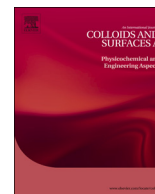




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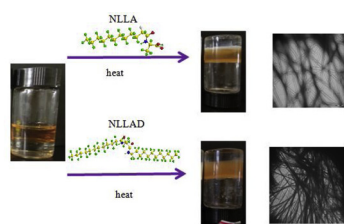
Gelation properties and application based on amino acids gelators with four kinds of edible oils

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GRAPHICAL ABSTRACT

Gelation process of gelator in sesame oils and water mixture



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ABSTRACT

The properties of the minimum gel concentration (MGC), gel-to-sol transition temperature (T_{gl}), gelation driving force, and oil binding capacity (OBC) by two amino acid gelators, namely, N-Lauroyl-L-alanine (NLLA) and N-Lauroyl-L-alanine dodecylamide (NLLAD) and four kinds of edible oils were studied. The crystal structure and microstructure of the gels were investigated by X-ray diffraction, polarizing microscopy, transmission electron microscopy, and scanning electron microscopy. Results showed that the hydrogen bond between the amide bonds in molecule was the intermolecular driving force for gel formation. The MGC of NLLAD was lower than that of NLLA, whereas its T_{gl} was higher than that of NLLA. NLLAD also had better crystal structures in four kinds of edible oils. At > 8% gelator concentration, the OBCs of NLLA were higher than those of NLLAD in the four oils. Moreover, the two gelators performed well in separating an oil–water mixture.

1. Introduction

As a soft material, gels are regularly used such as in toothpaste, hair spray, and jelly. Functional gels have also been extensively developed in recent years. A gel is composed of a 3D network structure formed by a gelator and the filling of solvent molecules [1]. The noncovalent intermolecular interactions within a gelator include intermolecular hydrogen bonds, π - π stacking, van der Waals force, and other weak interactions [2–4]. Gels can be classified into hydrogelators and

organogelators, depending on the type of solvent. Therefore, the phase selectivity of the gelator can be effectively used to choose the gel organic phase or the aqueous phase to separate oil from water [5].

Many gelators can be used to form gels. The common gelator units are amino acid, cholesterol, amide, urea, and sugar. Many new gelators can be designed by modifying these gelator units. N-acyl amino acid is a type of surfactant and a gelator derived from amino acid. In 2000, Bhattacharya discovered the gel property of N-acyl amino acid [6]. The efficiency of lauryl alanine gelatinization with aromatic and aliphatic

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hydrocarbon solvents have been investigated and initially used to simulate the recovery of oil during oil spills. Then, Ajinomoto first introduced a short-chain amine at the tail of the N-acyl amino acid and found the superior gel properties of the product. The product was non-toxic, tasteless, and very safe to sea creatures, such as fish and shellfish. This product can be used for oil recovery, medicine, cosmetics, paints, inks, and liquid explosives [7,8]. Ichikawa introduced an alcohol at the tail of the N-acyl amino acid to first produce an oil-soluble nonionic surfactant. The product had excellent emulsification and moisturizing properties and was used as an oily component for cosmetic fragrance. The product was subsequently found to have gel properties [9], but its gel ability was relatively weak. N-lauroyl-L-glutamic acid diethyl ester can form a white gel in liquid paraffin but cannot form a gel in most organic solvents [10]. Bastiat found that safflower oil gels by phenylalanine, tryptophan, and tyrosine-derived gelator [11]. Suzuki studied the gel properties of lysine-derived gelator on alkanes [12]. Amino acids are safe, non-toxic, widely available, and amino and carboxyl groups are easy to modify. Thus, the development of gelatins with amino acids as the main unit has been paid increasing attention. However, available amino acid varieties and modified substances are not sufficient. The types of amino acid gelator should be expanded.

Solid oils serve as raw materials for many foods, such as ice cream, chocolate, and butter [13]. Hydrogenation is the most common method for manufacturing solid oils. However, the trans-fatty acids produced by the incomplete hydrogenation of unsaturated fats may cause risks to the human heart and brain diseases. Hence, new methods for solid oil production are being explored [14]. Solid vegetable oil gels are new alternatives to unhealthy saturated fatty acids by capturing the liquid oils in a thermo-reversible 3D gel network. Thus, diseases caused by trans fatty acids in hydrogenated vegetable oils are avoided, and oil migration in foods is reduced [15–17]. Previous studies have shown that an amino acid gelator possesses good gel properties [2], but this gelator has not yet been applied to solidify vegetable oils.

Moreover, the easy separation of oil and water from disposed edible waste oil is also a problem in environmental protection [6]. Given the safety of the amino acid gelator, this compound can reduce pollution to water bodies and harm to aquatic organisms. Therefore, the amino acid gelator can be added to the oil–water mixture, and only the oil phase can be gelled to separate the oil–water phase. This property will also be important in the application of the amino acid gelator in grease [18,19]. Given that this gel was used to prepare cholinesterase inhibitors to treat Alzheimer's disease [11,20], amino acid gels are safe and can be used for edible oils.

In this study, the gels formed by N-Lauroyl-L-alanine (NLLA) and N-Lauroyl-L-alanine dodecylamide (NLLAD) and four kinds of edible oils were characterized using the minimum gel concentration (MGC), gel-to-sol transition temperature (T_{gl}), gelation driving force, crystal structure, and morphology. The oil binding capacity (OBC) of the gelators and their application in the gelation of edible oil and water separation were also discussed. The experiment provided a theoretical basis for the research and development of edible oil gels. The application of these gelators for treating kitchen waste and oil-water separation was also explored.

2. Materials and methods

2.1. Materials

NLLA and NLLAD (purity > 99%) were laboratory preparation by using fatty acid methyl ester [21]. Corn oil was purchased from Harbin Tiantong Agricultural Technology Development Co., Ltd. (China), soybean oil was purchased from China Food Products Marketing Co., Ltd. (China), olive oil was purchased from Shanghai Jiage Food Co., Ltd. (China), and sesame oil was purchased from Kerry Grain and Oil Co., Ltd (China).

2.2. Gelation preparation

The gelator was added to edible oil in a sealed vial, and the mixture was heated (> 80 °C) in an oil bath, until the solid was completely dissolved. Then, the mixture was cooled to room temperature in air, and the vial was inverted to determine whether the solution can still flow down under gravity. The standard for gel formation was the absence of fluid flow in the inverted tube. At the MGC, when the mixture was taken out to the room temperature, it formed a stable gel in 3 min.

The MGC was determined by adding the minimum mass fraction of the gelator. In a given solvent, gelation occurs when the MGC of the gelator was reached [3,11,22]. The T_{gl} was determined by placing the organogel in an inverted screw-capped glass vial with diameter of 10 mm into a thermostated water bath and raising the temperature at a rate of 2 °C min⁻¹. T_{gl} is the temperature at which the gel melts and shows gravitational flow. Each experiment was performed in triplicate.

2.3. FT-IR and UV measurements

To evaluate the driving forces, changes in the amide bonds were studied by FT-IR (Nicolet Avatar 370, Thermo Fisher Scientific, USA) and UV (UV2600, Shimadzu, Japan) spectra. The wave number range of FT-IR was 500–4500 cm⁻¹. The resolution of the instrument was 2 cm⁻¹, and KBr was used as background. The UV scanning wavelength ranges was from 200 to 800 nm. The concentration of gelator was MGC in gel, and was 10 mg/mL in solution.

2.4. X-ray diffraction (XRD)

The XRD was used to obtain information on the crystal structure of gel. Different edible oil gels were melted to solution, and the 2 mL solution were individually transferred carefully on a pre-cleaned sample cell and left to air dry, so it could make a self-supported cast films. In order to clarify the accumulation of gel molecules, the crystal structure of the gel was investigated by the XRD patterns of the organogels were recorded with the X'Pert X-ray diffractometer (Bruke, karlsruhe, Germany) and Cu X-ray source ($\lambda = 1.542 \text{ \AA}$, 40 kV and 10 mA). The 2 θ range of gelations was 5–30°.

2.5. Microscopy

A scanning electron microscope (SEM) (Bruke, Karlsruhe, Germany) was used to obtain information at higher resolution, and the accelerating voltage was 10 kV. The gel was first dispersed on the silicon slice after heating and then cooled to room temperature. The sample was frozen at -80°C and then frozen-dry in the machine to remove the oil. A small amount of gel was placed on a glass slide, covered with a cover glass, and placed under a polarized light microscope (PLM) (Axio Scope A1 pol, ZEISS, Germany). The sample for transmission electron microscopy (TEM) (JEOL, Tokyo, Japan) was prepared by placing a small amount of gel on the carbon coated copper grid (300 mesh), and then the sample was vacuum dried at 50°C, 0.08 MPa for 2 days to evaporate solvent.

2.6. Oil binding capacity

The experiment of the OBC was performed as follows. First, an empty centrifuge tube was weighed, and 5 mL of the edible oil and different mass fractions of the gelator were added. The tube was heated to form a gel and maintained at 5 °C for 24 h. The tube was weighed again and centrifuged at 10 000 rpm for 15 min at 25 °C. After centrifugation, the tube was inverted for 10 min. The liquid oil was discharged and weighed again. The OBC of each edible oil gel was calculated by the following equation. The results were averaged after three measurements [23].

Table 1
Gelation ability of two gelators in four edible oils.

	MGC (%)		T _{gl} (°C)	
	NLLA	NLLAD	NLLA	NLLAD
Olive oil	2.88	2.40	77	85.9
Sesame oil	2.85	1.93	76	79
Corn germ Oil	2.83	1.58	69.3	76.5
Soybean oil	2.61	1.26	66.8	75.5

$$\text{OBC (\%)} = 100 - \text{released Oil (\%)}$$

$$\text{Released Oil (\%)} = [(b - a) - (c - a)] / (b - a) \times 100$$

where a is the weight (g) of the empty centrifuge tube, b is the weight (g) of the oil gel, and c is the weight (g) of the discharged liquid oil.

3. Results and discussion

3.1. MGC and T_{gl}

The results of MGC and T_{gl} are summarized in Table 1. Table 1 showed that the MGCs of olive, sesame, corn, and soybean oils decreased. The fatty acid composition of the vegetable oil was consistent with the content of oleic acid in Table 2.

The phase transition temperatures of the various gels also showed the same trend. Comparison of the MGCs of the two gelators in the different vegetable oils showed that NLLAD had lower MGCs than NLLA because of difference in the amide bonds and hydrophobic alkyl chains of the gelators. The amide bonds of the different molecules can form hydrogen bonds, which are the primary cause for the formation of the 3D network structure [1,12]. The NLLAD molecule has two amide bonds, whereas NLLA only has one. On the other hand, the NLLAD molecules have two hydrophobic alkyl chains, whereas NLLA only has one such chain. The longer the hydrophobic chain, the lower the gelator concentration required for the nonflowing gel [11]. Therefore, NLLAD with a smaller MGC was more likely to form a complex network structure. The gel formed by NLLAD and edible oil had higher T_{gl} than NLLA (Table 1). T_{gl} also reflects the stability of the gels. Thus, the results indicated the better stability of the gels formed by NLLAD and edible oils [25–27]. The gel crystallization by NLLAD and edible oil needed higher temperature to be eliminated completely.

Photos of the gelators and four edible oils before and after gel formation are shown in Fig. 1. Fig. 1 showed that the color of the gel and oil hardly changed and the gel did not flow after the bottle was inverted.

3.2. Driving force for gelation

The intermolecular hydrogen bond is the main driving force to form oil gels. To evaluate the driving forces, changes in the amide bonds were studied by FT-IR and UV spectra.

The FT-IR spectra of the solutions and gels formed by the two gelators and edible oil are summarized in Figs. 2 and 3, respectively. The infrared absorption bands of the amide bond changed in the gels. First,

Table 2
Fatty acid composition of vegetable oils [23,24].

Oil	Saturated fatty acid	Unsaturated fatty acid			Other fatty acids
		Oleic acid	Linoleic acid	Linolenic acid	
Olive oil	10–20.89	75.21–83	5.99–7	0–0.73	0
Sesame oil	15	38	44.75–46	44.75	1
Corn oil	15	27	56	1.95	1
Soybean oil	16	22–25.22	47.15–52	7–7.95	3

in the 3100–3400 cm⁻¹ regions, the gel showed obvious characteristic absorption peaks. For example, the four gels formed by NLLA showed absorption peaks near 3348 cm⁻¹, whereas the gel formed by NLLAD showed absorption peak near 3296 cm⁻¹. Second, in Figs. 2 and 3, the $\nu_{\text{C=O}}$ (amide I) was red-shifted from the solution to the gel, whereas the $\nu_{\text{N-H}}$ (amide II) blue-shifted. As the gel was formed by NLLA and soybean oil, amide I moved from 1654 cm⁻¹ to 1647 cm⁻¹, and amide II moved from 1521 cm⁻¹ to 1527 cm⁻¹. For the solution and gel of NLLAD and soybean oil, amide I moved from 1634 cm⁻¹ to 1629 cm⁻¹, and amide II moved from 1528 cm⁻¹ to 1537 cm⁻¹. Third, the wave numbers of the characteristic absorption peaks of the gel formed by NLLAD were lower than those of the NLLA gel. This change was due to the hydrogen bonds generated between the different molecules by the amide bonds [1,12,28]. This result showed that hydrogen bonds were formed after the gels were formed.

The UV spectrum is another powerful tool for investigating gels, and the results are shown in Fig. 4. The absorbance and the maximum absorption wavelength changed after the gel was formed. For example, when converted from the solution to the gel, the maximum absorption wavelength of NLLA and soybean oil changed from 335 nm to 340 nm, and the maximum absorption wavelength of NLLAD and olive oil moved from 329 nm to 335 nm. Thus, both wavelengths were red-shifted. The maximum absorption wavelength red shifted because of the n- π conjugation of -CO-NHR- in the gelator. In the same vegetable oil gel, NLLA and NLLAD had different response. For example, the difference of maximum absorption wavelength was 6 nm in NLLAD olive oil gel and that was 3 nm in NLLA olive oil gel. The main reason was that there were two amide bonds in NLLAD and only one amide bond in NLLA. The maximum absorption wavelengths of the two gelators in the four edible oils were compared. The absorbances of the oil solution and gel were very different, because the gel was more opaque. Moreover, the maximum absorption wavelength of the two gelators and sesame oil were above 400 nm. The maximum absorption wavelength of NLLA and sesame oil gel was approximately 420 nm. The maximum absorption wavelength of NLLAD and sesame oil was approximately 400 nm, and those of other gels and oil solutions were lower than 400 nm. Hence, no remarkable difference was found.

3.3. Xrd

An X-ray is often used to obtain information on the composition of the material, the structure or morphology of atoms or molecules in the material, and the crystal structure [29–31]. The gelators and gels were analyzed by XRD, and the results are shown in Figs. 5 and 6.

Fig. 5 showed that NLLA and NLLAD showed multilayer ordered stacking mode. NLLA has multiple and small peaks, contrary to the sharp and neat peaks of NLLAD, which were especially noticeable at the d-spacing of 1 nm. The two gelators showed similar peaks around the d-spacing of 0.75, 0.4, and 0.38 nm, which indicated that the two gelators had similar lamellar arrangement, but NLLAD showed better degree of crystallization, which can also be observed in the optical microscope photographs at 500 \times magnification. The crystals of NLLA were short and small, whereas those of NLLAD were long and large.

The XRD results of the gelators showed that the crystallization of NLLAD was better than that of NLLA and had better crystallization in the gel systems with edible oil. As shown in Fig. 6(b), the peak shape of the gels by NLLAD and edible oil were sharper, and the d-spacing value was similar to its corresponding gelator sample. Moreover, a characteristic signal of the hexagonal subcell packing of the hydrocarbon chains in the self-assembled lipids (Bragg's peak at \sim 0.4 nm) was found in both gelators and the gels of NLLA and NLLAD [32]. The D-spacing values of other diffraction peaks in the gel factor changed after the gel formed. For example, the NLLA crystal showed diffraction peaks at 1 nm, 0.75 nm, 0.54 nm, 0.42 nm, 0.38 nm, and 0.36 nm, while the NLLA oil gels showed diffraction peaks at 0.77 nm and 0.42 nm. The NLLAD crystal showed diffraction peaks at 1 nm, 0.75 nm, 0.60 nm,

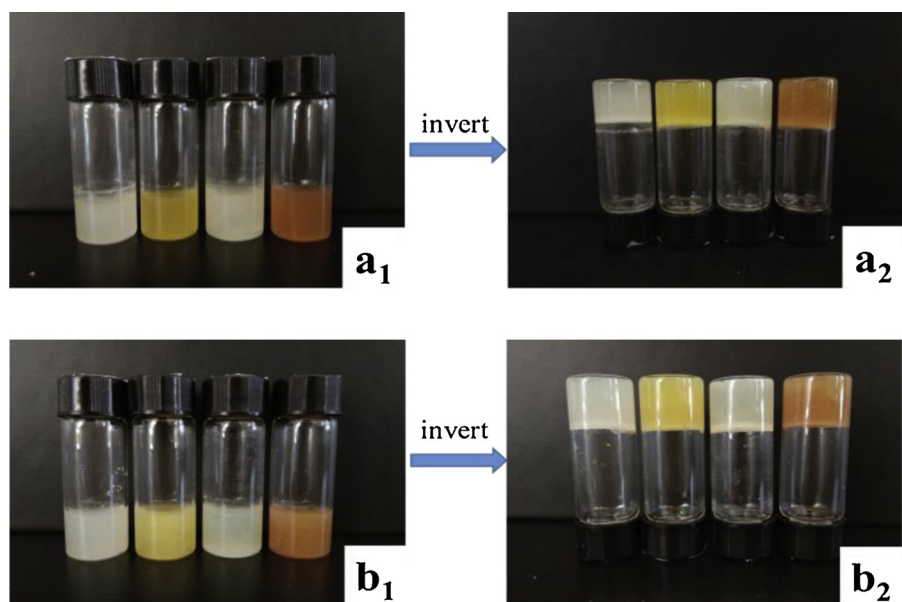


Fig. 1. Four kinds of edible oils gels with two gelators at MGC. a1 and a2 showed the gels of NLLA and the four kinds of edible oils before and after inverted. b1 and b2 showed the gels of NLLAD and the four kinds of edible oils before and after inverted. The edible oils are (from left to right) soybean oil, olive oil, corn oil, and sesame oil.

0.51 nm, 0.4 nm, and 0.38 nm, and the NLLAD oil gels showed diffraction peaks at 1.29 nm, 1.03 nm, 0.84 nm, and 0.4 nm. This indicated that the intermolecular arrangement changed after gel formed. Grease has three crystal forms, namely, α , β' , and β , and the β' -type crystal is characterized by strong diffraction peaks near 0.40 nm [23,33]. A small diffraction peak was found at approximately 0.42 nm in the NLLA gel [Fig. 6(a)] and a strong diffraction peak at approximately 0.4 nm in the NLLAD gel [Fig. 6(b)]. These results indicated that NLLAD gel had stronger crystal structure. Moreover, the gels by edible oil and NLLA had a dispersed bulge at approximately 0.7 nm, which demonstrated a

low degree of crystallization. When 2θ was less than 10° , the d-spacing values of the gels by NLLAD were 1.3, 0.84, and 0.4 nm, and the ratio of d-spacing was 1:1/2:1/3, which was the ratio of the inverse of the integer and manifested the layered structure [34].

In conclusion, the XRD results showed that the degree of crystallinity of the edible oil gels with NLLA were not as good as that of NLLAD edible oil gels. The primary reason was the two hydrogen bonds between the NLLAD molecules, which are responsible for the tighter intermolecular bonds in the gel molecules, whereas the NLLA molecules had only one hydrogen bond. A schematic of the hydrogen bond

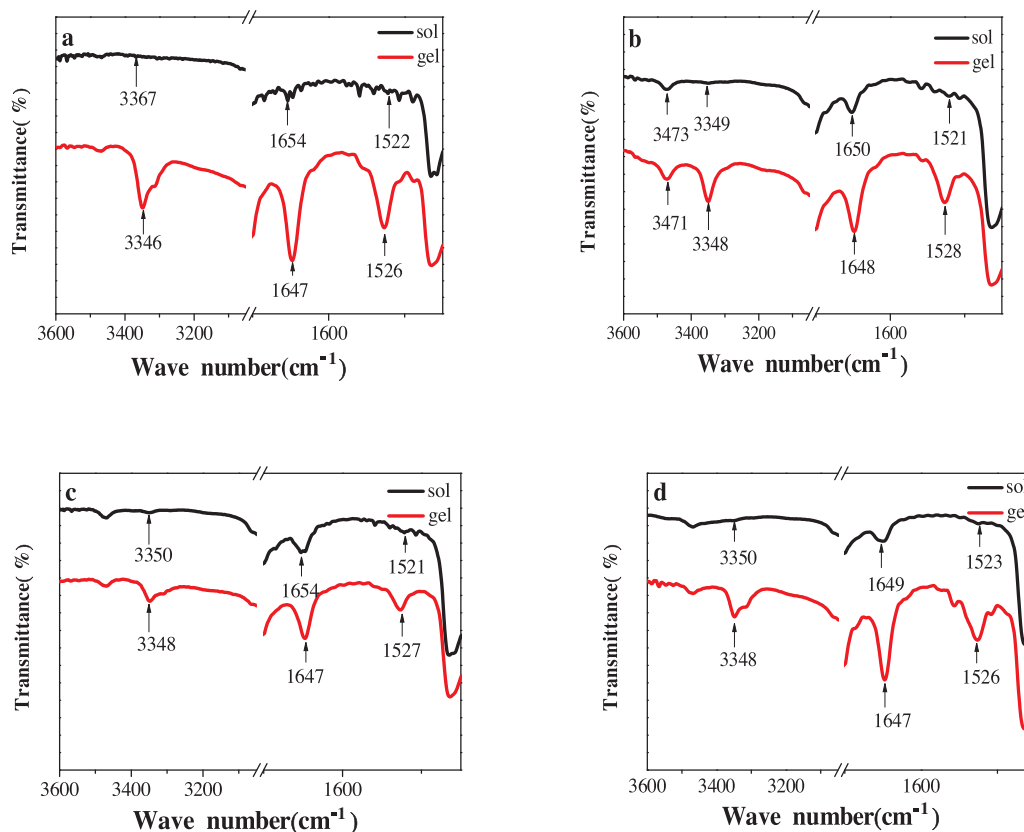


Fig. 2. FT-IR spectra of NLLA and edible oil: (a) sesame oil, (b) olive oil, (c) soybean oil, and (d) corn oil.

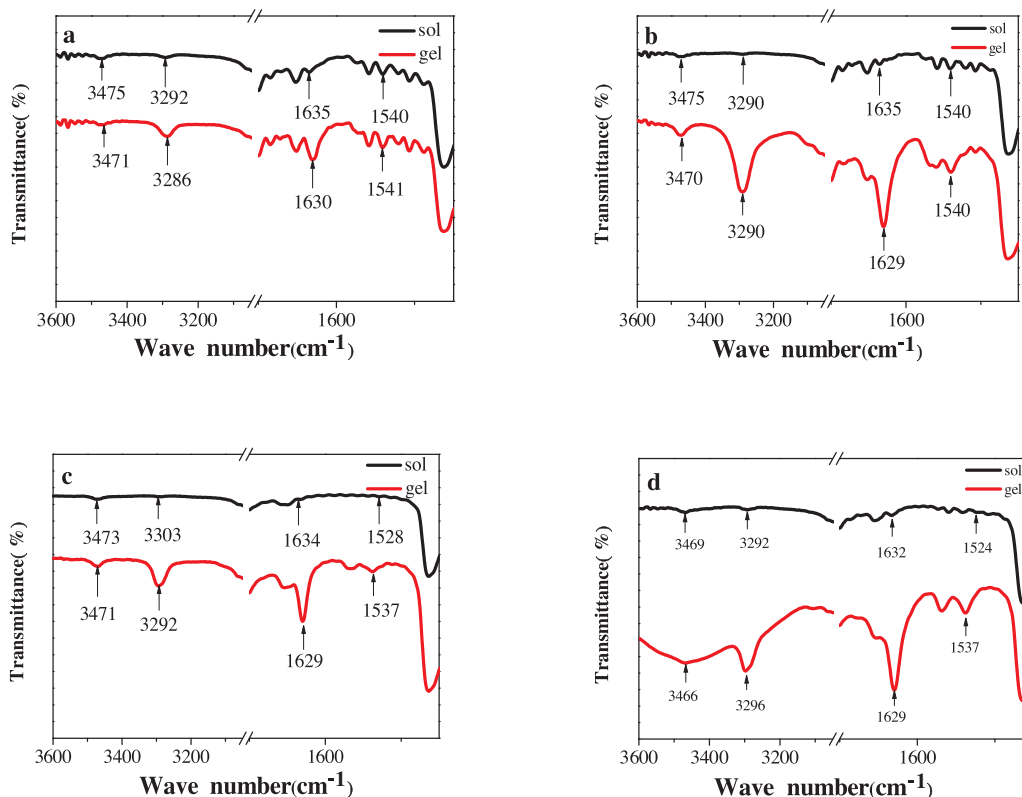


Fig. 3. FT-IR spectra of NLLAD and edible oil: (a) sesame oil, (b) olive oil, (c) soybean oil, and (d) corn oil.

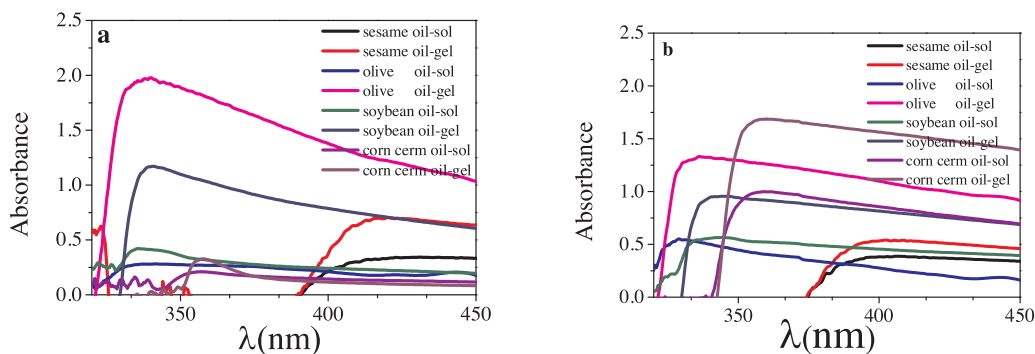


Fig. 4. UV spectra of the solution and gel by two gelators and four edible oils: (a) NLLA and (b) NLLAD.

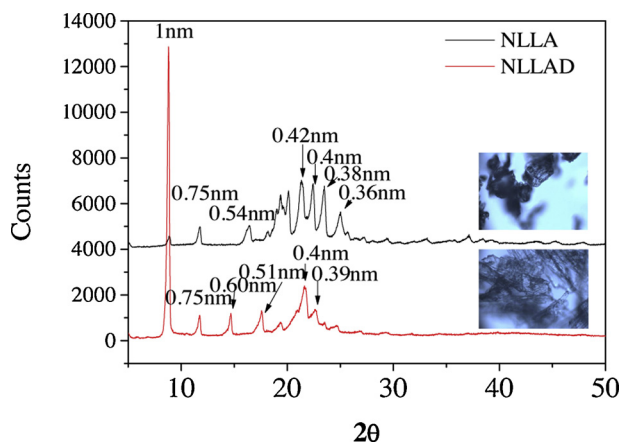


Fig. 5. XRD of NLLA and NLLAD and samples in an optical photo at 500 \times .

structure of the two molecules and the gel formation is shown in Fig. 7. The results in Fig. 6(b) also demonstrated that the peaks of the sesame and olive oil gels formed with NLLAD were more evident than those of the other two oil gels. Hence, the gels of sesame oil and olive oil had better crystallinity than the other two oils.

3.4. Morphologies of gels by edible oil and gelators

PLM, SEM and TEM were used to determine the microstructures of the different gels by edible oils and gelators, and the results are shown in Figs. 8–10. Fig. 8 shows that the sesame oil gel by NLLA had a flower-like structure, but other gels were fine and fibrous. Compared with the gel of NLLA and the edible oil, the gels of NLLAD and the edible oil were finer and had denser fibrous crystals. The SEM (Fig. 9) and TEM (Fig. 10) results were similar to those in Fig. 8. Moreover, the degrees of crystallization of the four edible oils were sequentially reduced, which were consistent with the XRD results.

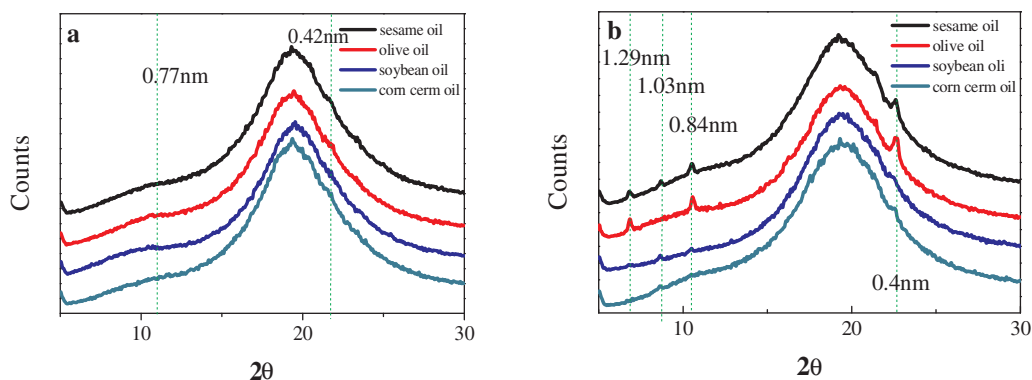


Fig. 6. XRD of gel by four edible oils and two gelators: (a) NLLA and (b) NLLAD.

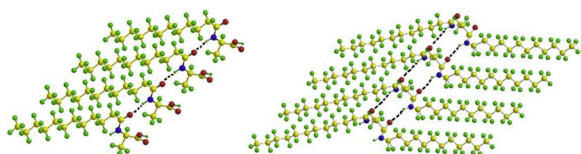


Fig. 7. Schematic of combination of two gelators and gel conformation.

3.5. OBC

The OBC indicates the ability of the gelator to retain oil. The OBC results at different gel concentrations are shown in Fig. 11. Fig. 11(a) shows that the OBC increased with increased NLLA concentration, and the ability to retain the liquid oil was enhanced. At 9% NLLA concentration, the OBC of NLLA for the four edible oils was more than 90%. At NLLA concentration of more than 9%, the OBC hardly changed. At the same NLLA concentration, the rule of the OBC of NLLA for the four edible oils was $OBC_{\text{soybean oil}} > OBC_{\text{corn oil}} > OBC_{\text{olive oil}} > OBC_{\text{sesame oil}}$. Thus, NLLA had the maximum OBC for soybean oil. This result was consistent with the MGC of NLLA in four kinds of edible oils. That is, the lower the MGC was, the stronger the OBC was. The results in Fig. 11(b) showed the same order of OBC in the four oils as those of Fig. 11(a). However, with increased NLLAD concentration, the OBC initially increased first and then decreased. When NLLAD concentration was 8%, the highest OBCs of NLLAD for the four oils were 92.06%, 83.33%, 75.17%, and 73.38%, respectively, and only $OBC_{\text{soybean oil}}$ exceeded 90%. When the NLLAD concentration was 9%, the OBC for the four oils were approximately 20% lower than those of the corresponding NLLA concentration.

This phenomenon was possibly due to the fact that at low NLLAD

concentration, the gel is formed by the intermolecular hydrogen bond and van Edward force interaction [28]. NLLAD is easy to form a dense network structure because of its two long alkyl chains, which is conducive to the interception of edible oil. Therefore, the OBC increased with increased NLLAD concentration. However, with the increase in NLLAD concentration, the gel network is more difficult to form because of the intermolecular hindrance between the two alkyl chains of NLLAD, which is not conducive to the OBC. Therefore, OBC decreased with increased NLLAD concentration. Given that the NLLA molecule has a single long alkyl chain, and the steric hindrance is smaller than that of NLLAD at high concentration, the OBC of NLLA was higher than that of NLLAD at high concentration. However, the OBC reached equilibrium when the NLLA concentration was 9%.

3.6. Application of the gelator in an oil-water mixed system

The two kinds of gelators formed gels in the oil–water mixture, and a picture of the gelation process of NLLAD is shown in Fig. 12. The left, middle, and right pictures were mixtures of oil and water, oil–water mixture with gelator, and gel photos after 20 days, respectively. The gel formed by the gelator and transparent oil became darker and less transparent but retained its good stability after 20 days.

Moreover, we also used the gelator to separate oil and water from kitchen waste, and the result is shown in Fig. 13. Hygrothermal treatment of kitchen waste has been a waste treatment method in the past decade [35]. The solid residue and oil–water mixture are obtained by heating and filtering kitchen waste. Solid residues can be used to prepare fertilizers, and mixed liquids can be used to separate oil and water. The recovered waste oil is used as industrial raw materials. Oil exists mostly in slick oil, dispersed oil, emulsified oil, and dissolved oil

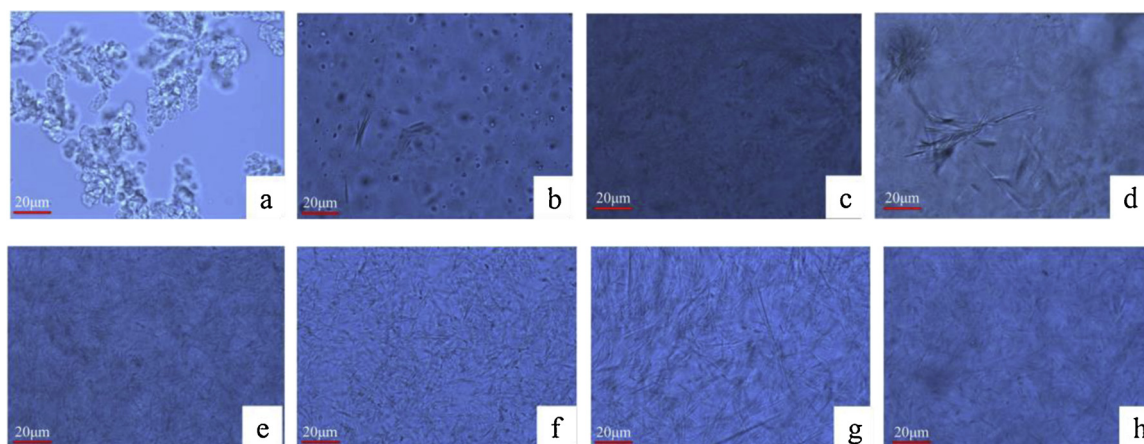


Fig. 8. PLM images of gels (a–d) gels of sesame oil, olive oil, soybean oil, and corn oil and NLLA, respectively; (e–h) gels of sesame oil, olive oil, soybean oil, corn oil, and NLLAD, respectively.

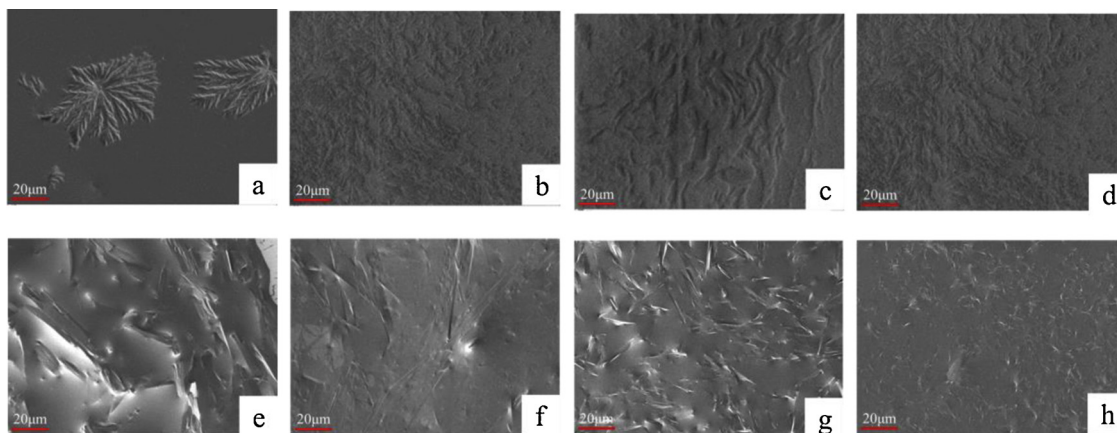


Fig. 9. SEM of gels. (a–d) gels of sesame oil, olive oil, soybean oil, and corn oil and NLLA, respectively; (e–h) gels of sesame oil, olive oil, soybean oil, and corn oil and NLLAD, respectively.

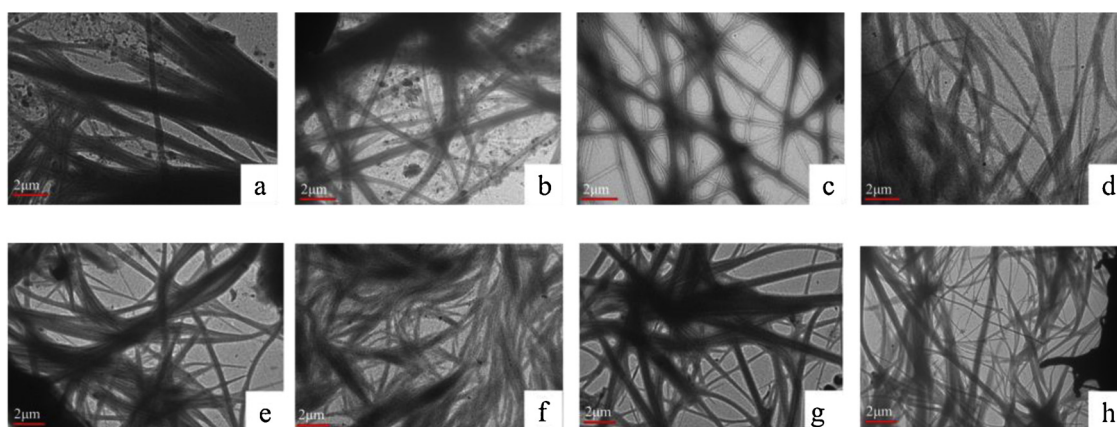


Fig. 10. Transmission electron micrographs of gels: (a–d) gels of sesame oil, olive oil, soybean oil, and corn oil and NLLA, respectively; (e–h) gels of sesame oil, olive oil, soybean oil, and corn oil and NLLAD, respectively.

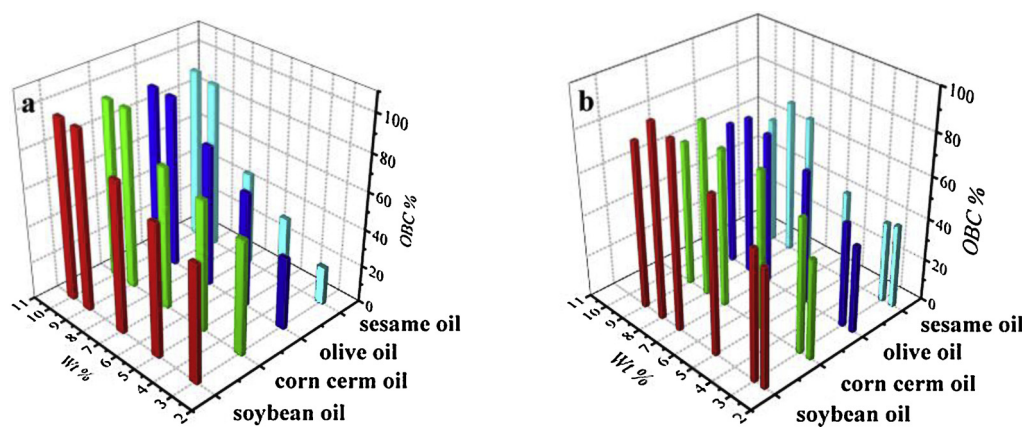


Fig. 11. OBC at different concentrations of gelators: (a) NLLA and (b) NLLAD.

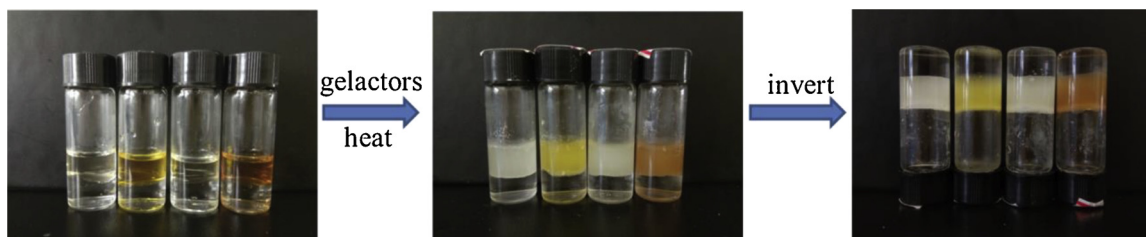


Fig. 12. Gelations of NLLAD were in edible oil and water mixture. The four edible oils were soybean oil, olive oil, corn oil, and sesame oil.

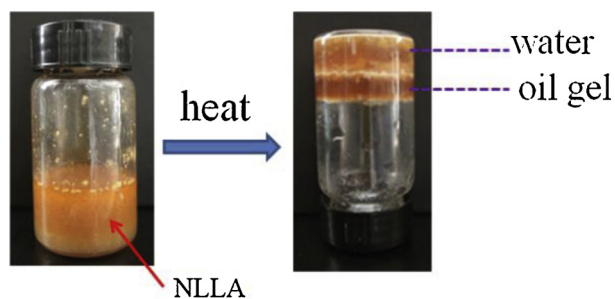


Fig. 13. Separated oil and water from kitchen waste using NLLA.

[36]. The floating oil droplets can float quickly after standing because of its larger diameter and can float on the water surface as a continuous oil film. Oil is dispersed in water as droplets with diameter larger than 1 μm , and oil with particle size of 0.5–15 μm is emulsified in water. At present, centrifugation and gravity sedimentation are used to separate oil and water. However, the density of emulsified oil is similar to that of water to form a homogeneous system. Thus, oil and water are difficult to separate using these two methods. Fig. 13 shows that when NLLA was added to the mixture, the oil formed the gel and separated oil from water. Thus, the oil phase can be used after the complete extraction.

4. Conclusion

Two amino acid gelators, namely, NLLA and NLLAD and their gel properties were compared. The FT-IR and UV indicated that the hydrogen bond between the amide bonds in the molecule was the intermolecular driving force of the gel. The two gelators formed good gels with four edible oils. NLLAD had stronger gel ability because of its two amide bonds. NLLAD showed smaller MGC, higher Tgl, and better crystal structure in the four edible oils. The variations in the OBCs of NLLA and NLLAD in the four edible oils were the same as that of the MGC, i.e., a lower MGC meant a stronger OBC. The two gelators also showed different OBCs with the four edible oils. The OBC of NLLA reached 96%, whereas the maximum OBC of NLLAD was only 92%. At NLLA concentration greater than 9%, the OBC hardly changed. However, when the NLLAD concentration exceeded 8%, the OBC of NLLAD with the four edible oils decreased. Moreover, the two gelators also showed good extraction of waste oil from kitchen waste. This study proved that NLLA and NLLAD can be used for the gelation of edible oils.

Declaration of competing interest

The authors declare no competing financial interest.

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References

- P. Duan, M. Liu, Design and self-assembly of l-glutamate-based aromatic dendrons as ambidextrous gelators of Water and organic solvents, *Langmuir*. 25 (2009) 8706–8713, <https://doi.org/10.1021/la8043335>.
- S. Bhattacharya, S.N.G. Acharya, Impressive gelation in organic solvents by synthetic, Low molecular mass, self-organizing urethane amides of l-phenylalanine, *Chem. Mater.* 11 (1999) 3121–3132, <https://doi.org/10.1021/cm990207v>.
- G. Feng, H. Chen, J. Cai, J. Wen, X. Liu, L-phenylalanine based Low-molecular-weight efficient organogelators and their selective gelation of oil from oil/Water mixtures, *Soft Mater.* 12 (2014) 403–410, <https://doi.org/10.1080/1539445X.2014.945042>.
- H. Guo, T. Jiao, X. Shen, Q. Zhang, A. Li, J. Zhou, F. Gao, Binary organogels based on glutamic acid derivatives and different acids: solvent effect and molecular skeletons on self-assembly and nanostructures, *Colloids Surf. A*. 447 (2014) 88–96, <https://doi.org/10.1016/j.colsurfa.2014.01.059>.
- X. Du, J. Zhou, J. Shi, B. Xu, Supramolecular hydrogelators and hydrogels: from soft matter to molecular biomaterials, *Chem. Rev* 115 (2015) 13165–13307, <https://doi.org/10.1021/acs.chemrev.5b00299>.
- S. Bhattacharya, Y. Krishnan-Ghos, First report of phase selective gelation of oil from oil/water mixtures. Possible implications toward containing oil spills, *Chem. Commun.* (2001) 185–186, <https://doi.org/10.1039/b007848o>.
- H. Toshihiko, K. Tabohashi, Production method of N-acyl amino acid amide China Patent CN 00131480.7 (2000).
- Z.Y. Li, Synthesis of gelling agent (G-1) for oils, *J. Dalian. Univ. Techno* 1 (1996) 120–122.
- T. Ichikawa, S. Fukami, T. Kobayashi, Oil-soluble n-long chained acyl acidic amino acid ester, mixture thereof and perfuming cosmetics containing the same. U.S. Patent 5153340 (1992).
- P.D. Sun, L.W. Zhu, Study on gelation properties of N-L-auroyl-L-glutamic acid and derivatives, *Chem Res Appl.* 21 (2009) 1140–1144.
- G. Bastiat, J. Leroux, Pharmaceutical organogels prepared from aromatic amino acid derivatives, *J. Mater. Chem* 19 (2009) 3867–3877, <https://doi.org/10.1039/b822657a>.
- M. Suzuki, M. Yumoto, H. Shirai, K. Hanabusa, A family of low-molecular-weight organogelators based on α,ω -diacyl-L-lysine: effect of alkyl chains on their organogelation behavior, *Tetrahedron*. 64 (2008) 10395–10400, <https://doi.org/10.1016/j.tet.2008.08.061>.
- A.R. Patel, P.S. Rajarethinem, A. Gredowska, O. Turhan, A. Lesaffer, W.H. De Vos, D. Van de Walle, K. Dewettinck, Edible applications of shellac oleogels: spreads, chocolate paste and cakes, *Food. Func.* 5 (2014) 645–652, <https://doi.org/10.1039/c4fo00034j>.
- M. Ögütçü, E. Yılmaz, Characterization of hazelnut oil oleogels prepared with sunflower and carnauba waxes, *Int. J. Food. Prop.* 8 (2015) 1741–1755, <https://doi.org/10.1080/10942912.2014.933352>.
- L.S.K. Dassanayake, D.R. Kodali, S. Ueno, Formation of oleogels based on edible lipid materials, *Curr. Opin. Colloid Interface Sci.* 16 (2011) 432–439, <https://doi.org/10.1016/j.cocis.2011.05.005>.
- D.C. Zulim Botega, A.G. Marangoni, A.K. Smith, H.D. Goff, The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream, *J. Food. Sci.* 78 (2013) 1334–1339, <https://doi.org/10.1111/1750-3841.12175>.
- A.J. Wright, A.G. Marangoni, Formation, structure, and rheological properties of ricinoleic acid-vegetable oil organogels, *J. Am. Oil. Chem. Soc.* 83 (2006) 497–503, <https://doi.org/10.1007/s11746-006-1232-9>.
- G.L. Feng, H.H. Chen, J.H. Cai, J.W. Wen, X.B. Liu, L-phenylalanine based Low-molecular-weight efficient organogelators and their selective gelation of oil from oil/Water mixtures, *Soft Mater.* 4 (2014) 403–410, <https://doi.org/10.1080/1539445X.2014.945042>.
- S. Basak, J. Nanda, A. Banerjee, A new aromatic amino acid based organogel for oil spill recovery, *J. Mater. Chem* 22 (2012) 11658–11664, <https://doi.org/10.1021/cm300739y>.
- A. Vintiloiu, M. Lafleur, G. Bastiat, J. Leroux, In situ-forming oleogel implant for rivastigmine delivery, *Pharm. Res.* 25 (2008) 845–852, <https://doi.org/10.1007/s11095-007-9384-3>.
- B.C. Xu, Y.W. Zhou, S.Z. Zhang, F. Han, G.J. Zhang, Method for Preparing N-Fatty Acyl Amino Acid Sodium Salt Surfactant with Fatty Acid Methyl Ester. China Patent CN 102,311,359 (2012).
- Y. Wang, Y. Wang, X. Yan, S. Wu, L. Shao, Y. Liu, Z. Guo, Toluene diisocyanate based phase-selective supramolecular oil gelator for effective removal of oil spills from polluted water, *Chemosphere* 153 (2016) 485–493, <https://doi.org/10.1016/j.chemosphere.2016.03.036>.
- G. Fayaz, S.A.H. Goli, M. Kadivar, A novel propolis wax-based organogel: effect of oil type on its formation, crystal structure and thermal properties, *J. Am. Oil. Chem. Soc.* 94 (2017) 47–55, <https://doi.org/10.1007/s11746-016-2915-5>.
- D. Li, Y. Zhao, T.T. Li, C. Liu, W. Wang, D.Y. Yu, L.Q. Wang, J. Wang, Effect of oil type on the formation and properties of cinnamic acid-based oleogels, *Food. Sci.* 39 (2018) 9–14, <https://doi.org/10.7506/spkx1002-6630-201812002>.
- A. Pal, J. Dey, L-cysteine-derived ambidextrous gelators of aromatic solvents and Ethanol/Water mixtures, *Langmuir*. 29 (2013) 2120–2127, <https://doi.org/10.1021/la3042764>.
- C. Wang, Z. Li, X. Wang, W. Wei, S. Chen, Z. Sui, Gelation mechanism and micro-structure of organogels formed with l-valine dihydrazide derivatives, *Colloids Surf. A*. 384 (2011) 490–495, <https://doi.org/10.1016/j.colsurfa.2011.05.027>.
- S. Samai, J. Dey, K. Biradha, Amino acid based low-molecular-weight tris(bis-amido) organogelators, *Soft Matter*. 7 (2011) 2121–2126, <https://doi.org/10.1039/c0sm01293a>.
- M. Suzuki, Y. Nakajima, M. Yumoto, M. Kimura, H. Shirai, K. Hanabusa, Effects of hydrogen bonding and van der Waals interactions on organogelation using designed Low-molecular-weight gelators and gel formation at room temperature, *Langmuir*. 19 (2003) 8622–8624, <https://doi.org/10.1021/la034772v>.
- L.M. Moreau, D. Ha, H. Zhang, R. Hovden, D.A. Muller, R.D. Robinson, Defining Crystalline/Amorphous phases of nanoparticles through X-ray absorption spectroscopy and X-ray diffraction: the case of nickel phosphide, *Chem. Mater.* 25 (2013) 2394–2403, <https://doi.org/10.1021/cm303490y>.
- M.A. Peck, M.A. Langell, Comparison of nanoscaled and bulk NiO structural and environmental characteristics by XRD, XAFS, and XPS, *Chem. Mater.* 24 (2012) 4483–4490, <https://doi.org/10.1021/cm300739y>.
- A. Tanaka, H. Kamikubo, Y. Doi, Y. Hinatsu, M. Kataoka, T. Kawai, Y. Hasegawa,

- Self-assembly and enhanced magnetic properties of Three-dimensional superlattice structures composed of cube-shaped EuS nanocrystals, *Chem. Mater.* 22 (2010) 1776–1781, <https://doi.org/10.1021/cm9032513>.
- [32] S.R. Jadhav, H. Hwang, Q. Huang, G. John, J. Agric, medium-Chain sugar amphiphiles: a New family of healthy vegetable oil structuring agents, *J. Agric. Food Chem.* 61 (2013) 12005–12011, <https://doi.org/10.1021/jf401987a>.
- [33] H.Y. Song, X.M. Xu, Effect of different propylene glycol esters on fat physical properties, *Science and Technology Food Industry* 33 (2012) 137-141 + 145.
- [34] F. Delbecq, K. Tsujimoto, Y. Ogue, H. Endo, T. Kawai, N-stearoyl amino acid derivatives: potent biomimetic hydro/organogelators as templates for preparation of gold nanoparticles, *J. Colloid Inter. Sci.* 390 (2013) 17–24, <https://doi.org/10.1016/j.jcis.2012.09.029>.
- [35] P. Wang, L.H. Ren, Y.Q. Qiu, X. Zhang, B.X. Li, Production of liquid bacterial manure with effluent of hydrothermal treated restaurant garbage, *Environ. Eng.* 35 (2017) 88–92, <https://doi.org/10.13205/j.hjgc.201706019>.
- [36] Z.X. Han, T.M. Hou, Technologies for determination of physicochemical properties and content of oil in wastewater, *Environmental Protection of Chemical Industry* 20 (2000) 38–43.