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Transformation of Soybean Oil to Various Self-Assembled Supramolecular Structures

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1. Introduction

Today's research worlds try to bring everything in nanosize and the tremendous development on nanosize and technology introduced numbers of molecules with immense applications. Though nanostructures from numbers of metals and materials are being synthesized, supramolecular structures attracts the research group at increasing level, because of the interest and urge to know the origin of life. Hence, research groups at global level are making attempts on how the self-assembly and the supramolecular structures have been formed from the single and /or from the combination molecules.

Thus the design and the construction of supramolecular assembly/structures are quite interesting and various hypothetical theories have been developed to substantiate the origin of life. Supramolecular structures are large molecules fashioned by binding of smaller molecules mutually and it often to develop molecules of preferred form including 2D triangles, squares, pentagons, hexagons and 3D octahedrons, cubes and some irregular shapes. Self-assembly is the most prevailing methodology in the design of large, distinct, ordered structures.

The objects of supramolecular chemistry are defined on one hand by the nature of the molecular components and on the other by the type of interactions that hold them together. Three major steps are involved in supramolecular systems; (i) selective binding, (ii) growth of the components in the correct relative orientation and (iii) termination requiring a built in feature which signifies the end process. The chemistry of supramolecular structure is a constitutional dynamic chemistry due to the reversibility of the connecting events. The kinetic liability confers the self-assembling systems to undergo annealing and self-healing of defects and to manifest tunable degree of polymerization and cohesive properties. In contrast, covalent linked, nonlabile type cannot heal spontaneously and the defects are permanent (Lehn, 2005).

According to Murakami, synthesis of supramolecular structure is based on the principle of molecular recognition and molecular self-assembly realized due to the formation of noncovalent interaction towards the cooperation of many weak bonds including electrostatic interaction, Van der Waals forces, dipole interaction, hydrogen bonding, hydrophobic interaction, and π–π interaction. Recently the interest was drawn to a new topological form of supramolecular structures by self-assembly and also by weak interactions.

Generally, supramolecular solid structures are commonly prepared by different templates; polymers, polystyrene, silica and some other metal nanoparticles. Vesicles and microemulsions are used as template to develop on an attractive and stable supramolecular structure. However, in the soft template approach, the control on the size and mechanical stability of the supramolecular structures could become a problem. Further, as pointed out by Shelnutt and his co-workers, it is not easy to prepare stable or large sized (e.g., > 100 nm in diameter) and thickly walled supramolecular spheres based on the soft template approach. Therefore, a new protocol using biological materials through which the rigid structure with controllable size and thickness can be made easily is of great interesting.

Amphiphilic and/or non-polar components further increase the structural diversity to include sponge and microemulsion phases, and even stable multiphase colloidal dispersions of one complex fluid in another – cubosomes and hexosomes. Many aspects of these nanostructures remain under exploited because self-assembled structures exist in dynamic equilibrium, and hence respond to changes in solution conditions. A great deal could potentially be achieved if amphiphilic self-assemblies could be rendered more robust *in situ*. One method for achieving this is to "lock-in" the self-assembled structure using polymerizable surfactants.

Simple, single-chain fatty acids have long been known to self-assemble into supramolecular structures such as micelles and vesicles (Gebicki & Hicks, 1973; Gebicki & Hicks, 1976). Fatty acids in a bilayer membrane are in rapid exchange with the aqueous environment (Walde et al., 1994). Such amphiphiles can also interact with solid surfaces. The interaction of amphiphiles with solid surfaces often involves adsorption due to chemical or physico-chemical forces through covalent bonds, hydrogen bonds, ion exchange, Van der Waals forces, and hydrophobic effects (Giles, 1982; Evans, 1986).

The interactions of simple, single-chain amphiphiles with many different surfaces results in the organization of membranes and the formation of vesicles. This effect could have played a key role in the organization and formation of the first cell-like structures on the early earth. Since mineral particles have been implicated in very early chemistries and polymerization reactions (Bernal, 1951; Wachtershauser, 1988; Ferris and Hill et al., 1996; Sowerby et al., 2001; Sowerby et al., 2002; Monnard, 2005), it is intriguing that minerals might have also been involved in the formation of yet another essential component of life-the cellular membrane. Mineral-mediated vesicle formation occurs with many disparate types of minerals and is therefore a more general property than clay-catalyzed RNA polymerization.

1.1 Current scenario

In general, as described, formation of supramolecular structures are mediated through individually or in combination of heating, cooling, hydration, solvent addition, refluxing, agitation, stirring, shaking and/or hydrothermal reaction. Further, the size, structure and reproducibility of supramolecular structures depend on the methods followed and the substrates employed in the study.

With regard to substrates, most of the researchers synthesized supramolecular structures using the following synthetic molecules; viz., Poly ethylene amine, 2,4,diaminopyrimidine-nitrobenzoate (Stanley et al., 2005), pyrrole-2-carboxylate dimer (Yin et al., 2006), Trichloromethane (Durov et al., 2006), polyoxovanadate (Duan et al., 2006), Cyclodextrin (zeng-guo & Sanping, 2003), Nitrobenzoic acid with ethylenediamine (Srinivasan & Rane, 2009), p-tert-butylcalix[6]arene, ammonium cations, 1-alkynlyl(phenyl) tetrafluroborate-

iodanes, 18 crown-6 (Ochiai et al., 2003) and etc. Similarly, semisynthetic or the combinational substrates such as galactocerebroside containing long chain unsaturated fatty acids, tris(hydroxylmethyl)- aminomethane based biosurfactant, hyperbranched polyethelenimine and fatty acids, glycolipid derivative with hydrogenated fluorinated mixed lipid tail, synthetic spingolipids, block copolymers and etc., are also in use.
In addition, a complete bio-based supramolecular structures from milk fat protein, lipids, DNA, RNA complex, nucleotides, aminoacids or doublechain aminoacids, phospholipids, glycolipids, peptides, gluconamides, bolamphiphilies, lipopeptide and biological amphiphilies compounds are also introduced by various researchers.

1.2 Vegetable oil / fatty acid based supramolecular structures

Even though supramolecular assemblies from above said molecules are in reports with varied hypothetical explanation, however, still the story behind the assembly of biological molecule is unclear. To understand the theory of self-assembly and supramolecular formation, researchers initiated the self-assembly studies using fatty acids and its derivatives. Montarnal et al., (2008) reported self-healing supramolecular rubber like material using vegetable oil, unsaturated fatty acid derivatives, combined with diethylene triamine and urea. Vegetable oil based supramolecular organogel is synthesized by Rogers et al., (2007). Chen et al., (2005) prepared supramolecular nanocapsules by electrostatic interaction between fatty acids palmitic acid and polyethylenimine. A mixture of fatty diacid and triacid is condensed first with diethylene triamine and then reacted with urea giving an oligomeric supramolecular self-assembled thermoreversible rubber having self-healing property (Cordier et al. 2008). Novales et al., (2008) reported self-assembly of fatty acids and hydroxyl derivative salts to form supramolecular assembly.
Maximum reported supramolecular assemblies involve complete synthetic or hybrid systems and or semi biological system. Complete biological means of supramolecular assemblies demand more time and the process of synthesize is a challenging task.

2. Transformation of soybean oil to supramolecular structures- a biomediated process

The present chapter covers the formation of various supramolecular structures from vegetable oils by microbial product mediated process. The experiments conducted in our laboratory revealed *in situ* transformation of vegetable oils to self-assembled different supramolecular structures viz., vesicle, stable vesicle, supramolecular capsules, colloidosomes, self-healing material, supramolecular rubber like material, organogels, sheet/ flims, bioadhesives, etc., mediated through microbial products. Three different experimental setups were run. In the first set of experiments, microbes were directly used for the transformation of vegetable oil to supramolecular structures. For the second set up, instead of microbes, microbial products were used. The third sets of experiments were executed without any microbes and microbial products but prior to exposure to the medium, the oil was heated at 100 °C.
Soybean and sunflower oil are directly procured from the manufacturers and used as a source for triglycerides. Microbes used in the present study are from the varied sources; marine and clinical origin. Microbial products are also from media suppliers; HiMedia Laboratories Pvt. Ltd and MERCK Ltd. The media used for present study are (i) mineral medium comprises of 1 g NH_4NO_3; 2.55 g NaH_2PO_4; 0.5 g $MgSO_4 \cdot 7H_2O$; 0.1 g $CaCl_2 \cdot H_2O$; 0.02 g $MnSO_4 \cdot H_2O$; 1 g Peptone; 0.5 g Glucose; Zobell marine broth containing 5g Peptic

digest of animal tissues; 1g yeast extract; 0.1g ferric citrate; 19.45g sodium chloride; 8.8g magnesium chloride; 3.24g sodium sulphate; 1.80g calcium chloride; 0.55g potassium chloride; 0.16g sodium bicarbonate; 0.08g potassium bromide; 0.034g; strontium chloride; 0.022 boric acid; 0.004 sodium silicate; 0.0024g sodium fluorate; 0.0016g ammonium nitrate; 0.008g disodium phosphate.

The selective microorganisms; marine *Bacillus* sps and clinical strain *Candida albicans* are cultured in the selective medium with triglycerides at different volumes (0.5, 1.0, 1.5, 2.0, 2.5, 4, 6, 8 and 10% w/v) and at cell concentration of 1X 10^5 cells per ml and incubated for the period of 5-10 days under shaking/ agitation at 180-200 rpm. Followed by inoculation, observations on cell growth, pH profile, hydrolytic enzyme production, fatty acids and glycerol release, surface-active agent production, transformation of oil, micelle formation, nano vesicle to macrosize supramolecular structures were made. The descriptions on various supramolecular structures are briefly explained below:

2.1 Transformation of soybean oil to fatty acid vesicles

In our study, the selected microbes, here in, *Candida* sp. grown in the medium containing carbohydrates, peptone, mineral salts and soybean oil at different percentages (w/v) for the period of more than 5-9 days at 37°C under agitation at 180-200rpm, we observed the slow transformation of these oils to micelle and then to vesicles. Though different concentrations of oils were attempted, only at higher concentrations (>5%) we observed the final transformed product as fatty acid vesicles. In addition to these observations, the physico-chemical analysis of the medium on different days clearly illustrates the steps involved in the process of transformations. We found, the microbes, in order to utilize the substrates released the enzymes and surface-active agents externally. Analysis of enzyme release suggests, lipase was released from 12 hours onwards at the rate of 3.5 U/ml. The produced lipase interacted with the oil present in the external aqueous medium and hydrolyzes it into fatty acids with in 48 hours. In the meantime, the organism produces surface-active agents (33 ±2 mN/m), which further starts interacting with the hydrolyzed fatty acids. Thus, a simultaneous reaction takes place between the fatty acids released upon enzymatic hydrolysis and the surface-active agents produced. Figure 1 illustrates the vesicle formed in the growth medium.

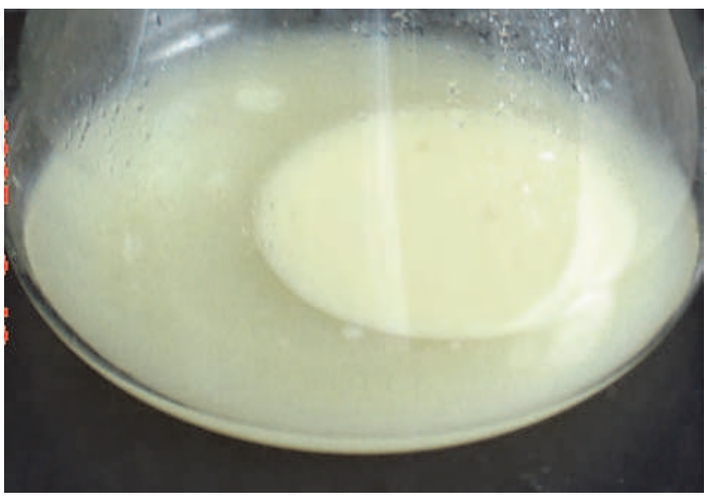


Fig. 1. Fatty acid vesicle from soybean oil.

Though, we couldn't observe the complete hydrolysis of oil with that of the lipase produced, however, the unhydrolyzed oil further solubilized by the released surface-active agents and interact with the already formed vesicles and helps in the assembly of vesicles. In addition, in the case of the chosen oils, the presence of lecithin increases the supramolecular self-assembly results with the increased gellation with multilamellar vesicles. The release of amino acids during the growth of the microorganism may also involved in the transformation of vegetable oil to vesicles.

2.2 Transformation of soybean oil to multilamellar stable vesicles (MLSV)

Multilamellar stable vesicles with different shapes and size formation starts with the micelle formation in the zobell marine broth during the growth of marine *Bacillus* sp. Though internal component facilitates the bilayer formation it has been followed by transformation to multilayer and then thickening of oil. In the present study, the external physical agitation (200 rpm), accelerates the transformation of multilayer vesicles (microscopic) to stable macroscopic structures. The varied macroscopic morphological patterns and the stability observed (spherical to cylindrical shapes) might be due to the available interactions between the components of the medium. The cylindrical morphology observed in the present study may be due to the aggregation of micelles followed by transformation to multilamellar vesicles or the bilayer formation followed by aggregates rolled and transformed to rod like giant vesicle with concentric rings.

According to Yan et al., (2009), bipolar nature of amphiphilic is mostly responsible for multilamellar vesicles. The hydrophobicity of released fatty acids mediates the close arrangement with biosurfactants molecule or it may be due to the non-ionic nature of biosurfactants leads to the layer-by-layer formation resulting with multilayer structures. Further, difference in the ratio of number of molecules in the monolayer or bilayers also decides the shape of the vesicles. The reasons for the different macroscopic structures generated could also be explained by (i) decrease in electrostatic interaction and other forces at the bifurcation time; (ii) presence of sensitive reaction diffusion system and (iii) presence of gravity or electric or magnetic fields; (iv) other factors responsible for the weak orientation and finally (v) mismatching of hydrophilic heads of biosurfactants. In addition, self-assembly formed in the experiments is neither uni-directional nor multi-directional, due to the continuous generation of biosurfactants, fatty acids, protein and carbohydrates resulting with assumed morphological features in the solutes. Jiang et al., (2006) reported macroscopic self-assembly of hyper-branched polyester by simple solvent volatilizing route and obtained multi-walled strucutres with millimeter in diameter and centimeters in length. They also found nature of the solvent ratio of the solution, temperature, and molecular concentrations are the parameters deciding the self-assembly of macroscopic structures. Nevertheless, the surface of the self-assembly obtained in the present study is uniform, nonsticky and flexible, emphasizes, formation of MLV initiated with the formation of uni-layer by the components as explained above followed by multilayer formation by action of external agents like agitation and finally transformed to stable macroscopic structures. The less bound water (<3%) in the individual macro-structures may be due to the dehydration of head groups, results with the decrease in effective area per molecule at interface (Singh et al., 2009). Further, we observed, salts present in the medium, also responsible for the stability of macroscopic structures.

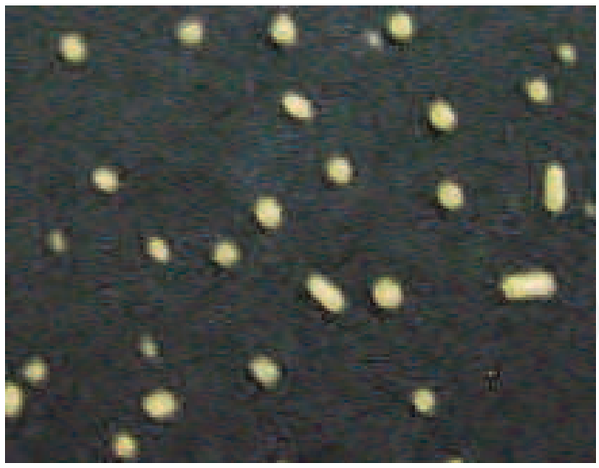


Fig. 2. Multilamellar stable vesicles (MLSV) from soybean oil.

Further, most of the reports suggests only alkaline pH mediates the self-assembly processes (Wang et al., 2004). However, in the experiments concerned, we observed stable vesicle formation at acidic pH (>4.0). The formation of fused structures may also due to the counter ions exist in the growth media. According to Lei & MacDonald (2003), because of the counter ions, there is compression in the bilayer. More the compression more the packing, which reduces the entering of outer molecules to the inner core of the vesicle, increases the diameter of the vesicle to the maximum size and the additional bilayer will leads to fusion of vesicles. Though Singh et al. (2009) reported, presence of cationic surfactant increases the packing of lamellar structures, in our study the produced biosurfactants is a non-ionic and the complete packing of lamellar structure may be due to the accumulation effect. The molecular network formation between fatty acids and biosurfactants provides high thermal stability to the macroscopic structures observed.

2.3 Transformation of sunflower oil to supramolecular capsules

Similar to the multilamellar stable vesicle, transformation of vegetable oil to supramolecular capsules is observed in the microbial mediated process of transformation. The selected microbe marine *Bacillus* sps., when grown in mineral medium with sunflower oil at 5% (v/v) at 37°C under 180-200 rpm agitation. As summarized above, hydrolysis of oil takes place at initial stage by enzymes released during the growth of the organism. The release of fatty acids and the unspent peptides mediates the self-assembly process results with the transparent capsule like structures and opaque structures of different shapes after 5 days and the percentage of transparency decreases and at final stage, more than 90% of capsules are opaque. Though two different shapes were observed during the experimental period, the one with spherical shape initially in the form of transparent spheres and upon increasing the incubation period it becomes opaque. The following figure demonstrates the transparent and opaque supramolecular structures of sunflower oil. The reason for the transparent and the opaque self-assembly structures may be due to the orientation of amphiphilic molecules assembly processes and the lecithin present at appreciable level. Furthermore, the dynamic molecular recognition, the reorientation and the packing parameters might have played the role in the formation of capsule like supramolecular assemblies.

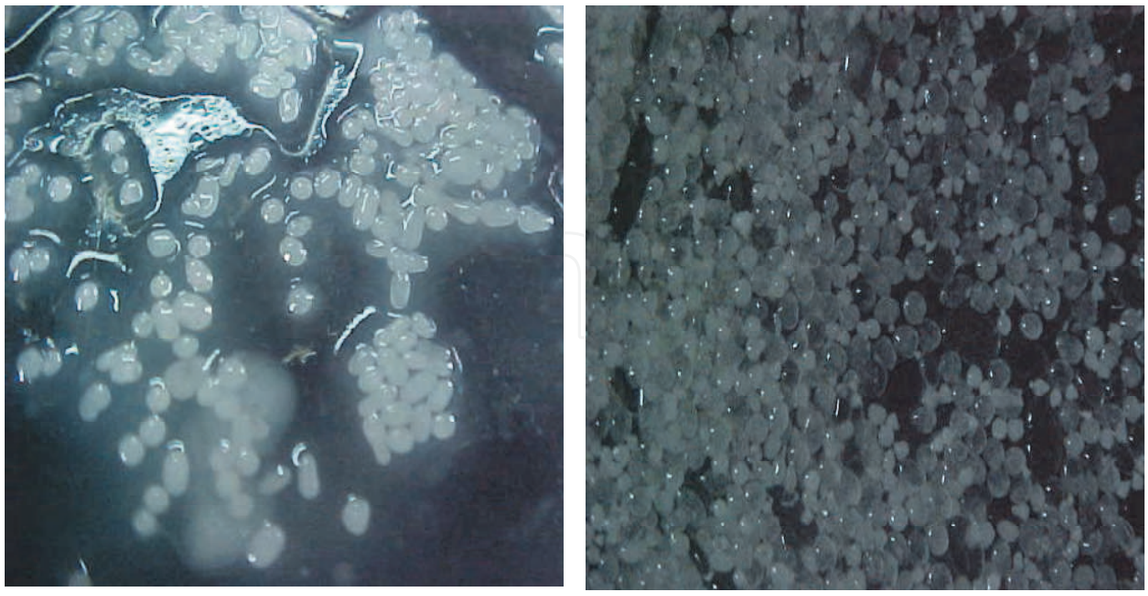


Fig. 3. Supramolecular capsules from sunflower oil.

2.4 Transformation of soybean and sunflower oil to colloidosomes

Colloidal particles are elementary to nature and technology. Self-assembly of colloids at liquid - liquid interface is well documented. Recently, there has been mounting concern in using this self-assembly system to form efficient superstructures, such as emulsions, microcapsules, particles and colloidal crystals. One of the most significant applications of this method is to formulate microcapsules known as colloidosomes, whose shells are composed of coagulated or fused colloid particles.

Based on this method, noval colloidosomes with coagulated or colloidal particles were produced in the presence of oil in water emulsion. Mineral medium with sunflower oil in the presence of marine *Bacillus* sp. and its hydrolytic enzyme and biosurfactants transform the oil into emulsion. Presence of Janus particle (amphiphilic compound nothing but the biosurfactant) stabilizes the emulsion and transform into stable colloidosomes. The presence of the particles at the water/oil interface minimizes the surface energy and therefore stabilizes the emulsion. The wettability and mobility of the particles will determine the stability of the emulsion and those factors are highly dependent on the hydrophobic/ hydrophilic character of the particles and transform into self-assembled supramolecular colloidosomes.

The largest yield of colloidosomes is obtained when using a surfactant to stabilize the oil/water interface. This introduces an electrostatic driving force to take the latex particle to the emulsion interface. The hydrophobicity of the latex particles is the driving force in the surfactant free case but it is evident that the particles are held a short distance apart, presumably due to an electrostatic repulsion in the plane of the emulsion. This repulsion is well known and is thought to operate through the organic phase. The following figure demonstrates the morphological features of colloidosomes obtained from soybean oil (A) and sunflower oil (B).



A B

Fig. 4. Colloidosomes from (A) Soybean oil; (B) Sunflower oil.

2.5 Transformation of soybean oil to self-healing material

An attempt was made on preparation of self–healing material using dimerized fatty acids. In the present study, dimerization of fatty acids has been initiated by use of soy triacylglycerol (STAG) in the presence of lipase (Fungal lipase, Sigma, USA), metal salts (alkali, alkaline earth and transition; Merck, India), monosaccharide and oligopeptides (HiMedia, India) in addition to biosurfactants and under agitation condition (200 rpm, Remi, India). And then self-assembly of dimers in the presence of biosurfactants (Lipopepetide, Sigma, USA) results with the transformation STAG to STLM (Soft Tissue like material).

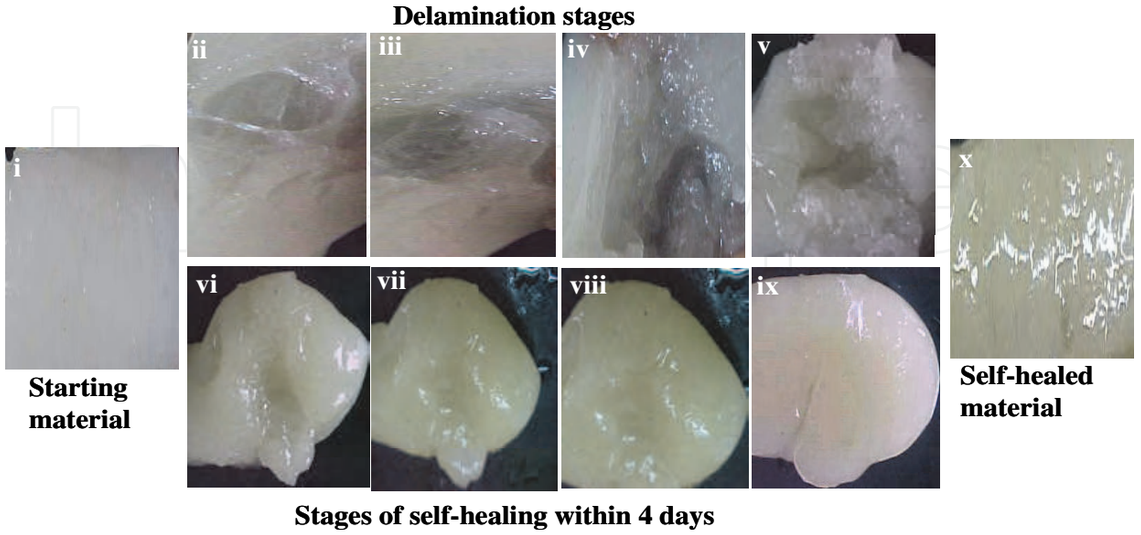


Fig. 5. Self-healing pattern of delamination damages of STLM.

The obtained STLM was creamy-white in colour with soft nature, partially soluble in polar and non-polar solvents, however, completely soluble in ethylacetate and methanol. STLM showed layered, honeycombed, porous structure with channeled network in Scanning electron microscope. Different damages mode such as cracking, punching, cutting and delamination were made. Since minor damages like cracking healed at the very faster rate (24 hours) and however, healing of punching, cutting and delamination damages, took more than 96 hours and the healing rate differs with the depth of the damage. Figure 5 illustrates the self-healing pattern of delamination damages of STLM.

However, STLM obtained in the present study, heal upon various damages (punching, delamination and cutting) without any inducers and also demonstrate more flexibility upon ageing (more than six months). Further, we found, surface rearrangement, diffusion and reunion of the self-healing material in the presence of aqueous atmosphere as evidenced through spread test conducted. The lower surface tension moieties at the end of the chain make the molecules migrate to the surface, and the diffusion and the interface results in the cross-linking and self-healing property. As reported by Wool (2008), healing of polymers proceeded with various stages of healing mechanisms, viz., surface rearrangement, wetting, diffusion and randomization and also suggest, the fibrillar morphology, nature of molecules at the end of the chain and *in situ* oxidation – reduction reactions.

Further, wetting and spreading of the fluid on the surface of the material, enhances the healing process (Brochard, 1986). In the present study, while damaging the self-assembled tissue like material, the released imbibed materials (hydrophobic and hydrophilic) diffuse through cut ends and trigger the repairing and healing process. The attractive force between the molecules present inside the material and on the surface of the material assembles by itself due to the Van der Waals forces. Here, the driving forces were the hydrophobic components (free fatty acid and unhydrolyzed oil) present in multilayered channeled structures.

With regard to wetting and dewetting processes of semi solid and liquid materials, in general, wetting makes the material to spread over the surface of the water, and in dewetting, the material shrinks and again wetting, spreading of a material transform the substrate to a very thin film (Scheludko, 1968 and lsraelachvili, 1985). However, in contradict to the said natural phenomena of wetting and dewetting, in the present study, we observed, a complete wetting (soaking), make STLM to shrink and the partial wetting, make it to spread. In the partial wetting state, (i) hydrostatic pressure makes the polymer to migrate towards the edge of the petriplate, which, (ii) further triggered by non-covalent bonding between the layers of the material and the hydrophobic components imbibed; (iii) the interface between the water and the material also acting as a driving force; (iv) Surface tension between the air and water interface also pull the material towards the edge. Presence of intramolecular bonding between the dimerized molecules gives the stability and it helps in the structure retrieval.

2.6 Transformation of soybean oil to organogel

We herein report, transformation of soybean oil to macro-sized self-assembled organogel in the aqueous medium containing mineral salts, glucose and peptone. Experiments were carried out at 37°C under agitation (200 rpm) for the period of 240 hours. Though different concentrations (0, 2.5, 5.0 and 10% (w/v)) of soybean oil was examined, the formation of macro-sized organogel was observed only with 10% concentration and the flasks receiving

lower concentrations displayed only the micellar structures. In the first stage, we visualized the transformation of soybean oil to micelle formation similar to the micelle of experimental flasks receiving 2.5 and 5.0% concentrations. Initial micellar formation could be due to agitation and the mineral salts present in the medium. Increasing the incubation period, further (after 6 days) results with vesicle formation and then to gellation. The formation of vesicle and gellation could be due to the primary aggregation of micelles. Similar to the report on self-assembly of peptides, in the present study, presence of glucose, peptone and the prevailing temperature (37°C) may initiate the primary aggregations. In addition, lecithin concentration and the phosphate moiety induce gellation and stabilization of micelles.

When the incubation period further increased to beyond 10 days we observed a formation of a single macro-sized organogel. The gel was spherical in shape with 2 cm in diameter. The inner structure of the cross sections showed multiple layers arranged like onion rings with no hallow space with tissue like appearance and feel in the center core. The thickness of the outer membrane was measured as 1 mm. According to Ai *et al*., (2003) and Liu *et al*., (2003) the layered assembly has molecular scale thickness and a few tens of layers can be easily achieved and the total layered area can be extended above the micrometer scale. Similarly, we observed continuous layering results with a macro-size organogel of 2 cm in diameter. Since, the directional and differential orientation of self-assembly decides the final size and structure of the secondary aggregates, in the present study, layering continues with directional orientation resulting with spherical size. Additional hydrogen bonding and the external agitation force may be responsible for the directionality, and the weak intermolecular forces (Van der Waals attractions) play the major role in the force balance, which results with multiple layering of bilayers in the secondary aggregations. Other than the above said driving forces, pH of the medium (6.0 ± 0.5), presence of divalent cations and anions (transition metal salts), and temperature may also instigate the secondary aggregations and the co-operation between the primary and the secondary aggregations.

There is a possibility of two different modes of primary aggregations for the existence of macrosized organogel. If the primary aggregation was a layered type, then the secondary aggregation could be a multi-layered with the space in between them able to hold either water or lipophilic compound depends on the nature of gel. In other words, if the self-aggregation was a fusion of micelles then the flower like aggregations takes place results with the circular/ spherical layered structures with same kind of holding nature.

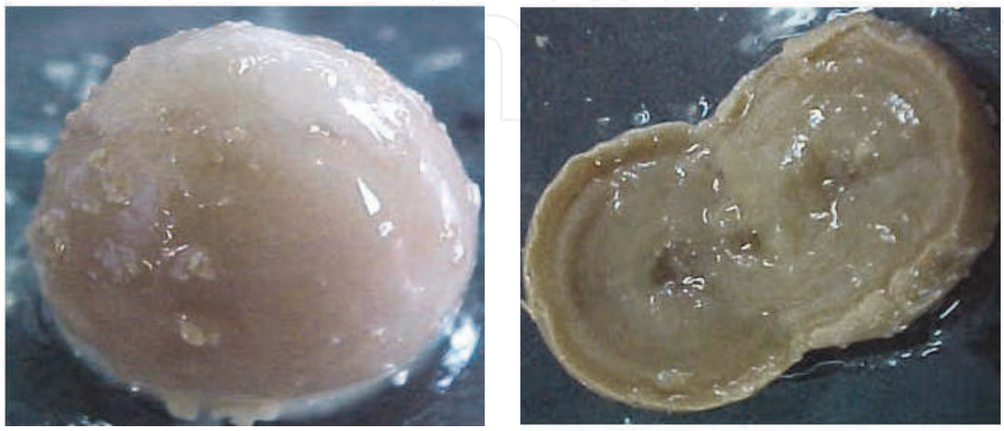


Fig. 6. Macrosized self-assembled organogel from soybean oil.

2.7 Transoformation of soybean oil, sunflower oil to bioadhesive

In the present study, dimerization of fatty acids of triglycerides have been realized during microbial growth. Growing the chosen marine microorganism in the medium increases the multiplication of cells and the doubling time (30 minutes). Though, triglycerides were given at varied concentrations (2 to 10 weight percent), only with >5.0 weight percent concentration, visible changes in the oil phase of the medium were observed.

At >5.0 percent concentration of oil we visualized the transformation of oil phase within 24 to 48 h of incubation. This might by due to the rapid *in situ* hydrolysis of triglycerides by the lipolytic enzymes produced by the organisms. Similarly, an increase in glycerol content in the cell free broth also substantiates the enzymatic process of the cleavage of triglycerides and the presence of a biosurfactant with appreciable surface activity of cell free broth may also contribute to the formation of thread like structures.

The presence of free fatty acids at trace levels evidenced throughout the experimental period in the form of oleic or linoleic acid further confirmed the hydrolysis of oil and the percentage of linoleic acid has been found at higher level compared to oleic acid. The formation of thread like structures further condensed to develop in to a solid mass with adhesive nature when the incubation period increases beyond 120-h.

In situ generation of biosurfactants plays a vital role in the condensation and polymerization as reported by Kestelman and Veselovsky (2001). The increased adhesive nature observed in the product of the present study might be due to the biosurfactants available in the broth during the formation of the adhesive product and its involvement in the intramolecular network of the product. Markevich et al., (1986) detailed the role of surfactant in increasing the adhesive nature of the product, where, they employed synthetic surfactants.

The thread like structures formed during the growth of the organism has been considered as the dimers of fatty acids or triglycerides polymers and these dimers are the precursors for the product formation, however, we couldn't ascertain the nature of dimers formed. Followed by dimerization, the reaction may further preceded and provide the product with adhesiveness. Dimerization followed by product formation might be affected by the presence of (i) biosurfactant; (ii) available amino acids (iii) unspent metal ions (iv) free glycerol and (v) monomers of triacylglycerols in the medium. With regard to dimerization in aqueous medium, Lyons (1969), Wheeler and Godfrey (1974) and Isbell (1994) reported less percentage of water increases the yield of dimers. However, in the present study, dimerization was evidenced in the aqueous medium. The following figure illustrate the adhesive nature of the supramolecular self-assembly structures of soybean (A) and sunflower (B).

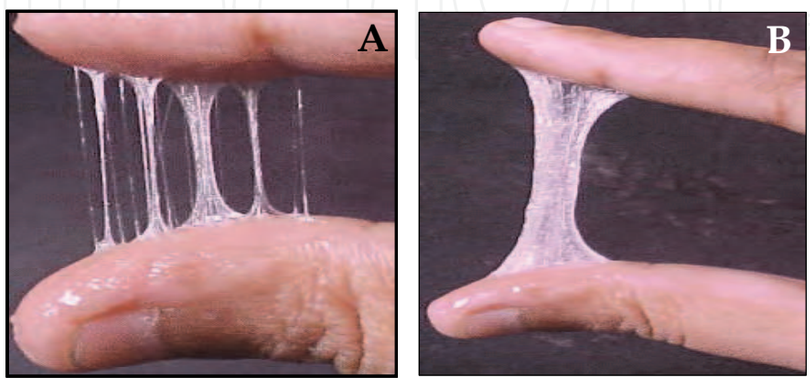


Fig. 7. Bioadhesive from soybean oil and sunflower oil.

2.8 Transformation of vegetable oils to other supramolecular structures

In addition to the above described wide numbers of supramolecular structures, we also received rubber like, membrane/sheet like and microemulsion structures from vegetable oil under insitu conditions. The following figure depicts the images of rubber like (a), membrane/sheet like (b) and microemulsion structures (c).

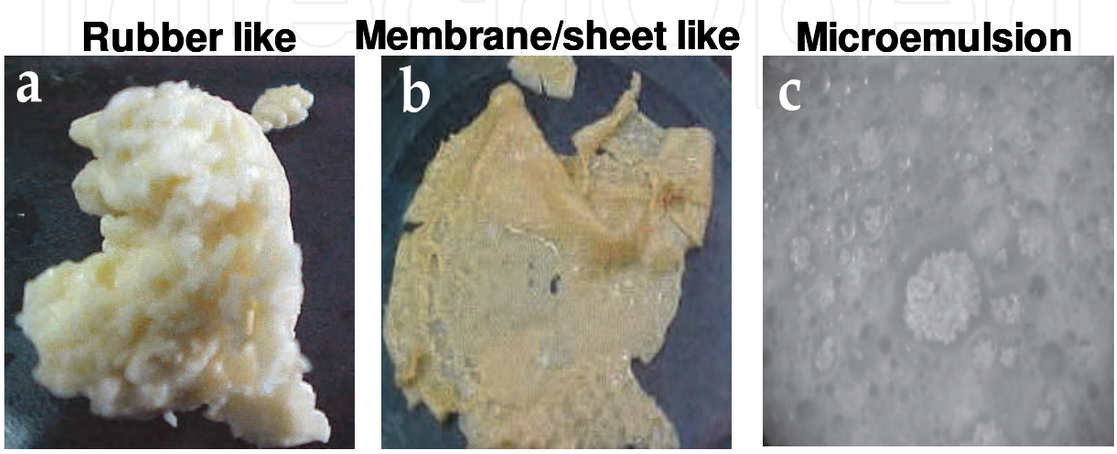


Fig. 8. Different supramolecular structures from vegetable oil (a) rubber like;
(b) membrane/sheet like; (c) microemulsion structures.

The major differences in the above said three structures are lies with the nature of the vegetable oil chosen. The rubber like material is obtained when the oil is heated near boiling point and then cooled and then incorporated in the mineral medium. The important message obtained from this material preparation is, the whole process is proceeded with out any microbes. Hence, self-assembly would have been takes place by mere self-assembly of the saturated fatty acids.

With reference to membrane/sheet like material and microemulsion structures, marine *Bacillus* sps is involved in the presence of mineral salts.

All these supramolecular structures received from vegetable oils under *in situ* condition during the growth of organisms pose a serious question on whether application of all the microbial products separately without microbes will provide the same kind of materials or not. Thus experiments were conducted separately with the selected oils with the enzyme lipase obtained from Sigma and the biosurfactants separated from the species used in the present study, mineral medium and the environmental conditions like agitation at 180-200 rpm. We received supramolecular structures of vesicles, multilamellar vesicles and self-healing materials. Other said structures could not be received and implies they will be formed only in the presence of microbes.

The following schematic representation revealed the formation of various supramolecular structures from vegetable oils and the transformation phases observed in the presence and the absence of microbes.

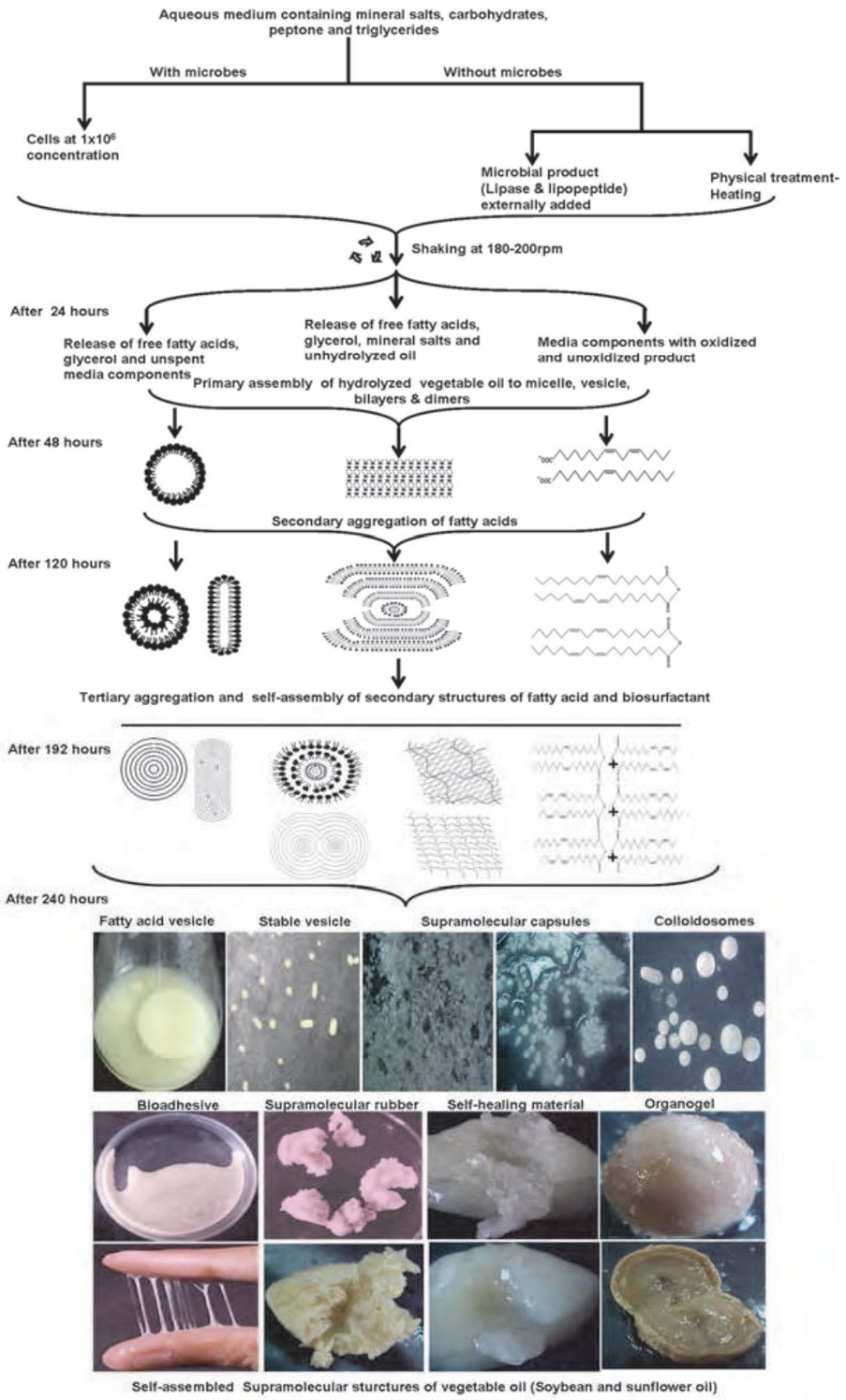


Fig. 9. Schematic representation of different self-assembled supramoelcular structures using plant triglycerides with microbes, with microbial products and by simple physical treatments.

3. Conclusion

As summarized in the introduction, self-assembled supramolecular structures and research on self-assembly of amphiliphilc molecules are always in limelight, since, any one of the hypothetical theories will provide the answer for the question on how the life is originated? Though supramolecular structures of synthetic chemicals and polymers were made under various environmental conditions, preparation of biological supramolecules needs intensive research. The results of our study emphasize the role of microbes and the microbial products on transformation of simple vegetable oils to supramolecular structures under *in situ* conditions. These findings have the pathway for the new approaches on how the live cells are involved in the formation of supramolecular structures. The reproducibility of the results of our study exemplifies, more avenues for future research.

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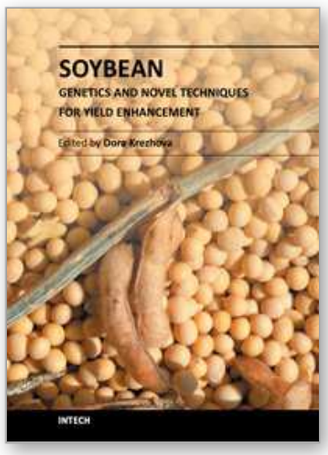
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