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Multiple light scattering as a preliminary tool for starch-based film formulation

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Abstract

Starch-based films are a good alternative to synthetic films in food packaging and are usually produced by casting. Their mechanical and optical properties were widely studied in literature, but the characteristics of the film-forming dispersions were poorly addressed. Since film-forming dispersions influence the formation and quality of films produced, we characterized different starch-based dispersions by the Turbiscan®. It is an instrument based on multiple light scattering and it gives the "fingerprint" of each dispersion by its transmission/backscattering profiles during time. We analyzed how the addition of additives (citric acid and sodium hexametaphosphate) and the preparation method (with or without sonication) influenced the aforementioned profiles and the film formation and quality. We focused particularly on the investigation of stability and destabilization phenomena in dispersions predicting good or scarce film formation and quality. In light of this, the Turbiscan® can be considered a very useful tool in the choice of the optimal dispersion formulation, even before performing tests on film formation.

Keywords: starch-based films, dispersions, characterization, Turbiscan, multiple light scattering.

Public Interest Statement

While many of the advances in materials science have been driven by breakthroughs in material design and fabrication, understanding the changes that occur in a material during its utilization or operation in devices is of immense importance for its successful integration. Considering these aspects and the continued growth in materials research, there is a clear need for new topical journals which can serve researchers to understand the phase transitions and exploit the phenomena to current, state-of-the-art research in the field of materials science, moreover with full accessibility.

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Introduction

Packaging in food industry is based mostly on synthetic polymeric films, because they are cheap, easy to be produced, flexible and durable. Nevertheless, they are petrochemically derived and resistant to degradation [1], therefore biopolymers – such as starch, cellulose, pectin, etc. – were recently proposed as green alternatives. Starch is a biodegradable, inexpensive and very abundant in nature biopolymer, obtained from different sources, such as wheat, corn, rice and potatoes. It consists of two main polysaccharides, that are amylose with a linear chain, and amylopectin with a highly branched structure. The amylose and amylopectin ratio depends on the starch origin and influences its crystallinity [2]. Starch-derived films are usually obtained by dry process or wet process. Actually, the wet process is preferred to produce edible films and provides for the solubilization of starch in water with potential additives and following drying of the film-forming dispersion. Since starch granules are not soluble in cold water, it is necessary to heat starch in excess of water to 80-90 °C [3]. This thermal process leads to starch gelatinization with structural changes caused by the breaking of hydrogen bonds and loss of crystalline structure [4,5]. When the starch gel is cooled, amylose and amylopectin chains go through the retrogradation phenomenon by forming a more ordered structure [6]. Differently from polymeric solutions, in polymeric dispersions also the drying temperature is a critical parameter. Indeed, below the minimum film forming temperature (MFFT), no clear continuous film is formed because particles have not sufficient energy for coalescence [7]. The MFFT depend on the polymer used, particle size of the polymer spheres, coating formulation and polymer concentration. Finally, the drying rate, influenced by ventilation and relative humidity, has important effect on film formation and properties.

Since starch-derived films have poor mechanical properties due to amorphous regions formed by amylose, it is necessary the addition of plasticizers and/or reinforcing fillers to improve flexibility and extensibility [3,8]. Glycerol is commonly used as a plasticizer with a concentration of 3-12% in most of hydrocolloid films to prevent film brittleness [9]. The mechanical properties of starch films can be improved also by the addition of a nontoxic cross-linking agent, such as citric acid, with proper concentration [1,10].

Researchers studied mainly the mechanical and optical properties of obtained films. These properties depend on rheological properties and stability of film forming dispersions. Sabbah *et al.* [11] proposed zeta potential measurements to investigate the interactions among polymeric chains. Dispersions are highly unstable when the zeta potential is very lower than -10 mV and very higher than 10 mV. Since the properties of dispersions depend on the preparation method, it is necessary to control several parameters – addition sequence of reagents, mixing rate, temperature – to make reproducible the dispersion preparation [12].

In this work, we investigated the properties of starch-based dispersions by the Turbiscan®. These dispersions were obtained with different additives amounts and preparation methods (included the presence or absence of sonication). The Turbiscan instrument, based on multiple light scattering, is mainly used in cosmetic and

pharmaceutical fields, but recently also on phase change materials, to investigate destabilization phenomena [13,14]. Indeed, it identifies phenomena of destabilization and phase separation before their visibility to the unaided eye. In addition, the gelatinization of nanosilica was studied by Turbiscan. Boul et al. [15] observed that the initial destabilization due to particles aggregation was followed by a gradual stabilization due to the formation of interactions among polymeric chains. This behavior should be observed also in film formation after the gelatinization step.

Our work aims at evaluating the use of Turbiscan as a preliminary tool to choose the optimal formulation of a film-forming dispersion, by linking the dispersion characteristics and the obtained film properties. Therefore, the main goal is to obtain information about the dispersion properties influencing the formation and quality of films. Film properties depend on casting and drying conditions too, but they were constant in this work. We investigated dispersions based on starch and glycerol, with or without additives and sonication. Citric acid as cross-linker and sodium hexametaphosphate as thickener were added in some tests to stabilize the dispersions, by increasing the viscosity and establishing interactions among starch chains and with glycerol. We prepared samples by three different formulation modes. At each formulation, two samples were dried at 30°C and 60°C. The obtained films were observed by visual and optical microscopy to evaluate their homogeneity.

Materials and Methods

Materials

Starch from potato (Sigma Aldrich), Sodium Hexametaphosphate (Sigma Aldrich) 65-70% P_2O_5 basis, Glycerol (Sigma Aldrich), Citric Acid (Sigma Aldrich) and distilled water were used in different ratios.

Preparation of film forming dispersion and casting

All film-forming dispersions were prepared with the same amounts of water (100 g), starch (5 g) and glycerol (2.52 g). The effect of additives, drying temperature and sonication was investigated by six tests described in Table 1.

Table 1. Operating conditions of different tests.

N° test	Citric acid (g)	Sodium hexametaphosphate (g)	Drying Temperature (°C)	Sonication
1	0	0	30	NO
2	0	0	60	NO
3	0.25	1	30	NO
4	0.25	1	60	NO
5	0.25	1	30	YES
6	0.25	1	60	YES

In all test, starch was dissolved in water by mixing for 5 minutes. Then, glycerol was added and samples were mixed for further 5 minutes. Citric acid and sodium hexametaphosphate were added together with glycerol in tests 3-6. Dispersions were heated to 90 °C for 30 minutes, then cooled and dried in oven at 30 °C (tests 1, 3, 5) or 60 °C (tests 2, 4, 6). In addition, samples were sonicated for 10 minutes in tests 5 and 6

(amplitude 80%).

The sonicator was provided by Hielscher (Teltow, Germany). UP200S compact ultrasonic homogenizer features include sturdiness, high degree of efficiency, and automatic determination of the ideal performance control by way of the amplitude or the pulse duration. The characteristics of the sonotrode are summarized in Table 2.

Table 2. Characteristics of the sonotrode used for sample preparation.

Probe for sonication						
Type	Max immersion	Diameter TIP	Max amplitude	Acoustic Power Density	Amplitude	Cycle
S14 – TIP 14	90 mm	14 mm	80µ	105 W/cm^2	100%	0.8

Films were obtained by casting. Dispersions were poured into Petri dishes and oven dried for 4 hours at 30 °C or 60 °C.

Characterization of dispersions by Turbiscan®

The operating principle of the Turbiscan® is based on multiple light scattering. The instrument scans samples at height about 3.5 cm and draws the transmission profiles (T) and back-scattering (BS). Scanning can be set for short or long periods at temperatures ranging from 0°C to 50°C. These profiles, at a given time, are like a sample fingerprint and can be used to test the reproducibility of its preparation method.

Transmission rate (T%) stablished whether regime is transmission or back-scattering: T>0.2% indicates a transmission regime, T<0.2% indicates back-scattering regime. The profiles along the cell, in transmission or back-scattering %, give information about the homogeneity of the sample but to identify the phenomena of destabilization it is right to take into consideration the value of ΔT(%) or ΔBS(%), since they consider the first profile as initial state of samples dispersion facilitating reading. The profiles of different destabilization phenomena was illustrated in Figure 1.

As regards the phenomena of particle migration, sedimentation occurs when the density of the dispersed phase is greater than in the continuous phase, vice versa when it is less we speak of creaming. Instead, the flocculation and the coalescence concern the particle interactions causing a reduction of particle number and an increase of particle size.

Phase separation due to particle migration is evident in the ΔBS% values corresponding to the top and bottom of samples, where creaming and sedimentation occurs, respectively. Instead, flocculation and coalescence affect the whole sample, appearing as shifted total ΔBS% profiles.

The instrument also calculates an overall stability index over time, the Stability Index (TSI) which considers all the variations in the sample to give a single number that reflects the destabilization of the sample.

Each scan is compared to the previous one, on a selected height, and the result is divided by the total height selected (Equation 1).

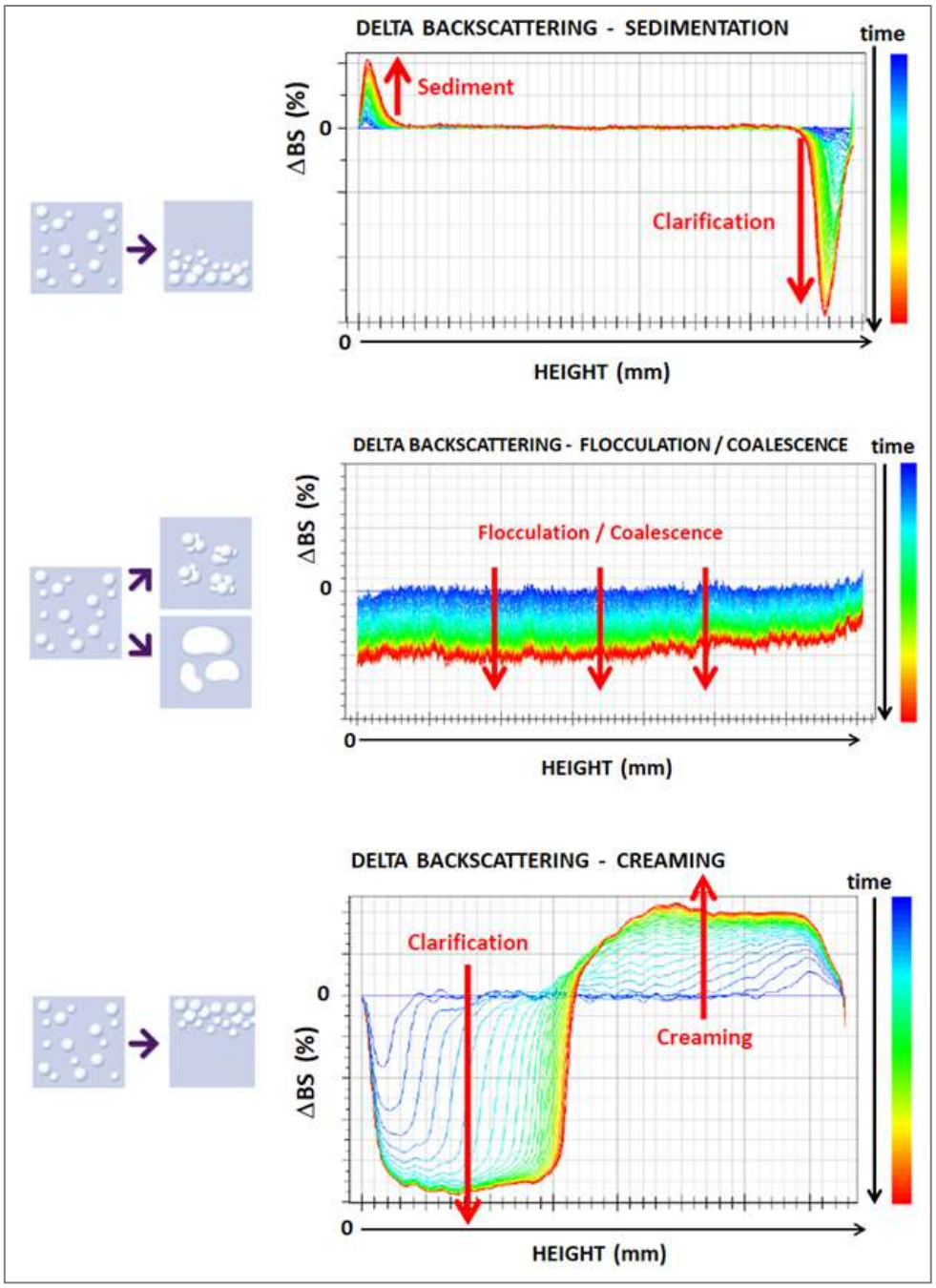

Figure 1. Main destabilization phenomena observed in dispersions by Turbiscan (adapted from De Paola et al. [13]).

$$\mathrm{TSI} = \sum_I \frac{\sum_h |scan_i(h) - scan_{i-1}(h)|}{H} \quad (1)$$

The TSI value increases as dispersion stability decreases. Moreover, the TSI *vs* time curve trend could give information about the gelatinization degree of a dispersion [16].

In this study, each sample was analyzed every 30 minutes for 24 hours at 30 or 60°C (drying temperatures investigated).

Morphological analysis by optical microscope

The investigation of film optical properties is important to get information about

film morphology. In order to analyze the film homogeneity, polymeric films (2 cm * 2 cm) from samples 4 and 6 were analyzed by a polarizing optical microscope "Leica" with a 5X objective. The film from sample 4 was analyzed by crossed polarizers, with the aim to detect possible birefringence effects due to not swollen starch granules.

Results

Since the T value of all samples was higher than 0.2%, Turbiscan worked in transmission mode [17]. Consequently, possible destabilization phenomena were detected by T% profiles. The BS% values depended on internal reflections and did not characterize the dispersions.

Profiles of T% in test tubes during time are shown in Figures 2 and 3 for samples number 1 and 2 (without additives and sonication), respectively.

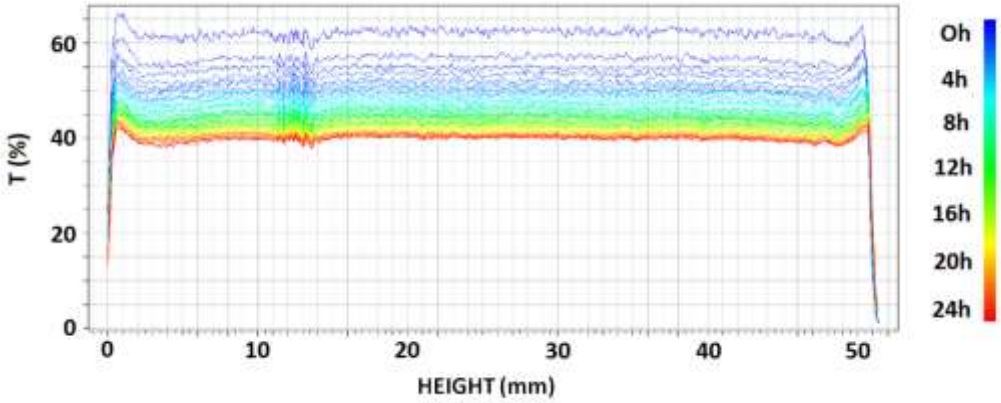

Figure 2. T% profiles of sample 1 (no additive, drying temperature=30°C, no sonication, ΔT%=20, TSI after 20 h=25).

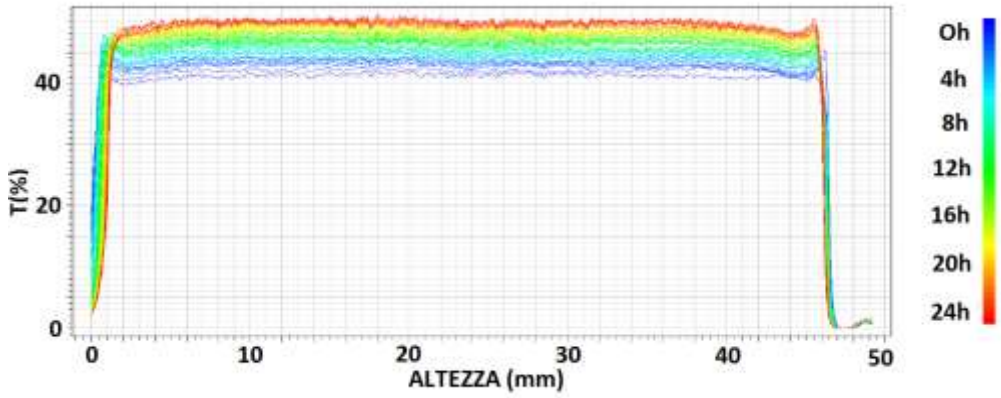

Figure 3. T% profiles of sample 2 (no additive, drying temperature=60°C, no sonication, ΔT%=8, TSI after 20 h=8.5).

Flocculation was evident in both samples along the whole cell by parallel lines shift during time. Flocculation is greater in the first sample (Fig. 2), resulting in higher TSI. Flocculation precedes gelatinization, at which systems are stabilized by interactions among particles with following film formation [16]. Nevertheless, when flocculation is too rapid, sizes of particles are higher than a certain critical value and migration phenomena (sedimentation/creaming) prevail over gelatinization. The low or missing

gelatinization in samples 1 and 2 was confirmed by no film formation. Instead, a crystallized material was obtained, as shown in Figure 4.

Figure 4. Product from sample 2.

Profiles of T% in test tubes during time are shown in Figures 5 and 6 for samples number 3 and 4 (with additives and no sonication), respectively.

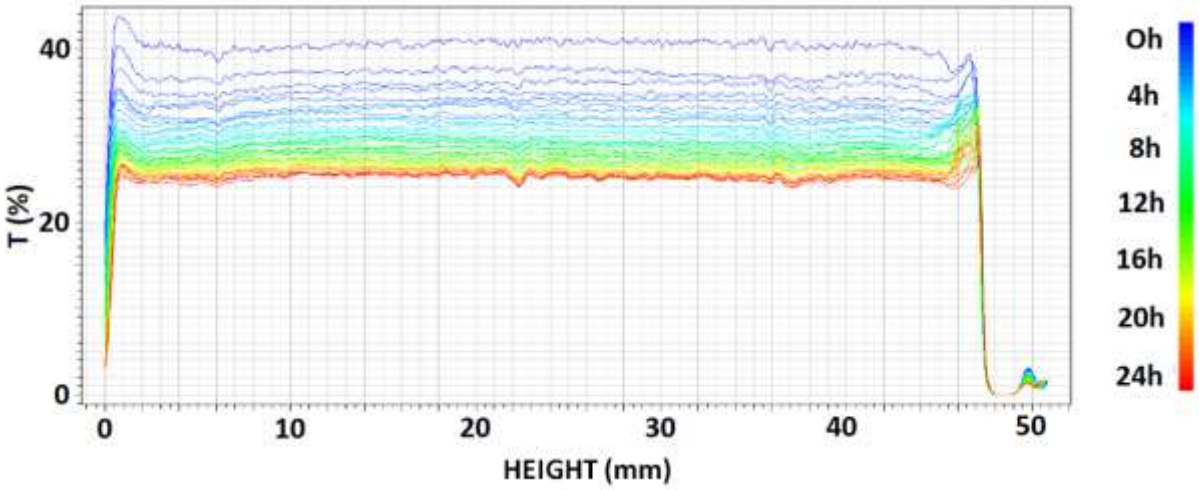

Figure 5. T% profiles of sample 3 (citric acid and hexametaphosphate as additives, no sonication, drying temperature=30°C, ΔT%=15, TSI after 20 h=14).

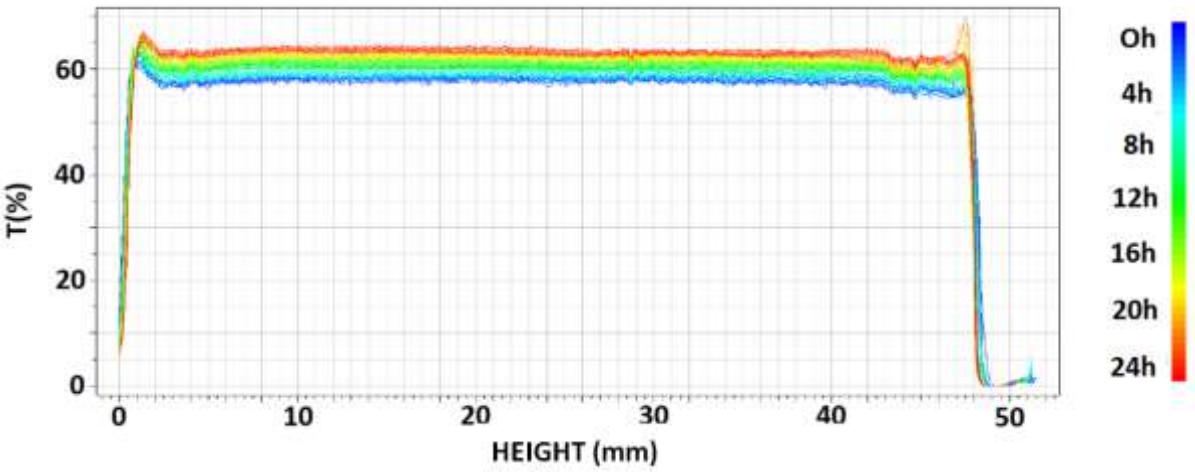

Figure 6. T% profiles of sample 4 (citric acid and hexametaphosphate as additives, no sonication, drying temperature=60°C, ΔT%=5, TSI after 20 h=5.5).

With equal temperature, TSI values lowered from 25 (sample 1) to 14 (sample 3) at 30 °C and from 8.5 (sample 2) to 5.5 (sample 4) at 60 °C. Generally, additives enhance the dispersion stability, but no film was produced from sample 3, which appeared very unstable in spite of the presence of additives. Instead, an irregular film was obtained from sample 4 (see Figure 7).

Figure 7. Irregular film from sample 4.

The microscopy analysis showed a peculiar optical behavior in presence of starch-based films. It is possible to observe birefringence phenomena, due to film heterogeneity. The image obtained by crossed polarizers (Figure 8) has a transparent area where molecules are aligned and a high birefringence zone where they are not uniform.

Figure 8. Detail of film from sample 4, seen by polarizing optical microscopy.

Birefringence is typically produced by not swollen starch granules. Their presence makes the film irregular and is an indicator of incomplete gelatinization. The presence of starch granules in samples 3 and 4 could be due to the insufficient breaking up promoted by the mixing.

It is usefull to remind that the starch gelatinization is preceded by the swelling of granules due to water absorption. This process is promoted by the breaking up of starch aggregates by sonication.

Concerning this, samples 5 and 6 were sonicated in order to reduce the size of starch granules aggregates and promote the water absorption, swelling and gelatinization.

Profiles of T% in test tubes of samples 5 and 6 during time are shown in Figures 9 and 10. Sonication of samples lead to reduced flocculation and TSI values both at 30 °C

(Fig. 8) and at 60 °C (Fig. 9).

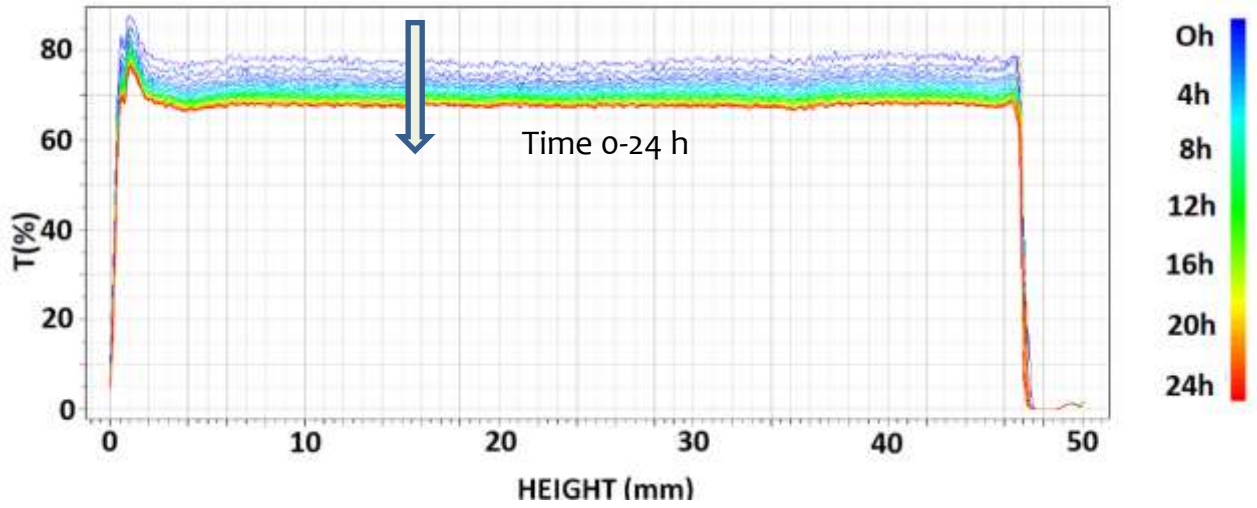

Figure 9. T% profiles of sample 5 (citric acid and hexametaphosphate as additives, sonication, drying temperature=30°C, ΔT%=9, TSI after 20 h=9.5).

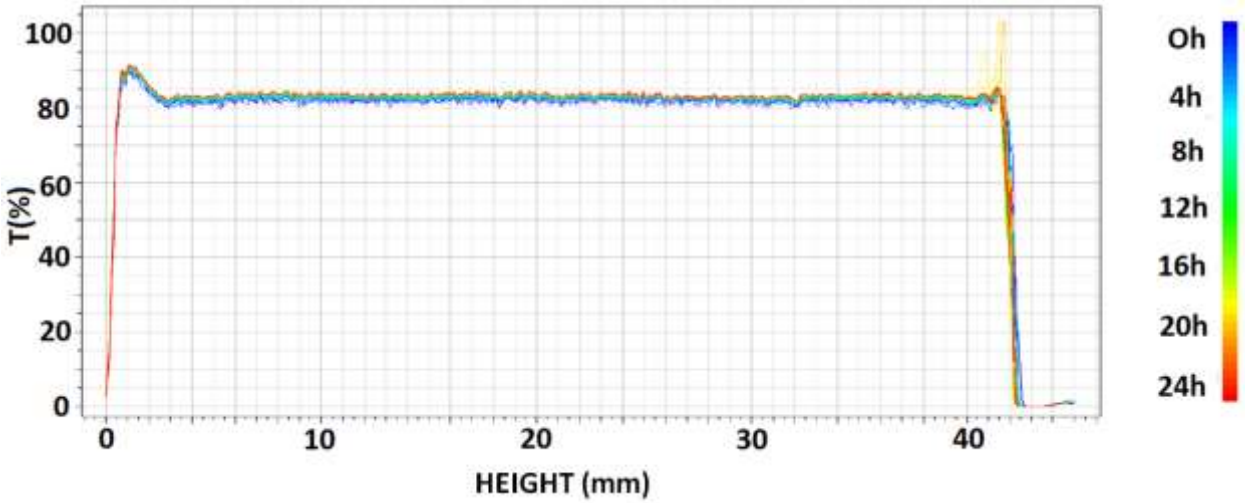

Figure 10. T% profiles of sample 6 (citric acid and hexametaphosphate as additives, sonication, drying temperature=60°C, ΔT%=2, TSI after 20 h=3.2).

In spite of a more stable dispersion, no film was produced from sample 5. Probably, the TSI value is associated also to the gelatinization degree of starch. Indeed, the TSI value of sample 5 is higher than the TSI value of sample 4 that lead to film formation (9.5 *vs* 5.5).

A transparent and homogeneous film was obtained from sample 6 (see Figure 11). Homogeneity of the film structure is evident in microscopy analysis by crossed polarizers (Figure 12). The aligned molecules lead to an optical image without asperity.

Figure 11. Film from sample 6.

Figure 12. Detail of film from sample 6, seen by polarizing optical microscopy.

No birefringence was observed in the film from the sample 6. This confirms the effectiveness of sonication in avoiding the presence of not swollen granules. Consequently, the film from sonicated dispersion was homogeneous and this is confirmed by polarized light optical microscopy.

Discussion

As shown in Figures 2, 3, 5, 6, 9 and 10, all samples had a similar behavior along the test tubes and lines are quite horizontal (constant %T-values in the whole cell height) and parallel during time. T%-trend is typical of flocculation for all samples. This phase precedes the gelatinization [15]. Different intensity of flocculation is evident on TSI value, as you can observe in Figure 13.

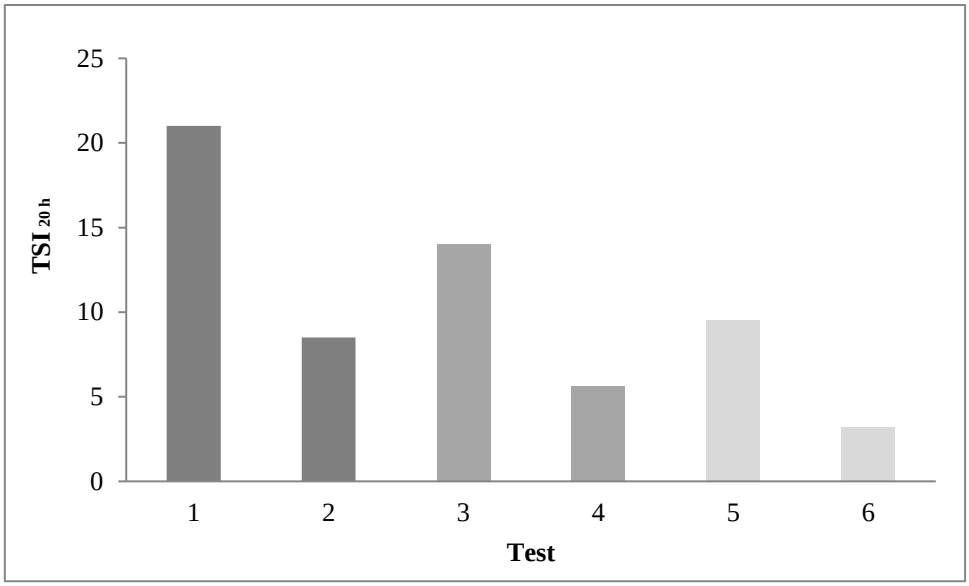

Figure 13. TSI value after 20 hours of all samples investigated.

Films were obtained from samples 4 and 6, which presented the lowest TSI values (5.5 and 3.2, respectively).

TSI *vs* time trends (Figure 14) show that the values were higher at 30 °C than at 60 °C for all samples. Moreover, the lowest variation of TSI during time was observed for sample 6 which produced a homogeneous film.

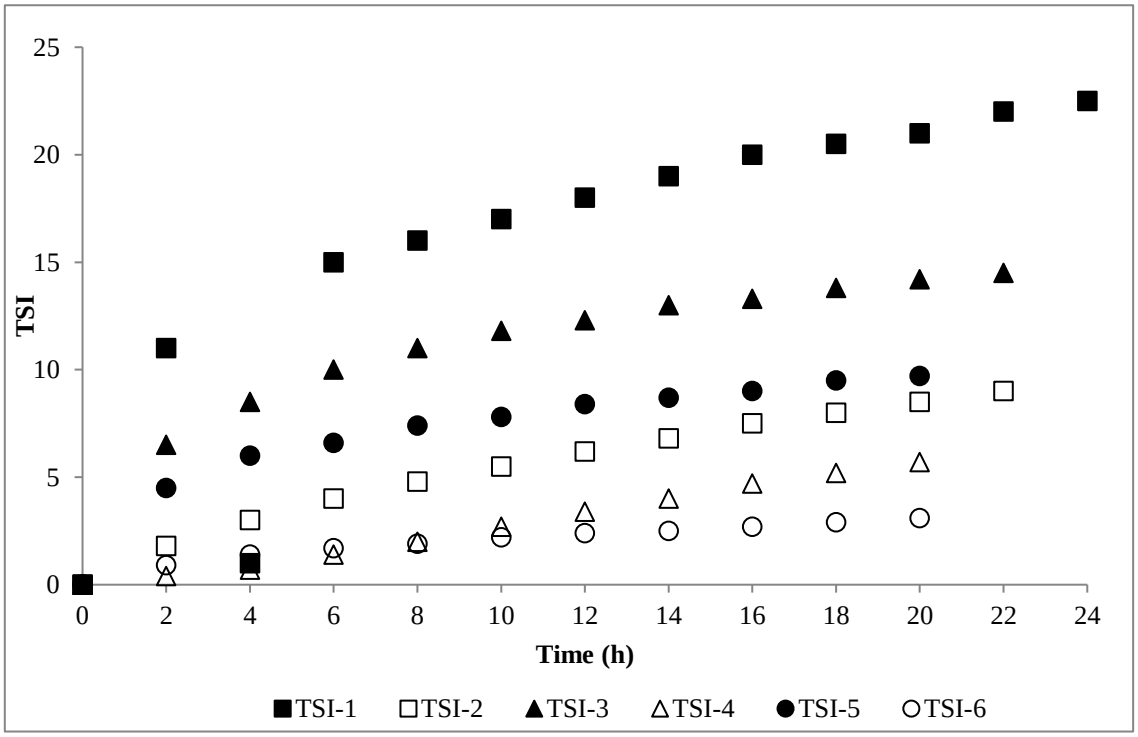

Figure 14. TSI *vs* time of all samples investigated.

Lower values of TSI and TSI variation rates during time correspond with improved film formation and quality. For this reason, the TSI could be used as a parameter to test the effectiveness of an additive or preparation method. In our case, citric acid and hexametaphosphate were effective as additives, because they reduced TSI variation in time. Moreover, sonication improved further the stability promoting the swelling of

starch granules and, consequently, the gelatinization, the increase of viscosity and the removal of possible air bubbles.

Moreover, the TSI value can be correlated to the film formation and quality. Indeed, no film was produced when TSI was higher than 8.5, whereas we obtained a crystallized material when TSI was 8.5, an irregular film when TSI was 5.6 and a homogeneous film when TSI was 3.2.

With equal other conditions, samples dried and analyzed at 30 °C were more unstable of samples dried and analyzed at 60 °C and did not produce any film. This can be due to starch retrogradation or to drying temperature that was lower than MFFT [7]. Starch retrogradation at 30 °C could impede the film formation. Instead, at 60 °C starch should be gelatinized.

Conclusion

Multiple light scattering by Turbiscan technology is very interesting and effective to characterize dispersions, because it identifies destabilization phenomena that are not observable with naked eye and that affect the following film formation and quality. TSI is an important parameter, depending on several factors and strictly correlated to the dispersion stability and to the degree of starch gelatinization. No film was produced from very unstable tested samples (TSI>8.5 in our tests), whereas the film quality increased with decreasing TSI.

Characterization of dispersions is essential to have reproducible films. The analysis of the initial profile is of particular interest and considered a "fingerprint" to be integrated with granulometry measurements. To this end, the Turbiscan instrument can evaluate average diameters, but not diameter distributions.

The optical microscopy analysis backed up the supposed connection between TSI and gelatinization. Indeed, sample 4 had higher TSI than sample 6 and lead to an irregular film showing birefringence due to not swollen starch granules. The sonication broke up starch aggregates and stabilized dispersions. Nevertheless, a temperature of 60 °C is necessary to produce a starch-based film. As expected, no film was produced at 30 °C because at this temperature there is the starch retrogradation and this was observable already in the dispersion analysis.

Our initial question was "Is it possible to predict the formation and quality of films by studying the initial dispersions?" and, in conclusion, we can confirm that yes, it is possible by Turbiscan. Therefore, the proposed method allows to investigate the effect of different modes of dispersion preparation – such as a supplement of additives or a sonication step – by a quantifiable parameters (TSI). This can help the selection of the most appropriate formulation. Nevertheless, it is evident that the film quality depends on the dispersion preparation, but also on following steps such as casting and drying.

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