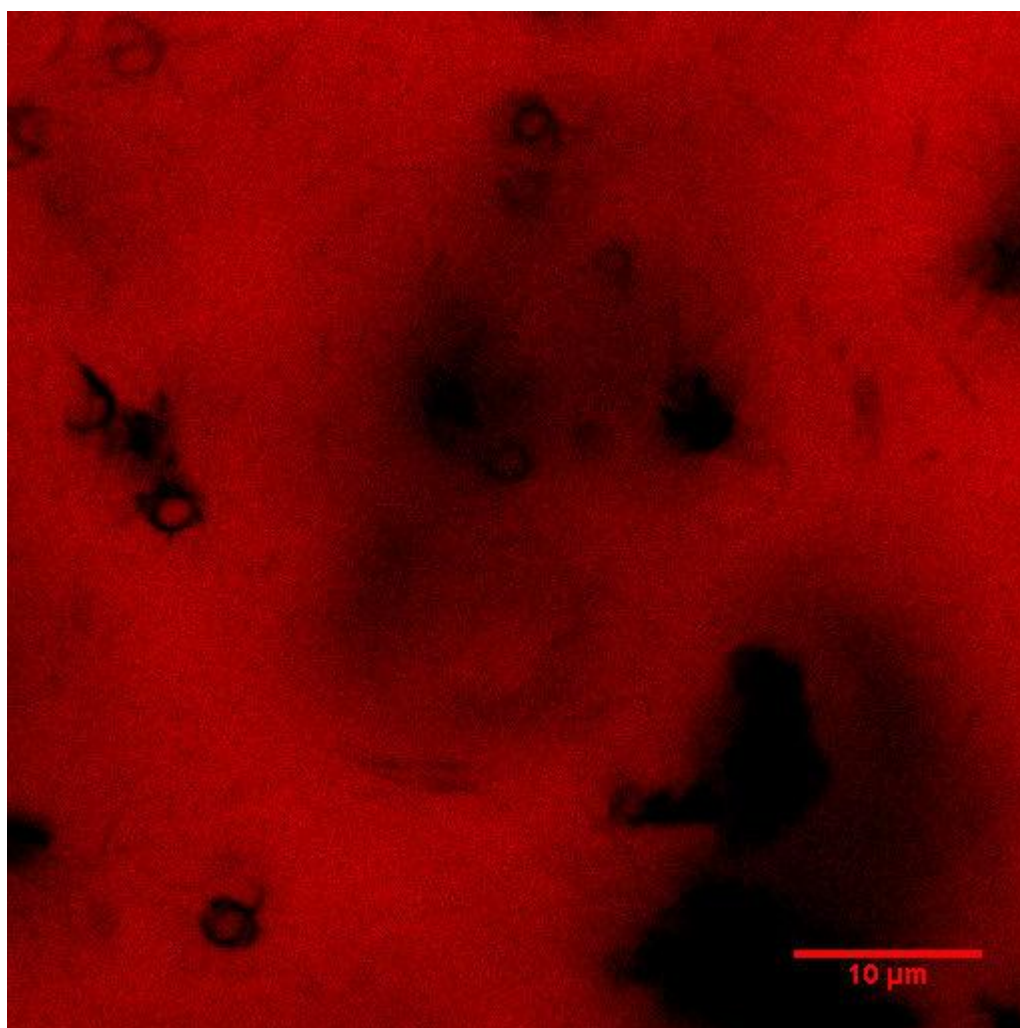


Fig S1: Enlarged image of Figure 2a for clearer viewing of the finer colloidal structures forming the network.

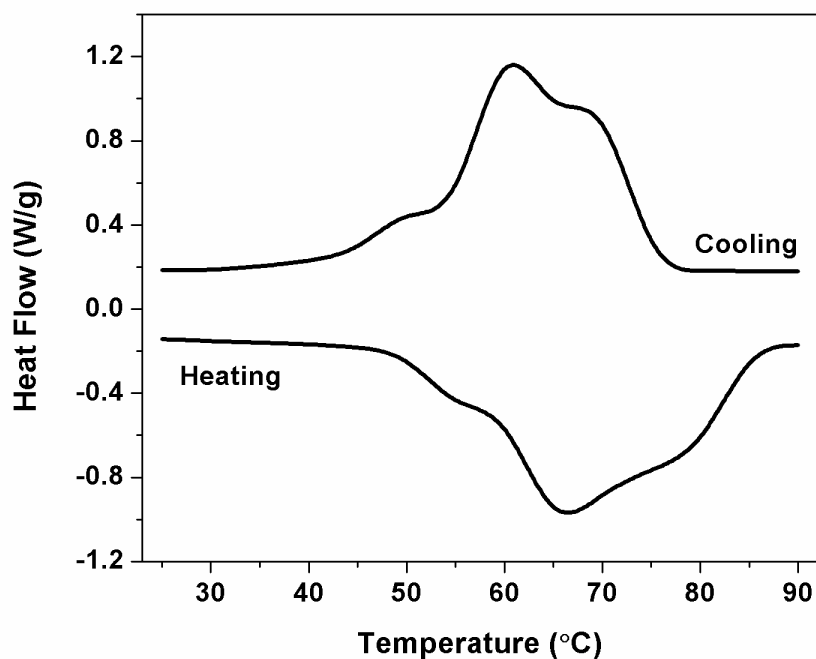


Fig. S2: DSC profile of shellac used in the study. The melting peaks at 55, 66.4 and 79.4 °C and the corresponding crystallization peaks at 69.9, 60.8 and 50.2 °C are attributed to the chemical composition of shellac.

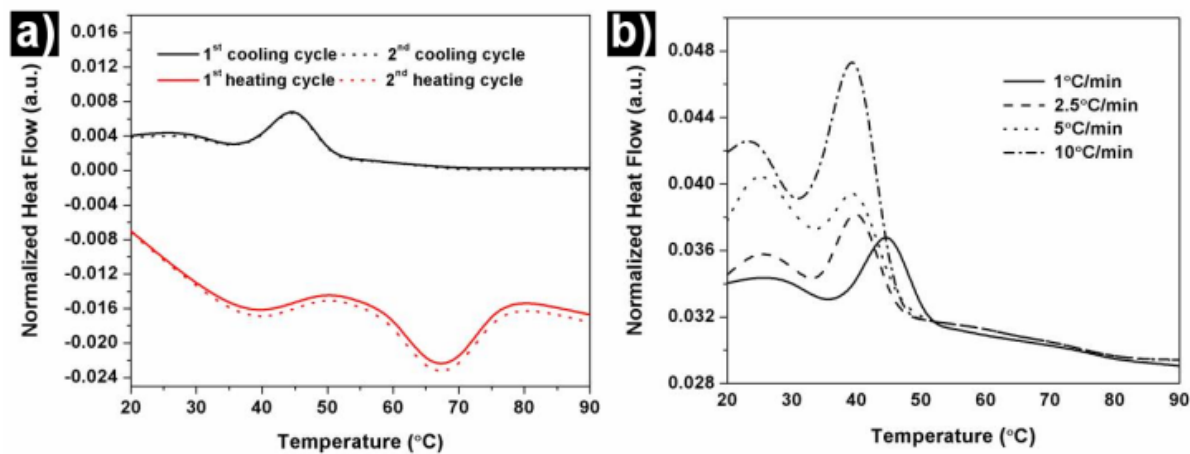


Fig. S3. a) DSC profiles of 2 %wt shellac oleogel during a consecutive cool-heat cycle at a constant rate of 5 °C/min; b) Normalized heat flow curves for 2 % wt shellac oleogel sample cooled at different rates.

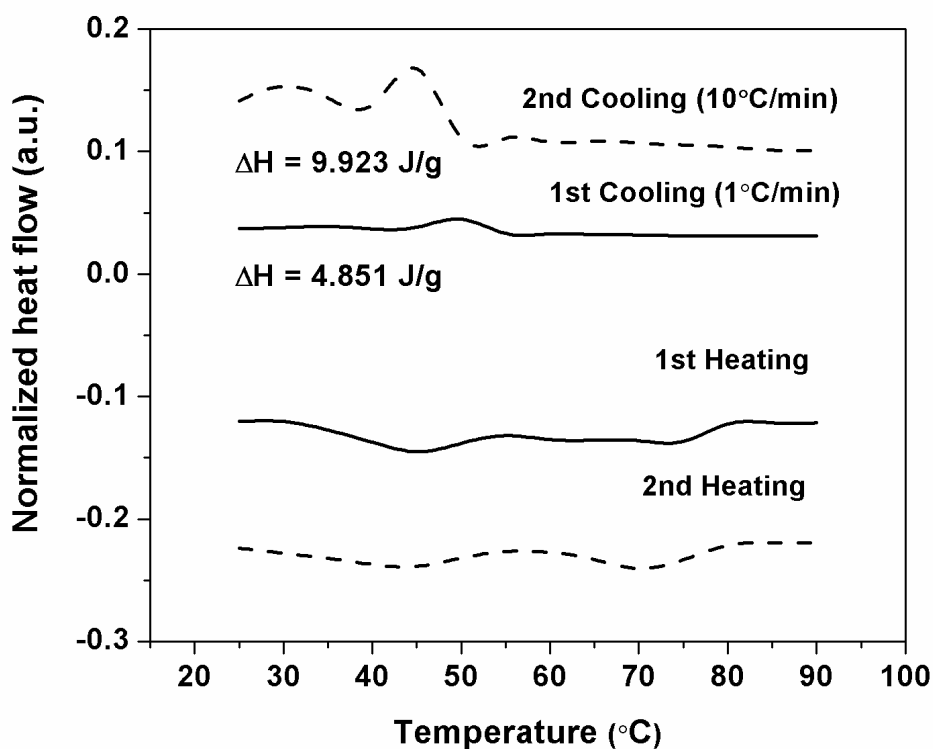


Fig. S4: Heating and cooling cycles of oleogels prepared using shellac at 5 %wt. The effect of cooling rate on thermal parameters (onset and crystallization temperature and the enthalpy of crystallization) was clearly seen.

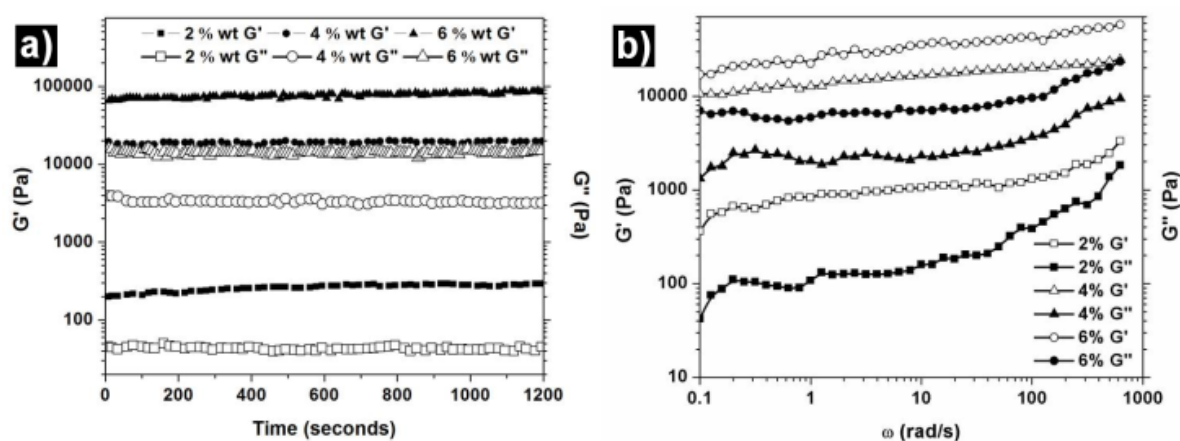


Fig. S5. a) Storage ( $G'$ ) and loss ( $G''$ ) moduli during time sweeps (at 0.25 Hz, 5 °C) for oleogels prepared at different shellac concentrations; b) Rheological data as a function of angular frequency (at 0.01% strain, 25 °C) for oleogels with 2, 4 and 6 % wt shellac.