Mechanical and Structural Properties of Maltodextrin/Agarose Microgels Composites

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Received: 30.11.2005, Final version: 30.10.2006

Abstract:
We present results from a new approach to the study of multicomponent gels, which allows independent investigation of the effect of phase volume and droplet size of the dispersed phase on the mechanical properties of the mixed gel composites. The method involves preparation of agarose microgels with different sizes, which are then embedded in maltodextrin gel matrices with different gel strengths. The effects of both phase volume and droplet size on composite properties are dependent on the phase modulus ratio. The higher the phase modulus ratio, the larger is the reinforcement effect and the effect of droplet size on mechanical properties of the maltodextrin/agarose composites. The observed behaviour was compared with literature models for the behaviour of composite materials.

Zusammenfassung:

Résumé:
Nous présentons des résultats issus d’une nouvelle méthode de préparation pour l’étude de gels multicomposés, laquelle permet de dissociée l’effet du volume et de la taille des particules de la phase dispersée sur les propriétés mécaniques des gels multicomposés. Des microgels d’agarose de taille différente ont été préparés puis inclus dans une matrice gélifiée de maltodextrine avec des rigidités différentes. L’effet tant du volume de phase ainsi que de la taille des particules dépend du ratio des modules des phases. L’augmentation du ratio des modules entre les phases dispersée et continue accentue l’effet de renforcement ainsi que l’effet de la taille des particules sur les propriétés mécaniques des composites de maltodextrine/agarose. Le comportement observé a été comparé à des modèles de la littérature décrivant le comportement de matériaux composites.

Key words: biopolymer mixtures, maltodextrin, agarose, microgels, mechanical properties, microscopy

1 INTRODUCTION

Previous studies have shown that using phase separated maltodextrin/agarose mixed gels to study the effect of phase volume and droplet size on the mechanical properties of food composites were made difficult because of problems with fractionation of maltodextrin [5]. It also proved impossible to control the inclusion size independently of the phase volume. Another approach to understand the effect of the inclusion of one ingredient in a matrix of another is to prepare filled gels, which consist of a gel matrix with inclusions of pre-made microgel particles [2]. A few studies have been conducted using filled gels to model food composites [3 - 6]. Ring and Stainsby [3] used different fillers to show that the small
deformation properties of composites depend on the phase volume of the filler, the deformability of the filler and the strength of the unfilled gel matrix. Increasing the phase volume of the filler results in a reinforcement effect of the composites (increase of the stiffness of the composites), which depends on the modulus of the matrix for deformable fillers. Whilst Brownsey et al. [5] and Richardson et al. [7] did not notice a significant effect of particle size on the dynamic moduli (they conducted studies of spherical glass particles ranging from 40 to 80 μm and sephadex particles ranging from 20 to 300 μm), Ross-Murphy and Todd [4], who studied glass beads ranging from 35 to 550 μm, found that the effect of particle size depends on the volume fraction. This observation was confirmed by Langley and Green [6], who studied the effect of glass spheres on whey protein gels. At high phase volume, the effect of particle size was enhanced and the smaller particles increased the stiffness of the composites most. However, they could only observe this effect if a strong interaction between the filler and the matrix was present. Thus, the particle size effect is not obvious and depends on other factors such as the phase volume of the filler and the interface strength between the filler and the matrix. Brownsey et al. [5], Langley and Green [6] and Langely et al. [8,9] have also shown that at high deformation, the affinity between the filler particle and matrix can profoundly affect the strength and failure properties of the material. Most of these studies used either a synthetic polymer such as cross-linked dextran particles or glass spheres, neither of which are really comparable to a food filler such as starch granules, fat globules or seeds. Here we employ a method that allows the use of food biopolymer microgels as fillers.

We employ an emulsion route to produce the microgels. This technique has been used to prepare alginate [10], agarose and κ-carrageenan microgels [11,12]. Frith and Norton [11] and Frith et al. [12] obtained agarose and κ-carrageenan microgels by mixing and stirring the hot solutions in oil with a surfactant (admol WOL) and then quenching the mixture. The oil and surfactant were then removed by washing the microgel suspension with water. By this method, Frith and Norton [11] were able to prepare filled gels with two biopolymer gels involved. It was decided to use the method proposed by Frith and Norton [11] to prepare maltodextrin/agarose composites and investigate their mechanical properties. Agarose microgel suspensions were prepared first and then incorporated in a maltodextrin matrix. The only requirement in preparing these gels was to be able to mix the two at a temperature where agarose microgel did not melt and maltodextrin was in the solution state.

In the following, the effects of phase volume, phase modulus ratio and droplet size on the large deformation properties of maltodextrin/agarose composites were studied using the above method of preparation. Results were compared to models for synthetic blends and composites. The microstructure of the composites was also characterised using confocal microscopy.

2 MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Maltodextrin and agarose

The food grade maltodextrin (Paselli SA2) used in this work was obtained from Avebe (The Netherlands). Paselli SA2 is an enzymatically converted potato starch based product with a dextrose equivalent (DE) of less than 3. There was no glucose present in the sample (information from the supplier). Paselli SA2 is available as a white powder, with a water content of 5 % (by dry weight). In all the figures, the term “SA2” was used as a synonym for maltodextrin. Agarose type Ia (Sigma-Aldrich, U.K.) was used. The sample had a sulphate content of less than 0.2 % and an ash content lower than 0.6 % (information from supplier). In all the figures, the term “Ag” was used as a synonym for agarose.

2.1.2 Preparation of agarose microgels

Agarose microgels were prepared by an emulsification method that has been reported previously [11,12]. 8% agarose solutions were prepared by dispersing the required amount of powder in deionised water (18 MΩ/cm) at room temperature for 10 minutes and then heating in a boiling water bath for 30 minutes. This solution was poured progressively into sunflower oil in a 1:2 ratio. The sunflower oil had been pre-heated at 80°C to avoid the gelation of agarose. To facilitate emulsification, a strong lipophilic water-in-oil emulsifier (Hydrophilic Lipophilic Balance (HLB) value of
around 4 - 5), admul WOL (1 %) (Quest international, The Netherlands) was dissolved in the oil phase. Whilst the agarose solution was added to the oil, the mixture was stirred with an L4R Silverson homogeniser at different speeds to create different agarose droplet sizes. In order to prepare the smaller sized microgels, the rotor of the Silverson homogeniser was fitted with the supplied mesh screen, containing round holes of diameter of 1 mm. For the largest sized microgel, the screen was removed. Three different samples were prepared: “high shear” microgels (maximum speed of Silverson homogeniser ≈ 8000 rpm), “low shear” microgels (minimum speed of Silverson homogeniser ≈ 2000 rpm) and “no screen” microgels (minimum speed without screen). The mixtures were stirred during 30 minutes to allow a steady state droplet size to develop. The emulsion was then left to cool in a beaker filled with ice and stirred slowly, to prevent aggregation and coalescence. On cooling, the aqueous polysaccharide phase gelled, forming agarose microgel particles. The sample was then centrifuged to separate the microgel from the oil phase (Sorvall centrifuge, RC 3C, U.K.). The speed of the centrifugation used depended on the size of the agarose droplets formed. The speeds selected were those where clear separation could be observed between the oil top phase and the sedimented microgels. Microgel suspensions were also observed under phase contrast microscopy to check if they stayed intact after the centrifugation. Table 1 summarises the speeds applied for the different samples.

As produced, the sedimented microgel solution has got still a significant amount contamination of oil. Therefore, a second emulsification process was conducted using 1% tween, which favours an oil in water emulsion. Samples were then subsequently purified by repeated centrifugation (5 times for 15 minutes) and redispersion in de-ionised water to eliminate the surfactant and oil left. The speed of centrifugation applied to the different samples is the same as mentioned in Table 1.

Earlier studies [12] showed that once gelled, the microgels have little tendency to swell or shrink, thus the concentration of biopolymer inside the microgel particle should be the same as that of the original solution, here 8%. This allows the volume fraction of an aqueous suspension of microgels to be determined from the weight solids: \( \phi = W_s/W_o \), where \( \phi \) is the volume fraction of the microgel suspension, and \( W_s \) and \( W_o \) are the weight concentrations of the microgel suspension and the original polymer solution, respectively. A microgel stock was produced by diluting the sediment in distilled water from the last centrifugation step to a constant concentration of microgel (60 %) as determined by dry weight measurement (16 h at 60°C). Therefore, the agarose microgel suspension concentration for the three samples with different droplet sizes was 4.8 % (w/w).

2.1.3 Preparation of maltodextrin/agarose microgel solutions

Composites of maltodextrin/agarose microgels were prepared by mixing 51 g of the stock microgel with 170 g of maltodextrin solutions at different concentrations. Agarose microgel suspensions were composed of 60 % by volume. Therefore when the maltodextrin solution was mixed with the microgel suspension, the solution was diluted. Hence, for initial concentrations of 30, 35, and 40 % maltodextrin, the concentration of maltodextrin in the mixed solutions was respectively estimated to be 25.5, 29.5, and 33.9 %. The maltodextrin and agarose microgel solutions were mixed for 15 minutes at 60°C, at which temperature the agarose microgels do not melt and maltodextrin solutions do not gel [13]. The mixture was then centrifuged at 60°C for 45 minutes (Beckman, L-8M, U.S.A.), using a speed that depended on the size of the agarose microgels (see Table 2).

The two phases (maltodextrin as supernatant and agarose microgel suspension as sediment) were separated, stored in the oven at

<table>
<thead>
<tr>
<th>Composites</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>maltodextrin/“High shear” microgel</td>
<td>13000 g – 45 min – 60°C</td>
</tr>
<tr>
<td>maltodextrin/“Low shear” microgel</td>
<td>3300 g – 45 min – 60°C</td>
</tr>
<tr>
<td>maltodextrin/“No screen” microgel</td>
<td>800 g – 45 min – 60°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Microgel</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>“High shear”</td>
<td>5 200 g – 1h – room temperature</td>
</tr>
<tr>
<td>“Low shear”</td>
<td>1 900 g – 1h – room temperature</td>
</tr>
<tr>
<td>“No screen”</td>
<td>500 g – 1h – room temperature</td>
</tr>
</tbody>
</table>

Table 1 (above): Speed applied during centrifugation for different agarose microgel solutions: “high shear” microgels, “low shear” microgels and “no screen” microgels.

Table 2: Speed applied during centrifugation for different maltodextrin/agarose microgel solutions: “high shear” microgels, “low shear” microgels and “no screen” microgels.
60°C and mixed again in different proportions. This centrifugation procedure was used in order to always have the same concentration in each phase when they are mixed in different proportions. Knowing the agarose concentration of the initial microgel samples (4.8 %) and the quantities of supernatant and sediment obtained, the volume fraction of agarose microgel in the sediment could be determined as could the phase volume of agarose microgels in each of the samples prepared.

2.1.4 Preparation of maltodextrin and composites gel samples

The mixed solutions were poured into moulds (13.5 mm deep and 12.3 mm diameter), which were initially stored in the fridge. They were overfilled to avoid air bubbles and the excess gel was forced out while sealing. The moulds were stored overnight, in a water bath at 10°C. Confocal microscopic examination of the top and bottom surface of the mixed gels as well as a section thought the samples confirmed a uniform distribution of the agarose microgels within the maltodextrin matrix.

2.2 METHODS

2.2.1 Large deformation measurements

Uniaxial compression experiments were performed on an Instron Universal Testing Machine, Model 4501 (Instron SFL, U.K.), equipped with an environmental chamber held at 10°C. The compression tests were carried out with a 100 N capacity load cell at a displacement rate of 25 mm/min. The samples were extracted from the perspex moulds after 18 h and aligned in the centre of the stainless steel compression platens. A defined distance between the sample and the top plate was left before compression to avoid any compression before measurement. In order to ensure slip boundary conditions, the plates were lubricated with mineral oil. A minimum of five compression tests was performed for each experimental condition to maintain reasonable statistical validity and analyse the variability in the data.

Corrected true stress and strain were calculated due to the potentially large change in sample cross-sectional area at high deformations (i.e. > 0.1 or 10%) [14]. The corrected “true” stress is approximated by:

\[ \sigma = \frac{F \cdot H}{A_0 \cdot H_0} \]  

where \( F \) is the load applied, \( A_0 \) is the original specimen cross-sectional area, \( H \) is the instantaneous specimen height and \( A_0 \) is the original height. The corrected “true” (or Hencky) strain, \( \epsilon \), is defined as:

\[ \epsilon = \ln \left( \frac{H}{H_0} \right) \]  

The apparent compressive elastic modulus, \( E_{app} \) (Pa), is then given by the initial linear region of the stress/strain curve following:

\[ E_{app} = \frac{\sigma}{\epsilon} \]  

The apparent compressive elastic modulus was measured within a low strain region, i.e. between 0.02 to 0.05. The true stress and strain at failure were taken as the maximum of the true stress/strain response, \( \sigma_f \) and \( \epsilon_f \), and their relative values, \( \sigma_r \) and \( \epsilon_r \), were calculated as follows:

\[ \sigma_r = \frac{\sigma_r}{\sigma_f} \]  

\[ \epsilon_r = \frac{\epsilon_r}{\epsilon_f} \]  

Also, the relative apparent elastic modulus was defined as:

\[ E_{app} = \frac{E_{app}}{E_{app_0}} \]  

The subscript 0 refers to the mechanical properties of the matrix phase.

2.2.2 Confocal Scanning Laser Microscopy (CSLM)

Maltodextrin/agarose microgel composites were observed under confocal microscopy. The system consisted of a MRC 600 CSLM (Bio-Rad Laboratories, U.K.) attached to an Ortholux II microscope (Leica Microsystems, U.K.). The CSLM was operated with an argon-krypton laser with an excitation at 568 nm and an emission collected at 585 nm. A 20x objective lens with no zoom
was used. Structural observation was typically conducted about 100 μm underneath the top surface of the sample being examined. Imaging at this depth minimised any surface related optical artefacts. To increase the signal to noise in the images, multiple scans were averaged (Kalman filtered) during data collection. The samples were stained with Rhodamine-B to provide a high level of contrast between the agarose and maltodextrin phases. For the micrographs presented here, the maltodextrin stains more intensely and appears light, whereas the agarose appears dark.

### 2.2.3 Size distribution of agarose droplets in maltodextrin/agarose composites using a mastersizer
To determine the size distribution of the agarose microgel, a Mastersizer Χ (Malvern Instrument, UK) was used. A 300 mm lens, which allows the particle sizes between 1.2 and 600 μm to be measured, was set up and a sample cell with a 2.6 mm path length was selected.

3 RESULTS AND DISCUSSION

#### 3.1 EFFECT OF PHASE VOLUME ON LARGE DEFORMATION PROPERTIES OF MALTODEXTRIN/AGAROSE COMPOSITES
In this section, we discuss, as one example, the effect of phase volume on large deformation properties of maltodextrin/agarose composites using composites consisting of the “low shear” microgel in 30% maltodextrin gel. Figure 1a and b show the effect of agarose microgel phase volume on the true stress/strain response of maltodextrin/agarose composites prepared at different phase volumes for one size of microgels (“low shear” microgel) and one matrix concentration (30 %) using the Instron. For clarity, data are given on two figures. Two types of behaviour are seen: (i) at low phase volume (φ < 28 %), the composites show a true stress/strain response similar to the maltodextrin gel, with a strain softening behaviour, i.e. the gradient of stress versus strain after a linear response decreases before fracture and (ii) at high phase volume (φ > 28 %), a linear relation between stress and strain is observed nearer fracture. This behaviour is similar to that of agarose gels at high concentrations [15]. Increasing the phase volume of agarose microgels changes the true stress/strain behaviour of the mixed composites bringing it closer to that of the filler.

From Figure 1a and b, the apparent elastic modulus and the strain and stress at failure can be determined. Table 3 gives the values of the different parameters as a function of agarose microgel phase volume. The relative values of these parameters are plotted as a function of the phase volume of agarose microgels in Figures 2, 3, and 4 (EAg/ESa2 = 9). Increasing the phase volume of agarose microgel increases the apparent elastic modulus and the true stress at failure and decreases the true strain at failure. Composites with high phase volume of agarose microgel are thus stiffer and less deformable.

In contrast to the method of preparation of the composites by phase separation and remix reported in an previous article [2], this inclusion of agarose microgel in maltodextrin matrix allows the effect of phase volume on mechanical

<table>
<thead>
<tr>
<th>Agarose phase volume (w/w%)</th>
<th>Apparent elastic modulus (kPa)</th>
<th>True stress at failure (kPa)</th>
<th>True strain at failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>224.6 ± 7</td>
<td>17.1 ± 1.07</td>
<td>0.1306 ± 0.0098</td>
</tr>
<tr>
<td>7</td>
<td>291.1 ± 8.1</td>
<td>21.3 ± 0.87</td>
<td>0.1151 ± 0.0084</td>
</tr>
<tr>
<td>17</td>
<td>373.9 ± 10</td>
<td>25.2 ± 1.7</td>
<td>0.1038 ± 0.0084</td>
</tr>
<tr>
<td>28</td>
<td>599 ± 9.6</td>
<td>37.5 ± 1.13</td>
<td>0.098 ± 0.0025</td>
</tr>
<tr>
<td>35</td>
<td>765.5 ± 10</td>
<td>41.5 ± 0.6</td>
<td>0.0902 ± 0.0025</td>
</tr>
<tr>
<td>43</td>
<td>799.8 ± 10</td>
<td>47.1 ± 0.5</td>
<td>0.0892 ± 0.0038</td>
</tr>
<tr>
<td>53</td>
<td>1056.3 ± 54</td>
<td>73.4 ± 0.32</td>
<td>0.0843 ± 0.0055</td>
</tr>
</tbody>
</table>
properties of the mixed composites to be studied without an influence of the droplet size. However as noticed in the literature, this reinforcement effect observed may also depend on the phase modulus ratio and droplet size. The influence of these two parameters on the large deformation properties of maltodextrin/agarose composites are discussed in section 3.2 and 3.3.

3.2.1 Mechanical properties of agarose microgels and maltodextrin matrices

Agarose gels in excess water do not swell [12]. Therefore, the polymer concentration within the microgel is supposed to be the same as the bulk concentration of the solution used to make it, here 8%. Therefore, the apparent elastic modulus of the agarose microgel was approximated to be the same as 8% agarose, i.e. 2060 ± 165 kPa.

Large deformation measurements were conducted on the gelled maltodextrin matrix (the top phase obtained after centrifugation of the initial maltodextrin/agarose mixture). Table 4 summarises the apparent elastic modulus and the stress and strain at failure for the different matrices. In a previous study [1], a power law relation was established between the concentration and the apparent elastic modulus of maltodextrin gels: $E_{\text{app}} = 10^{-4.7c^{6.9}}$.

Assuming that the top phase is only composed of maltodextrin, the concentration of the maltodextrin gel matrix can be determined using this equation and the data from Table 4. Concentrations are very close to the estimated concentrations (see Table 5), which suggests both that solutions of maltodextrin do not diffuse into the agarose particles and that agarose microgels do not swell or shrink. From the previous data, the values of the modulus ratio for the different composites prepared can be calculated and are summarised in Table 6.

3.2.2 Effect of phase modulus ratio on large deformation properties of maltodextrin/agarose composites prepared at different phase volumes

The relative values of apparent elastic modulus, true stress and strain at failure as a function of phase volume for different phase modulus ratios are plotted on figure 2, 3 and 4, respectively. These figures show that increasing the modulus ratio between the agarose microgel and the maltodextrin gel matrix affects the reinforcement properties of agarose microgels. Composites with a small phase modulus ratio show a smaller relative apparent elastic modulus than those with a high phase modulus ratio. This difference is enhanced for high phase volumes of agarose microgel. The same effect of the phase modulus ratio on the true stress at failure can be observed. The effect of...
modulus ratio on the relative true strain at failure is less pronounced than on the two other parameters. At agarose microgel phase volumes lower than 0.2, the phase modulus ratio does not seem to influence the true strain at failure of the composites. When the phase volume of agarose microgels is increased, composites with the higher modulus ratio show the higher relative true strain at failure. These results are in accordance with Ring and Stanley [3], who showed that reinforcement by a deformable filler (sepharose) becomes less pronounced when the gel matrix (gelatin) is stronger.

3.2.3 Comparison of the experimental data with different models from the literature
A very extensive literature exists on the theory and use of particle fillers in polymeric materials [16 - 18]. Although the forces applied are much smaller than for plastics and metals, an engineering approach to model the elasticity and fracture of food model composites should be possible. A variety of approaches have been proposed to predict the mechanical properties of filled systems, ranging from curve fitting to sophisticated analytical treatments. Evaluation of semi-empirical relationships, which rely upon the determination of adjustable parameters by curve fitting techniques, is beyond the intent of this work. Rather, attention will be directed to those models for which the parameters can be fixed by other considerations so that the resulting relationships can be used predictively.

Models for the relative apparent elastic modulus
As the apparent elastic modulus is related to the shear modulus by the following equation:

\[ G = \frac{E}{2(1+\nu)} \]  

(7)
Models developed for the dynamic modulus should be applicable to the apparent elastic modulus. One of the most versatile and elaborate equations for a composite consisting of spherical particles in a matrix is due to Kerner [19]. This model was improved by Nielsen [20], who included the maximum packing fraction parameter. Here, the maximum packing fraction was estimated to be 0.7. The modified Kerner equation was written as follows:

\[ G = \frac{1+AB\phi_f}{1-B\phi_f} \]  

(8)

where

\[ A = \frac{7-5\nu}{8-10\nu} \]
\[ B = \frac{G_r/G_t - 1}{G_f/G_o + A} \]
\[ \psi = 1-e^{-\frac{\phi_m}{\nu_m}} \]

and

\[ G_r/G_t = \left( \frac{\phi_f-\phi}{\phi_m} \right)^{\frac{1}{\psi}} \]  

(9)

Figure 2a shows that Eq. 8 does not fit the data, either at low or high phase volume. The model first underestimates the data, then at high phase volume, it overestimates them. However, the model does capture the effect of modulus ratio quite well.

Two other models were considered, the Sudduth model [21] and the isostress model [22], with no better success (Figures 2b and c). Sudduth also developed an equation taking into account the maximum packing fraction using a generalised viscosity model based on the Smallwood equation [23]:

<table>
<thead>
<tr>
<th>Initial concentration of maltodextrin solution (%w/w)</th>
<th>Apparent elastic modulus ( E_{SA2} ) (kPa)</th>
<th>True stress at failure (kPa)</th>
<th>True strain at failure</th>
<th>( E_{SA2}/E_{SA2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>77.5 ± 3.6</td>
<td>6.9 ± 3</td>
<td>0.1128 ± 0.0086</td>
<td>27</td>
</tr>
<tr>
<td>35</td>
<td>225 ± 7</td>
<td>17 ± 1</td>
<td>0.1306 ± 0.0098</td>
<td>9</td>
</tr>
<tr>
<td>40</td>
<td>1000 ± 23</td>
<td>85 ± 4</td>
<td>0.1327 ± 0.0068</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 4 (above): Apparent elastic modulus and fracture properties of gelled top phases (maltodextrin matrices) at different concentrations, and phase modulus ratios for mixture of 8 % agarose microgel with maltodextrin at different concentrations \( E_{Ag}/E_{m} \), where elastic modulus of the agarose microgel is approximated to be 2030 ± 165 kPa. The errors were determined by repetition of the measurements five times.

Table 5:
Comparison of the estimated concentration of maltdextrin gel matrix due to dilution of mixing with the agarose microgel suspension, with the concentration calculated using equation relating the apparent elastic modulus.
where

$$G = \frac{(G_f / G_m)\phi_f (1-\phi_f)}{(8-10\phi_f)(G_f / G_m) + (7-5\phi_f)}$$

Concerning the isostress model [22], Frith and Norton [11] modified it to describe the behaviour of the apparent elastic modulus for agarose/gelatin and $\kappa$-carrageenan/gelatin composites replacing the volume fraction by the reduced volume fraction ($f / f_m$) and assuming an infinite value for the filler modulus. In this study, the filler modulus was not assumed to be infinite and the modified equation of the isostress was written:

$$\frac{G_f}{G_m} = \left[ \frac{1 - \phi_f}{1 - \phi_m} \left( \frac{G_f}{G_m} \right) \right]^n$$

Models for the fracture properties (relative stress and strain at failure)

Models for fracture properties of composites, such as the true stress and strain at failure, have been less studied than those for the apparent elastic modulus. Nielsen [24] proposed a model to describe the behaviour of the true stress at failure as a function of spherical filler phase volume for composites where particles and matrix adhere together. Ross-Murphy and Todd [4] provided the equation for a non adhesive composite. The equations are for composites with adhesive particles:

$$\frac{\sigma_f}{\sigma_o} = 1 - b\phi_f^n$$

(13)

where $S$ is the stress concentration factor introduced by Nielsen [24]. For simplicity, Ross-Murphy and Todd [4] assumed that $S = 1$. Figure 4 shows the behaviour of the relative true stress at failure as a function of phase volume for maltodextrin/agarose composites with different phase modulus ratios. Equations 11 and 12 are also plotted.

Equations 11 and 12 do not include phase modulus ratio or maximum packing fraction, therefore, they would not be expected to describe the data well. Of the two models, Eq. 12 for non adhesive particles describes best the behaviour of the true stress at failure as a function of agarose microgel phase volume. The Ross-Murphy model, assuming no adhesion between the particles and the matrix, fits the data for composites with a high phase modulus ratio very well indeed. This model is valid when there is a larger difference between the modulus of the filler and the one of the matrix. These results suggest that the weak interfacial strength already described by Loret et al. [22] controls the failure behaviour.

Concerning the true stress at failure as a function of filler phase volume, some authors [24 - 27] suggested that, assuming no adhesion between the matrix and the filler and no stress concentration effects, the relative stress could be described by a power law relation:

$$\frac{\sigma_f}{\sigma_o} = 1 - b\phi_f^n$$

(13)

where $\sigma_f$ and $\sigma_o$ are the strengths of the composite and the matrix, respectively, $\phi_f$ is the volume fraction of the filler and $b$ and $n$ are constants depending on the assumed particle shape and arrangement in the model composite. For a cubic matrix with uniformly dispersed spherical particles, Nicolais et al. [25] transformed Eq. 13 by:

$$\frac{\sigma_f}{\sigma_o} = 1 - 1.24(\phi_f^n)$$

(14)
These models predict that the true stress at failure decreases with increasing filler phase volume.

Another approach was proposed by Ross-Murphy and Todd [4]. As the relation of the relative stress at failure to the modulus and the relative strain at failure is:

\[ \frac{\sigma_r}{\sigma_o} = E_r \cdot e_r \]

using the Nielsen model for relative strain at failure as a function of phase volume (Eqs. 11 or 12, assuming \( S \) equals 1) and Landel equation [28] (Eq. 15) to describe the modulus as a function of phase volume, Ross-Murphy and Todd [4] developed new models to describe the stress at failure for adhesive and non adhesive composites. The Landel equation is:

\[ \frac{\sigma_r}{\sigma_o} = (1 - \phi_f)^{1/2} \]

Therefore, for adhesion between the filler and the matrix, the relative stress at failure can be defined for good interfacial adhesion by:

\[ \frac{\sigma_r}{\sigma_o} = (1 - \phi_f)^{1/2} \]

and for no interfacial adhesion by:

\[ \frac{\sigma_r}{\sigma_o} = (1 - \phi_f) \]

In the case of good interfacial adhesion, when \( \phi_f \) is less than 0.42, the relative stress at failure is lower than for the modified matrix, whereas for \( \phi_f > 0.42 \), it increases. Whereas, in the case of no interfacial adhesion, the stress at failure is always increased with \( \phi_f \) compared to the unfilled matrix. Since it appears that there is a weak interface between the filler and matrix in the maltodextrin/agarose composites [2], only the models for non adhesive particles will be considered.

Langley and Green [6] modified the Ross-Murphy model [4] to take into account the maximum packing fraction. They showed that data on Sephadex/whey protein gel composites with weak interaction between the components were better fitted by:

\[ \frac{\sigma_r}{\sigma_o} = \left(1 - \phi_f \cdot \phi_m \right)^{1/2} \]

Equation 17 and 18 are also plotted to show the effect of the introduction of the maximum packing fraction parameter in the model.

As can be seen in Figure 3, the Ross-Murphy model (Eq. 17) best describes the behaviour of the true stress at failure as a function of phase volume of agarose microgels for composites with low phase modulus ratio. In contrast, composites with high phase modulus ratio are better described by the Langley model (Eq. 18), although that at high phase volume this model overestimates the relative true stress at failure.

3.3 EFFECT OF MICROGEL SIZE ON LARGE DEFORMATION PROPERTIES OF MALTODEXTRIN/AGAROSE COMPOSITES

3.3.1 Size distributions of agarose microgels

Size distributions of the microgel suspensions are shown in Figure 5. In this figure, two sets of preparation are shown indicating the reproducibility of the process. Figure 10 shows that agarose microgels could be prepared with different sizes from 5 to 150 \( \mu \)m. In each case, the microgel suspensions show a broad monomodal distribution. The “no screen” agarose microgel suspension shows a broader distribution than the two others, and its reproducibility seems somewhat poorer.

3.3.2 Confocal microscopic observation of the maltodextrin/agarose composites with different agarose droplet sizes

For all samples, the composite microstructure was observed under confocal microscopy. Examples of the microstructures obtained for the
30% maltodextrin / 8% agarose composites made with different size of agarose microgels and at different phase volumes is given. The observations were identical for the composites prepared at lower and higher phase modulus ratio (35% maltodextrin / 8% agarose and 40% maltodextrin / 8% agarose).

Figure 6 shows that (i) increasing the phase volume of the agarose microgels, increases the number of droplets present in the samples and (ii) for each phase volume shown, composites with different droplet size could be obtained using the different agarose microgels prepared. The micrographs for composites prepared with “no screen” microgel show a broader distribution of droplet size. This is due to the broader size distribution of droplets in the agarose microgel suspension prepared (see Section 3.3.1).

3.3.3 - Effect of droplet size on mechanical properties of maltodextrin/agarose composites

The effect of droplet size on large deformation properties of maltodextrin/agarose composites was studied for composites at different phase volumes and modulus ratios and is shown on Figures 7, 8, and 9a, b and c for, respectively, the relative apparent elastic modulus, the relative true stress and strain at failure. For clarity, the behaviour of the relative true strain at failure as a function of droplet size and phase volume is shown on different graphs for different matrix concentrations (Figure 9a, b and c).

As shown in figures 7, 8 and 9a, b and c, the effect of droplet size on the mechanical properties of maltodextrin/agarose composites depends on the phase modulus ratio. For composites with low phase modulus ratio ($E_{Ag}/E_{SA2} = 2$) no effect of droplet size could be observed (in all cases, data for the three composites with different droplet size overlap), whereas an effect of droplet size could be seen for composites with higher phase modulus ratios ($E_{Ag}/E_{SA2} = 9$ and 27).

This observation confirms the previous observation that the filler has a larger effect if the phase modulus ratio is high. This could explain why some authors did not observe an effect of droplet size on mechanical properties [5, 7].

Moreover, the effect of droplet size on the mechanical properties of maltodextrin/agarose composites depends on the phase volume. For composites with $E_{Ag}/E_{SA2} = 9$, an effect of droplet size can only be observed (i) for the apparent elastic modulus at phase volume of agarose microgel higher than 0.3 and (ii) for the fracture properties, at phase volumes above 0.4.

For composites with higher phase modulus ratio ($E_{Ag}/E_{SA2} = 27$), the effect of droplet size is observed earlier (at phase volume higher than 0.2). This latter observation is in accordance with the observations of Ross-Murphy and Todd [4] and Langley & Green [6]. Ross-Murphy & Todd [4] showed that for the spherical glass/gelatin
composites, the size of the glass spheres has an effect only at phase volumes higher than 0.48.

For the present study, when an effect of droplet size on the mechanical properties of maltodextrin/agarose composites is observed the composites made with the largest droplets are the strongest. For example, for composites with 44% agarose microgels and high phase modulus ratio, the apparent elastic modulus of the composites with the smallest droplets is $284 \pm 4$ kPa, whereas it is $483 \pm 15$ kPa in presence of largest droplets. The true stress at failure increases from $19.5 \pm 0.7$ to $34 \pm 0.9$ kPa and the true strain at failure decreases from $0.1042 \pm 5.1 \cdot 10^{-3}$ to $0.0807 \pm 5 \cdot 10^{-3}$. This effect contradicts other studies of the effect of glass sphere sizes on the large deformation properties of gelatin and whey protein gels [4, 6]. These authors found that smaller particles increase the moduli of the composites most. There have also been attempts to correlate the stress at failure with the diameter of the filler particles, which show a linear relationship between either (i) the stress at failure and the reciprocal of the particle diameter (for particles lower than $0.12 \, \mu m$) [29] or (ii) with the reciprocal of the square root of the particle diameter [30]. They all found a decrease of the stress at failure with an increase of particle size, the opposite of the present case. Our conclusions are surprising and difficult to explain. One hypothesis could be that the differing size distribution of the microgels affects their packing in such a way as to make the larger microgels have a lower maximum packing fraction, and thus higher modulus.

4 CONCLUSIONS

Studies have been made of model food based composites consisting of two biopolymer phases, maltodextrin and agarose. The materials were produced by embedding agarose microgel particles in a maltodextrin matrix. In contrast to the more classic method of preparation of the composites used by Loret et al. [2], this process allows independent control of dispersed phase volume, particle size and the mechanical properties of either phase. The moduli and fracture properties of maltodextrin/agarose composites were measured in compression as a function of phase volume, phase modulus ratio and droplet size. The modulus of the filler (agarose microgel) was always higher than the modulus of the matrix.

Increasing the phase volume of agarose microgels in maltodextrin/agarose composites changes the general behaviour of the composites under large deformation, going from a strain softening behaviour similar to maltodextrin gel behaviour ($\phi < 28\%$) to a more linear behaviour similar to agarose gel behaviour for high concentrations. This increase of the phase volume of hard filler in a composite also reinforces the com-
posite by increasing its modulus and stress at failure and decreasing its strain at failure. This effect is more pronounced if the difference in modulus between filler and matrix is large. The effect of phase modulus ratio on the true strain at failure is less pronounced, with a bigger decrease of the true strain at failure only at high phase volume for composites with high phase modulus ratio.

Despite the multitude of models proposed to describe the behaviour of the relative modulus with phase volume, none was able to fit the data correctly. However, these models described the effect of phase modulus ratio well. For fracture properties, the Ross-Murphy models describe well the behaviour of the true stress at failure as a function of phase volume. If the filler modulus is much higher than that of the matrix, the behaviour of the true strain at failure can be well described by the simple relation: \( e = 1 - \phi \). The Ross-Murphy model (Eq. 17) describes relatively well the behaviour of the true stress at failure as a function of agarose microgel phase volume for maltodextrin/agarose composites with low phase modulus ratio. The introduction of the maximum packing fraction helps the description of the behaviour of the true stress at failure as a function of phase volume for composites with high phase modulus ratio.

By including agarose microgels of different sizes in maltodextrin gels of different strengths, the effect of droplet size on large deformation properties of maltodextrin/agarose composites was studied for different phase volumes of agarose microgels. The effect of droplet size on mechanical properties of maltodextrin/agarose composites depends on both the phase modulus ratio and the phase volume. It was found that higher the phase modulus ratio, the bigger was the reinforcement effect, i.e. higher apparent elastic modulus and the true stress at failure and smaller the true strain at failure. This effect was observed at lower phase volumes for composites with high phase modulus ratio. For the system with a small modulus ratio between filler and matrix, no effect of droplet size could be observed. Contrary to previous studies, the composites with the larger droplets had the bigger reinforcement effect. They were stronger and stiffer.

These observations are very relevant for the food industry. To develop products with new textures by mixing two biopolymer gels together, certain conditions need to be fulfilled. To see an effect of reinforcement of the filler, the stiffness of the filler needs to be higher than to the matrix. This modulus ratio between filler and matrix also determines the phase volume at which the filler must be included. The larger the phase modulus ratio, the less filler has to be incorporated to see a reinforcement effect.

**REFERENCES**


