Rheology of interfacial layers of composite materials intended for encapsulation technology

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Introduction

A key element in the encapsulation technology is the control of the diffusion phenomena troughout the surface layer in contact with air phase.

Mass transfer is mediated by both steric hyndrace effects and polymer chain dynamics.
A useful approach to quantify these factors is rheological evaluation of the material structuring at the interface (P. Erni, 2006). Aim of the work was to quantify the interfacial rheological behaviour of a composite material suitable as shell material for capsules manufacturing.

Materials and Methods

Soy Protein Isolates (SPI) were purchased from Cargill (Baupte, France). Soy protein solutions were prepared by dispersing soy protein powders in deionized water for one night at room temperature, under magnetic stirring.

High Methoxyl Pectins (HMP) were purchased from Sigma Aldrich (Milano, Italy). Pectin solutions were prepared by dispersing HMP powders in deionized water for one night under magnetic stirring.

Soy protein - High Methoxyl Pectins composite systems were prepared by adding pectin solution to soy protein solutions under magnetic stirring The HMP/SPI ratio in the mixed systems varied from 1/1 to 1/10.

Interfacial shear rheological measurements were carried out by means of two commercial rheometers (Camtel CIR 100; a Physica MCR 300). Dilatational measurements were performed on a NIMA Langmuir trough. Layer thickness were determined by means of a UVISEL ellipsometer.

Results and Discussion

High methoxyl pectin (DE 58%)/ soy protein isolates in aqueous dispersion were studied.
It is well known that the co-solubility of pectins and soy proteins is not favourite for the occurrence of phase separation due to thermodynamic incompatibility between biopolymers with different polarity. By increasing the pectin/soy proteins concentration ratio (up to 5:1) and by acting opportunely on the chemico-physical conditions of the medium, the occurrence of phase separation phenomenon has been efficaciously restrained (J. Gigli, 2008).

In order to design an HM pectins/soy protein interface with taylor made properties, the following aspects as to be considered:

1) interfacial layer thickness;
2) interfacial layer formation kinetic (Fig. 1);
3) viscoelasticity of the interfacial layer;
4) interfacial viscosity of the adsorbed interfacial layer;
5) the effect of polysaccharidic sub-phase on the interfacial layer.

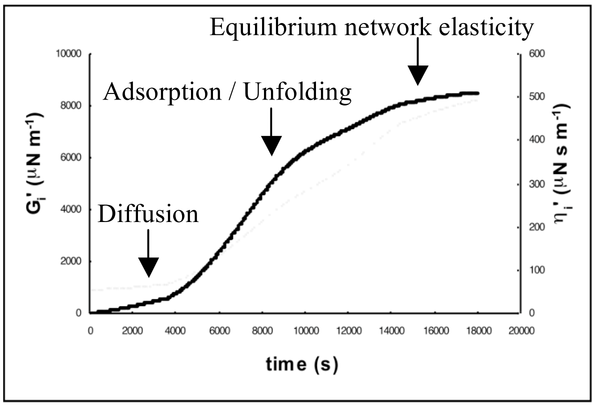

Fig 1: Development of the interfacial elasticity (Gi’, bold line) and of the interfacial shear viscosity (ηs’, normal line) plotted vs. time for HM pectins/soy protein isolates composite systems (Piazza et al., 2008).

Different physical analyses were carried out to quantify the above mentioned aspects: ellipsometry investigation, interfacial shear rheology and dilation rheology. The useful aims of this study not only lies in the developments of theoretical models on interfacial structuring and dynamics, but also in the development and validation of instrumental techniques.

It can be postulated that interfacial shear rheology combined with interfacial dilatational rheology could be a powerful tools for investigating the formation and resultant network properties of adsorbed layers at the air-water interface.

The protein layer formation was monitered using an ellipsometer durign adsoprtion on a Langmuir trough. The layer thickness was derived from standard simulation algorithm provided by the instrument software. After complete adsorption, the equilibrium film thickness was equal to 2 nm.

Static measurements of surface pressure vs. time and transient relaxation test were performed on SPI solutions at various concentration by means of a Langmuir film balance.

The relaxation spectra were fitted with a generalized Maxwell model and the viscoelastic moduli $E'(\omega)$ and $E''(\omega)$ readily calculated. The behaviour of SPI solutions is that of a light cross-linked polymer network with a more stable character of the network obtained at the surface of the less concentrated solution (J. Lefebvre, 2006).

Steady state and oscillatory measurements were performed using a rheometer adapted for interfacial rheometry. Suitable operative conditions for dynamic rheological evaluations of the SPI layer formed at the air/water interface, were defined. It was concluded that the limit of the linear viscoelasicty is very low, that means a high sensitivity rheometer is required at very low strain amplitudes.

SPI progressively accumulate at the air/water interface: the higher the protein content in the solution, the higher the delay in the saturation coverage. Moreover, the low bulk viscosity of the SPI solutions resulted to limit the instrumental detectability. The rheological behaviour at air/water interface of composite SPI-HMP water solutions was then studied.

The coupled surface structuring action of SPI and HMP was investigated by means of small amplitude oscillatory test. By increasing the HMP concentration the elastic interfacial modulus Gi' adjusts to an asymptotic value after an extended lag phase, thus indicating the thickener role played by the polysaccharide in the bulk. The stabilizing effect, that was observed in presence of the high-molecular-weight polysaccharide may be attributed to a greater enhancement of the local viscosity in the interface. It can be therefore considered licit to discuss the role of the surface layer of capsules shell material in terms of the structural contribution of the surface biopolymer network.

Conclusions

In conclusion, in order to design biopolymer interfacial layers with desired physical properties, two main phenomena are to be taken into account that drive the viscoelastic character of the 2D interfacial network:

1) if the rate of biopolymers diffusion from the bulk to the surface overcomes the rate of the interfacial structuring, no viscoleastic film will results. On the contrary,

2) if the rate of diffusion from the bulk to the surface is lower than the rate of the interfacial structuring, a viscoleastic 2D gel will be formed, that reduces the mass transfer towards the external environment.

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