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Sol–gel transition and gelatinization kinetics of wheat starch

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ABSTRACT

Rheological and optical microscopy experiments were conducted to monitor the sol–gel transition during gelatinization process of starch granules. During the gelatinization phenomenon, the grains grow and dissolve into the plasticizer leading to a drastic increase of the elastic modulus (G') and the loss modulus (G''), and to their crossover as a consequence of the formation of a physical gel. The kinetics of gelation were studied by oscillatory shear experiments and the influence of parameters such as temperature or volume fraction on the gelation process was investigated. The variation of the gel time with temperature for any composition of glycerol/starch suspension was predicted from the Dickinson model. The relaxation exponent ($n = 0.73$) was calculated by varying the frequency at constant volume fraction and temperature. The deduced value indicates that the gelation process is described by percolation theory. Apparent activation energies were estimated from the rheological data as well as from the optical microscopy data and were found to be nearly the same. At last the ability of two polyols to act as plasticizer was assessed and compared to that of glycerol.

1. Introduction

During the last decades, biopolymers and particularly starch-based materials showed growing interest in replacing oil-based materials. Their large availability and very low cost make thermoplastic starch one of the main renewable resource materials to be used as a raw material or to be blended with synthetic polymers. Compared to other natural polymers, their processing properties are very complex since they involve numerous physical processes and chemical reactions (water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization) (Liu, Xie, Yu, Chen, & Li, 2009; Septo, 2003). Gelatinization, which is closely connected to the other phase transitions, is the main phenomenon involved in the conversion process from starch to thermoplastic starch since it refers to the destruction of the crystalline structure that includes granular swelling, native crystalline melting and molecular solubilization (Liu et al., 2009).

Many techniques can be used to characterize phase transitions that occur during plasticization of starch. They can be divided into two main groups whether or not they involve shear stress. The techniques involving shear stress include DSC, X-ray diffraction, nuclear magnetic resonance, and microscopy with hot stage. DSC method was used by Yu and Christie to study starch transitions temperature as well as transition enthalpies (Yu & Christie, 2001). X-ray diffraction can be used to monitor the crystal structure, thus allowing to determine the relative amounts of crystalline and amorphous phases in starch. X-ray diffraction was accordingly used to study the internal structure of starch and thus to check the degree of gelatinization since starch granules possess both short-range and long-range orders (Cameron & Donald, 1993; Vermeylen et al., 2006a, 2006b). NMR can be used as a complementary method to provide information on the secondary structure and molecular order of a number of molecular systems (Cheetham & Tao, 1998). The last technique belonging to the first group is optical microscopy, which is a relevant tool for quantitative analysis of the modifications occurring in starch granule. Both photomicrographs and use of polarized light microscope to observe the loss of birefringence can be used for that purpose (Bhavesh & Koushik, 2006). The second group includes rheoscopy, rheometry and DMA. Rheoscope combines a rheometer with a video camera and allows measuring viscosity together with the observation of starch particles (Chen, Yu, Kealy, Chen, & Li, 2007). DMA is also an attractive tool to observe starch gelatinization by monitoring the variations in tan δ during heating (Xie, Yu, Chen, & Lin, 2008). The gelatinization process can be as well basically investigated by monitoring the rheological properties using a rheometer.

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Only few authors employed dynamic rheology to characterize the gelation process occurring during the gelatinization phenomenon. One should precise the difference between gelatinization and gelation since confusions might appear between those two terms. Gelatinization is a phase transition that corresponds to the destruction of the crystalline structure, granular swelling and molecular solubilization. The gelation process is a percolation process. It is a statistical concept related to the formation of long-range clusters of connected particles or pathways in random systems. In the studied system, the gelation results from the formation of macromolecular aggregates that connect to each other to form a sample spanning network. These two phenomena are closely related since gelatinization involves gelation phenomenon. Martin, Averous, and Della Valle (2003) studied the viscoelastic properties of plasticized wheat starch by means of an instrumented slit and a cylindrical viscometer dies attached to the end of a single-screw extruder. They confirmed the plasticizing role of glycerol and studied the influence of temperature and moisture content on the viscosity of starch. Singh, Singh, Kaur, Singh Sodhi, and Singh Gill (2003) used viscoelastic measurements to continuously monitor the variation of dynamic moduli during temperature and frequency sweep tests of various starchs coming from different botanical sources. They observed a strong increase in both elastic and loss moduli due to the degree of granular swelling that tends to fill the entire available volume of the system and a further decrease of the moduli due to the destruction of the gel structure during prolonged heating. They found that the rheological properties are strongly dependent on the variety of starch. The same authors carried out morphological, thermal, rheological and retrogradation studies on the properties of potato starch of different granule sizes (Singh & Kaur, 2004). Varying the granule starch size, they observed changes in G', G'' and $\tan\delta$ of starch suspensions as a function of temperature heating rates. As already observed in their previous study, they noticed an increase of several decades of the two dynamic moduli as a consequence of the swelling of starch granule. They also pointed out that the size fraction influences the induction temperature of the G' and G'' rise and the value of the final plateau. They revealed that the larger the particles are, the shorter the induction temperature is and the bigger the final plateau is. Finally, Hsu, Lu, and Huang (2000) used dynamic rheometry to characterize viscoelastic changes during heat-induced gelatinization of two types of rice starch suspensions. As the previous authors they monitored the variations of G' and G'' during temperature ramp, and time and frequency sweeps. They observed the crossover of G' and G'' characterizing the sol–gel transition and calculated the relaxation exponent ($n = 0.5$) from the frequency sweep tests.

A good understanding of the gelation process occurring during plasticization of starch is required. Rheology is a convenient tool to improve our understanding of this process since a physical gel is formed as the result of the penetration of the plasticizer into the starch granules. This penetration is responsible for the swelling, the solubilization and at last the interpenetration of the granules as well as a decrease of the amount of free plasticizer. Dynamic viscoelastic measurements carried out during gelatinization process in aqueous suspensions are mentioned in the literature, however, we were not able to found any work mentioning dynamic viscoelastic measurements carried out with other plasticizers. This is the reason why we took a particular interest in the gelatinization of starch using glycerol and two other plasticizers. Glycerol is the most common plasticizer used in the literature (Rodriguez-Gonzales, Ramsay, & Favis, 2004; Lin & Tung, 2009). The molecule includes three hydroxyl groups that can easily form hydrogen bonds with the hydroxyl groups of starch chains. Temperature, concentration and type of plasticizer are the main parameters controlling dynamic viscoelastic behavior. We studied the influence of these parameters on the sol–gel transition. The ability of polyethylene glycol 200 and propylene glycol to act as a plasticizer was estimated. We observed and measured the granule growth during gelatinization by use of optical microscopy.

2. Experimental

2.1. Materials

Wheat starch from Sigma–Aldrich at 10% moisture content was employed throughout the study. Moisture content having a great influence on gelatinization process of starch, it has to be controlled and kept constant all along the study. Starch powder was conditioning in the same manner during all the study and moisture content was verified by means of TGA (thermo gravimetric analysis) prior to each experiment and was found to be constant and close to 10%. Several plasticizers such as glycerol, propylene glycol and polyethylene glycol 200 (PEG 200—Mw = 200 g/Mol) were tested and compared. These plasticizers come from Sigma–Aldrich.

Both light diffraction measurements and scanning electron microscopy (SEM) were used to characterize the native starch particles. The particle size distribution were determined using a Malvern Mastersizer 2000 fitted up with a laser ($\lambda = 235$ nm) that enables measuring particle sizes in the range of 0.02–200 μm. The volume size distribution of wheat starch particles is centered at 80 μm and relatively dispersed (ranging from 1 to 200 μm). The SEM observations carried out on a SEM Hitachi S800 at 120 kV revealed non-spherical particles, not well defined and differing from a particle to another.

2.2. Rheology measurements

Rheology experiments were carried out on a controlled stress AR2000 (TA instruments) rheometer equipped with a Peltier module to regulate the temperature. In order to monitor the viscoelastic properties of starch suspension in the plasticizer during plasticization, 25 mm diameter parallel-plates in oscillatory mode were used. The thickness of the sample was set to 1 mm. The plasticizer and starch mixture was premixed manually and further injected with a syringe. The influence of volume fraction (ϕ_0) on plasticization was checked in the range 0.15–0.25. The volume fraction is defined by the following equation (1):

$$\phi_0 = \frac{(m_{\mathrm{solid}}/\rho_{\mathrm{solid}})}{(m_{\mathrm{solid}}/\rho_{\mathrm{solid}}) + (m_{\mathrm{liquid}}/\rho_{\mathrm{liquid}})} \qquad (1)$$

with $\rho_{\mathrm{solid}} = 1.5\ \mathrm{g\,cm^{-3}}$ and ρ_{liquid} equal to 1.26, 1.036 and $1.12\ \mathrm{g\,cm^{-3}}$ for glycerol, propylene glycol and PEG 200, respectively.

The linear viscoelastic domain of the samples was first determined by stress sweep experiments. Temperature sweep tests at constant heating rate ($5\,^{\circ}\mathrm{C\,min^{-1}}$) and frequency ($6.283\ \mathrm{rad\,s^{-1}}$) were carried out to determine the gel temperature. The storage and loss moduli varying over several order of magnitudes, the imposed stress during each experiment had to be continuously adjusted. The stress was initially set to 0.5 Pa to provide a detectable response in the liquid state, and further progressively increased to reach 50 Pa at the end of the experiment in the solid state. This stress modification procedure was also applied to the other experiments of this study such as isothermal time sweep tests.

2.3. Optical microscopy observations

The swelling of the granules during the sorption and the gelatinization process has been monitored by means of an optical microscopy (Leitz Wetzlar) equipped with a video camera Sony (Exwave HAD) and a heating plate Mettler FP52 with a programmed cooling/heating apparatus Mettler FP5. The surface of the granules during isotherms was measured with the Linksys software.

3. Results and discussion

Winter et al. chose to use the term "physical gelation" in the widest possible sense for polymeric systems which undergo liquid–solid transition due to any type of physical mechanism that is able to connect the polymer into large scale structures. These mechanisms are quite diverse:

(a) Polymers lose their chain flexibility near their glass transition temperature and molecular motion correlates over longer and longer distances.
(b) Liquid crystalline polymers at their transition from nematic to smectic state gradually lose their molecular mobility.
(c) Suspensions in which the filler particles aggregate into sample spanning complexes.

The liquid–solid transition of these systems seems to present the same features as for chemical gelation, namely divergence of the longest relaxation time and power law spectrum with negative exponent (Winter & Mours, 1997). In our case, the gelatinization of starch in plasticizer is considered as the last instance, since the starch granules is playing the part of filler in suspension in the plasticizer. The diffusion of the plasticizer into starch granules generates the growth, the dissolution and finally the aggregation or interpenetration of the particles. Since a physical gelation is appearing during the plasticization due to the formation of macromolecular aggregates that connect into a sample spanning network, a good way to observe this phenomenon is to monitor the viscoelastic properties of the suspension.

3.1. Influence of volume fraction on viscoelasticity properties

Time sweep measurements at different volume fractions (ranging from 0.15 to 0.25) at constant temperature ($T = 60\,^\circ C$) and frequency ($\omega = 6.283$ rad s^{-1}) using glycerol as the plasticizer were carried out to characterize the influence of the volume fraction on the sol–gel transition. The gelation process (Fig. 1) is directly influenced by the volume fraction. As expected, the sol–gel transition appears earlier when the volume fraction increases. The final plateaux of the elastic and loss moduli are reached more rapidly and are higher when the volume fraction rises. The increase of the level of the plateau can be explained at higher volume fraction by a larger number of particles interpenetrating and resulting in a more packed network.

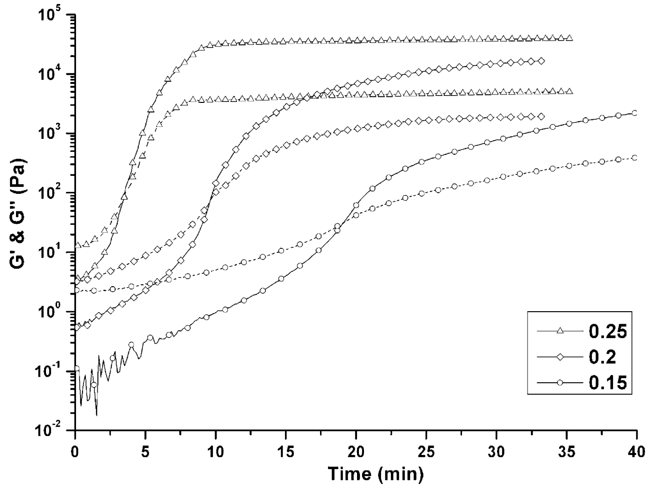


Fig. 1. Variation of G' and G'' versus time at different volume fractions (0.15–0.25) at constant temperature ($T = 60\,^\circ C$) and frequency ($\omega = 6.283$ rad s^{-1}).

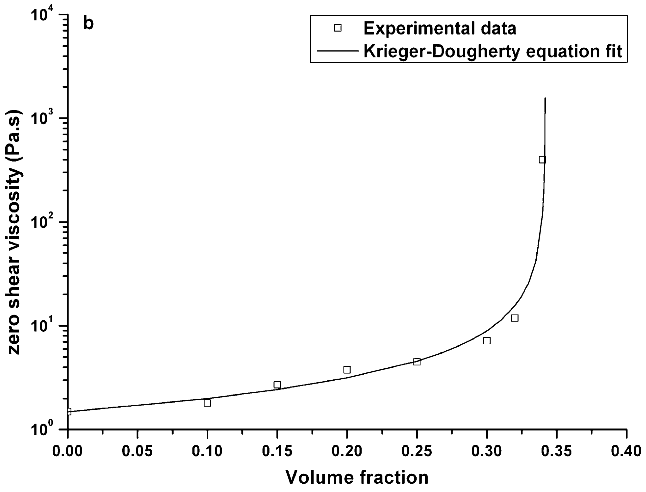


Fig. 2. Variation of the zero-shear viscosity versus volume fraction along with the Krieger–Dougherty equation fit (straight line).

SEM observations at different scales of gelatinized starch after isothermal measurements at 50 and 60 °C revealed that the starch granules were totally interpenetrated and formed a three-dimensional network. These results confirm the good ability of glycerol to diffuse into the starch grains, leading to their swelling, their percolation and finally their interpenetration (gelatinization).

To determine the maximal packing fraction (Φ_m) in the suspension that corresponds to the maximum volume of solid particles that can fill a given volume of fluid, rheological experiments and frequency sweep tests were carried out. By sweeping the frequency from 100 to 0.01 rad s^{-1}, we observed the variation of the complex viscosity as a function of volume fraction in order to determine the zero-shear viscosity. For volume fraction varying from 0.1 to 0.34, the absolute complex viscosity is almost Newtonian and a poor shear thinning behavior is observed. Beyond a concentration of about 0.34, the zero-shear viscosity clearly diverges toward infinity meaning that we are at the sol–gel limit and close to Φ_m. For larger volume fractions, the zero-shear viscosity cannot be determined anymore, and the viscosity varies as $\omega^{-\beta}$ with $\beta \approx 1$. This indicates the onset of yield stress type behavior. The Krieger–Dougherty equation (Krieger & Dougherty, 1959) is an empirical expression that describes the variation of the zero-shear viscosity as a function of volume fraction for suspensions of particles. It is expressed as follows:

$$\eta_0 = \eta_s \left(1 - \frac{\Phi}{\Phi_m}\right)^{-[\eta]\Phi_m} \qquad (2)$$

where η_0 is the zero-shear viscosity of the suspension, η_s is the viscosity of the solvent, Φ_m is the maximal packing fraction, $[\eta]$ is the intrinsic viscosity and Φ is the solid volume fraction. This correlation explains the increase of the viscosity with the increase of the volume fraction. As the volume fraction of solids in the system increases, the particles become more closely packed together, impeding them to move freely. Thus, particle–particle interactions increase and resistance to flow (viscosity) rises. As the volume fraction nears maximum for the sample, viscosity rises very steeply.

The zero-shear viscosity values obtained from the previous frequency sweep tests are reported in Fig. 2 as a function of solid volume fraction. As expected, the zero-shear viscosity increases progressively by raising the solid fraction volume and tends toward infinity when approaching the maximal packing fraction. By fitting the Krieger–Dougherty equation to the experimental data, we

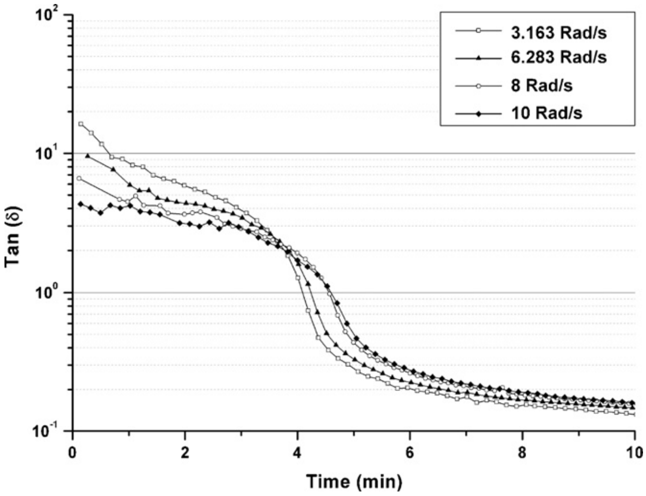


Fig. 3. Variation of the loss tangent delta (tan(δ)) versus time at constant temperature ($T = 70\,^\circ$C) and volume fraction ($\Phi_0 = 0.15$) for different frequencies.

were able to determine both $[\eta]$ and Φ_m. We found $\Phi_m = 0.341$ and $[\eta] = 2.5$. The value of the intrinsic viscosity corresponds to the famous Einstein coefficient that corresponds to a model of rigid spheres without any electrosteric interaction. The above mentioned maximal packing fraction is quite low for a suspension whose value usually ranges from 0.58 to 0.63 assuming hard spheres. This may probably result from the variable shapes of the starch granules.

3.2. *Influence of temperature on the gelatinization kinetic*

First, Tung and Dynes (1982) suggested that the gel point could correspond to the crossover of G' and G''. This definition was not rigorous since the storage and the loss modulus crossover depends on frequency. More recently, Winter and Chambon (1986) introduced that at the gel point for crosslinking polymer, the critical gel was shown to present a power law relaxation modulus $G(t)$:

$$G(t) = St^{-n} \tag{3}$$

where S is defined as the gel strength, and n is the relaxation exponent that is physically restricted to $0 \leq n < 1$. This exponent must be lower than unity to ensure that the zero-shear viscosity is not diverging at the gel point. The case $n = 0$ corresponds to a Hookean solid behavior. The relaxation exponent is not a universal value, as one might expect for a property at a critical point. The critical gel is generally very soft and fragile when the relaxation exponent is large (n close to 1) and the front factor S is small (Richter, 2007). While small n and large S correspond to a stiff critical gel. As a consequence of the power law behavior, the storage modulus (G') and the loss modulus (G'') are expressed as:

$$G'(\omega) = \frac{G''(\omega)}{\tan(n\pi/2)} = \Gamma(1-n)\cos\left(\frac{n\pi}{2}\right) S\omega^n \tag{4}$$

The phase angle between stress and strain, δ, is independent of frequency but proportional to the relaxation exponent at the gel point:

$$\delta = \frac{n\pi}{2} \tag{5}$$

This gel point feature is shown in Fig. 3. As a consequence of the formation of an elastic, three-dimensional polymer network, the increase of G' is larger than that of G'' and thus the tangent delta is decreasing progressively with time. Viscoelasticity experiments were carried out at several frequencies (ranging from 3.163 to 10 rad s^{-1}) at constant temperature ($T = 70\,^\circ$C) and volume fraction ($\Phi_0 = 0.15$) to characterize the independence of tan(δ) with frequency at the gel point. Thus, as shown in Fig. 3, the gel point can be determined from the crossover of the different curves. In this case the gel time is equal to 3.7 min and tan(δ) ≈ 2.2 resulting in a relaxation exponent approximately equal to 0.73. Dynamic scaling based on percolation theory does not yield unique results for the dynamic exponents as it does for the static exponents (Winter & Mours, 1997). Several models can be found that result in different values for the relaxation exponent (n), the viscosity exponent (s) and the elastic modulus exponent (z). These models use either Rouse and Zimm limits of hydrodynamic interactions or electrical network analogies. De Gennes proposed an analogy between the divergence of the viscosity and the divergence in the conductivity in a random superconductor-resistor network (Richter, 2007; De Gennes, 1978). If the De Gennes values of the exponents z ($z = 1.94$) and s ($s = 0.75$), obtained from simulations are substituted into $n = z/(z + s)$, one obtains $n \approx 0.72 \pm 0.02$ (Martin & Adolf, 1991). The relaxation exponent obtained previously ($n \approx 0.73$) is very close to that obtained by De Gennes, meaning that this gelation process is described by percolation and supports De Gennes analogy between the viscosity of the gelation bath and percolating superconductivity. Pishvaei, Graillat, McKenna, and Cassagnau (2005) made an analogy between the percolation theory and the Krieger–Dougherty theory. They assumed: $s \equiv [\eta]\Phi_m$. Using the values of $[\eta]$ and Φ_m previously deduced from the Krieger–Dougherty equation, we obtain $s = 0.85$. This value is relatively close to the one of De Gennes ($s = 0.75$).

Knowing the value of n, one can calculate from equation (4), the gel strength (S), which is here equal to 1.4 Pa S^n. The value of the relaxation exponent relatively close to 1 and the small value of the gel strength indicate that we are in presence of a soft critical gel.

Temperature is one of the main parameters controlling diffusion mechanisms. Indeed, migration of small molecules will extensively depend on thermal agitation. As a general rule, as temperature rises, glycerol molecules will better diffuse in starch granules leading to a faster formation of the physical gel. Thus at a constant volume fraction ($\Phi_0 = 0.15$), dynamic viscoelastic measurements were carried out in order to observe the influence of temperature on the sol–gel transition. Isothermal experiments were carried out for temperatures ranging from 60 to 90 °C. The trends of the curves are similar for all temperatures. As seen in Table 1, at all temperatures, the elastic and viscous moduli reach final values that are very close, meaning that the final network is slightly dependent on temperature. In contrast, the sol–gel transition which occurs at the gelation time determined by assuming that $\tan\delta = G''/G' = 2.2$ was constant for each temperatures, is greatly influenced by the temperature. At the sol–gel transition, the material no longer behaves as a liquid but not yet as a solid. The gelation process is much slower while decreasing temperature and thus the plateau region requires longer curing time to be reached. At 60 °C the gelation time is about 16 min while at 90 °C it is only 30 s. All the gelation times (t_{gel}) are summarized in Table 1. The values of the dynamic moduli are close to15 Pa. These results are in agreement with the work of Boudhani, Lainé, Fulchiron, and Cassagnau (2007) who carried out the same kind

Table 1
Obtained gelation time (t_{gel}) and dynamic moduli at different temperatures.

Temperature (°C)	t_{gel} (min)	Dynamic moduli at t_{gel} ($G' = G''$, Pa)
60	16.2	15
65	9	13
70	3.7	18
75	1.9	15
80	1.4	16
90	0.5	19

of experiments on PVC plastisols. They found, as we did, a strong dependence of the time of gelation on temperature for PVC particles in suspension in a plasticizer.

As previously described, the gelation time is greatly influenced by temperature. When the gelation is kinetically controlled, apparent activation energy of gelation E_a can be deduced from the integration of the following kinetic Arrhenius equation:

$$t_{\mathrm{gel}} = C \exp\left(\frac{E_a}{RT}\right) \tag{6}$$

where C is the pre-exponential factor, R the perfect gas constant and T the absolute temperature. The gelation times were determined from the crossover of the elastic and viscous moduli of the isothermal experiments by assuming that the relaxation exponent was constant as a function of temperature. As expected the variation logarithmic of t_{gel} versus the inverse of the absolute temperature is linear for each volume fractions.

To predict the t_{gel} variation as a function of temperature for any composition of the system, one can re-scale the Y-axis using a shift factor to obtain a master curve. Boudhani et al. (2007) already established a master curve from the variation of t_{gel} versus $1000/T$ for PVC plastisols. In their work they used the following shift factor (7) obtained from the Dickinson model (Dickinson, 1997):

$$f(\Phi) = \left[\left|\frac{(\Phi_m/\Phi)^{d_f/(3-d_f)} - 1}{(\Phi_m/\Phi_{\mathrm{ref}})^{d_f/(3-d_f)} - 1}\right|\right]^{3/d_f} \tag{7}$$

where Φ_m is the maximal packing fraction previously calculated by means of the Kriege--Dougherty equation, Φ_{ref} is the reference volume fraction, Φ is the volume fraction and d_f is the fractal dimension that measures how opened or packed a structure is. d_f can be calculated from the relaxation exponent (n) with the following equation (8):

$$n = \frac{d(d+2-2d_f)}{2(d+2-d_f)} \tag{8}$$

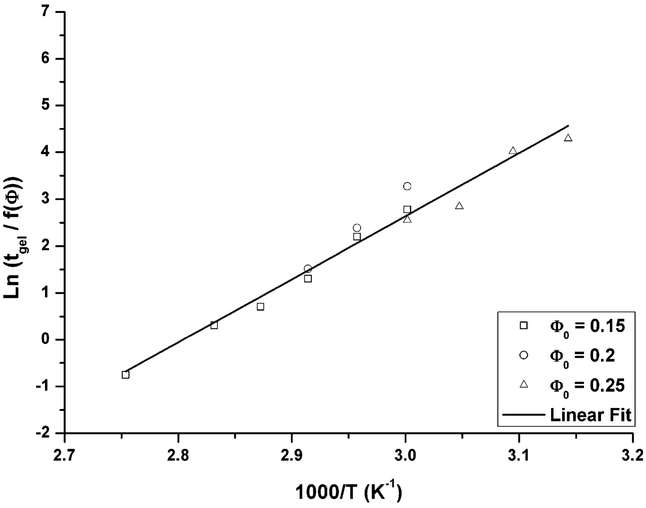
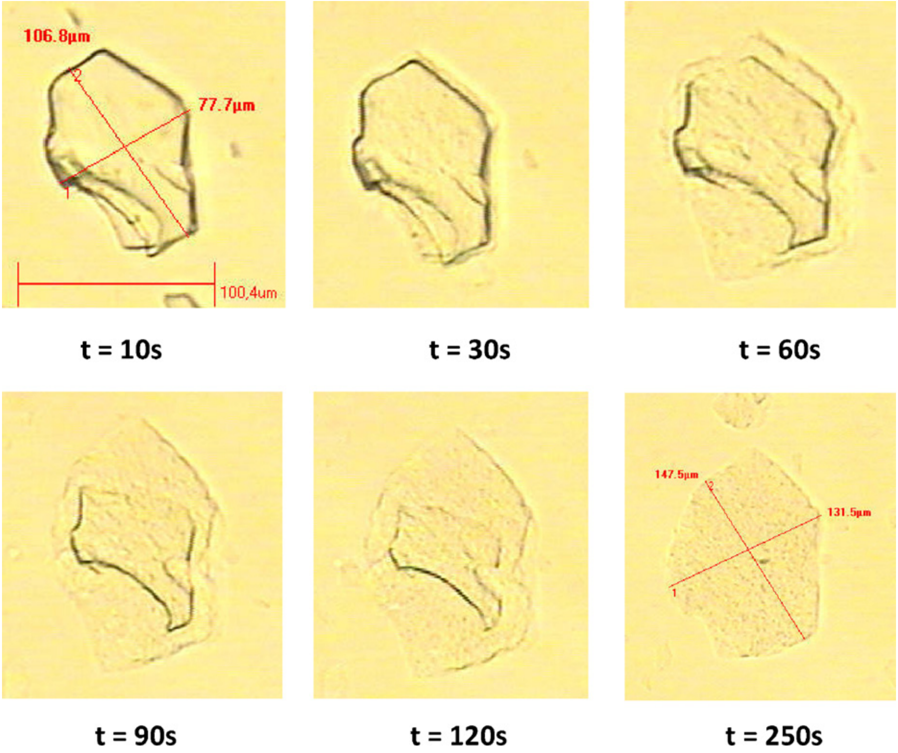


Fig. 4. Master curve of the variation of t_{gel} versus the inverse absolute temperature at different volume fractions (0.15, 0.2 and 0.25).

where d is the space dimension ($d = 3$). In our case with $n = 0.73$, we found $d_f = 1.69$. Knowing this fractal dimension, one can calculate for each concentration the shift factor ($f(\Phi)$) and plot the master curve. Fig. 4 shows the shifted data points with $\Phi_{\mathrm{ref}} = 0.15$ fitted by a straight line. Using a linear regression we were able to calculate the apparent activation energy and the pre-exponential factor that we found respectively equal to $E_a = 112\,\mathrm{kJ\,mol^{-1}}$ and $C = 4.7\,\mathrm{e}^{-17}$ min.

In addition to the rheological experiments, the kinetics of gelatinization were monitored using an optical microscope. During an isothermal heating, the growth of an isolated grain in glycerol was observed. As seen in Fig. 5, the different phases (i.e. sorption and gelatinization) of the plasticization are observable: first the outer layer of the granule starts to dissolve in the plasticizer and the grain swells progressively until the total dissolution is reached.



t = 10s

t = 30s

t = 60s

t = 90s

t = 120s

t = 250s

Fig. 5. Optical microscopy observations of the gelatinization of an isolated grain at 90 °C.

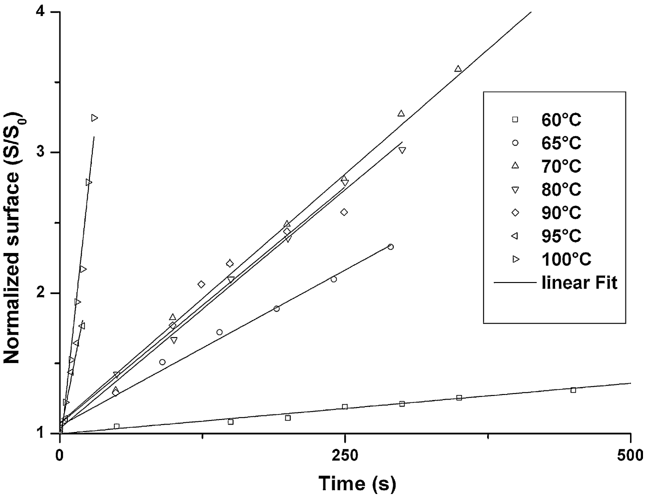


Fig. 6. Variation of the normalized surface of the grain versus time during isothermal heating.

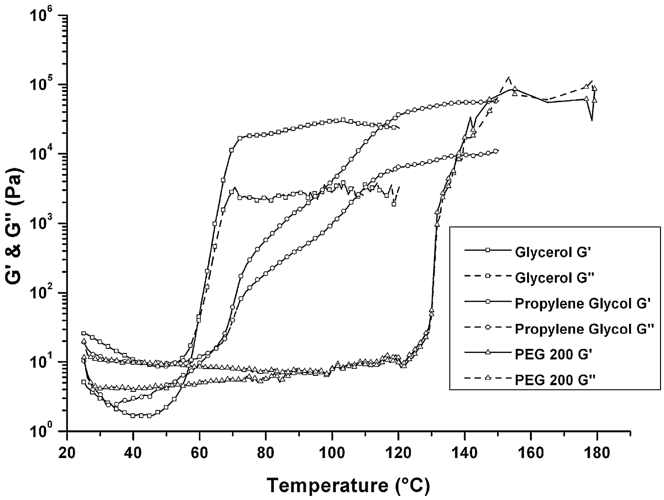


Fig. 7. Evolution of the complex shear modulus versus temperature at constant volume fraction ($\Phi_0 = 0.3$) and frequency ($\omega = 6.283$ rad s^{-1}) for different plasticizers.

These pictures were recorded during an isotherm at 90 °C. In less than 250 s, the grain grows from an initial size of 107 μm long and 78 μm large to a final size of 148 μm long and 132 μm large.

The same experiments were carried out for temperatures ranging from 60 to 100 °C. The variations of the normalized surfaces of each grain during isotherms are plotted against time in Fig. 6. The growth rate of the grains can be easily modeled by a linear regression. As expected and in agreement with the rheological results, the granule growth rate considerably increases with temperature. While at 60 °C, the growth rate of the granule is relatively slow, at higher temperatures the growth rate considerably increases and at 100 °C the granule swells in only a few seconds.

In the same way used to calculate an activation energy from the rheological results, it can be deduced from the variation of the granule surface as a function of temperature. From the linear variation of the surface with time (Fig. 6), we are able to determine the slope of each curve and to plot it versus 1000/*T*. The activation energy is deduced from the slope of the straight line fitted to the experimental data. We found an activation energy equal to approximately 100 kJ mol^{-1}. This result is in accordance with the activation energy previously deduced from the rheological results ($E_a \approx 110$ kJ mol^{-1}). We can notice that an activation energy was also deduced from the variation of the volume with time, and found to be equal to 93 kJ mol^{-1}, which is a value close to the two others.

3.3. Comparison of glycerol with two others plasticizers

Generally, a molecule that possesses hydroxyl groups like glycerol should be able to disrupt intermolecular hydrogen bonds between starch chains. We selected two polyols to be compared with glycerol: the first one is propylene glycol ($M_w = 76$ g mol^{-1}), which presents a molecular structure very close to glycerol, and the second one is PEG 200 ($M_w = 200$ g mol^{-1}), which has a larger molar mass as compared to the two others. As in the previous part of this study dealing with gelatinization of starch with glycerol, both rheological and optical microscopy experiments were carried out. The elastic and loss moduli of evolving suspensions of starch into the plasticizers were monitored during a temperature ramp (5 °C min^{-1}) as shown in Fig. 7. All the curves start from an initial modulus which is approximately the same, and after a quick increased characteristic of the gelatinization process, reach a final plateau. This means that propylene glycol and polyethylene glycol as well as glycerol act as plasticizer for starch. But if all the curves present the same trends, the temperature of gel depends on the nature of the plasticizer. While the temperature of onset of gelation is approximately equal to 50 °C in the case of glycerol, they are 60 and 120 °C for suspensions using respectively propylene glycol and polyethylene glycol 200. This difference in induction temperature between glycerol and propylene glycol can be explained by the difference of number of hydroxyl groups in each molecule. As propylene glycol has a smaller molar mass, it should better diffuse in granule starch, but hydrogen bonding also plays a major role. Hydrogen bonding is a major structural element in the starch granule and hence is also a major determinant for the effectiveness of a plasticizer of starch (Perry & Donald, 2000). Glycerol possesses three hydroxyl groups on his backbone while propylene glycol has only two. That is why the onset of gelation is delayed for the propylene glycol. In this case the hydrogen bonding has more influence than molar mass. Concerning the polyethylene glycol, the molar mass plays a major role on induction temperature compared with the hydrogen bonding. Its high molecular weight considerably increases this temperature since the polyethylene glycol molecules diffuse slowly into the starch granules. The slope of the curve during the sol–gel transition that characterizes the gelatinization rate of starch granules varies significantly according to the nature of the polyol. Whereas the gelatinization process takes place rapidly in the cases of glycerol and polyethylene glycol, it is slower for propylene glycol. The slope of the corresponding curve in Fig. 7 is less steep for this latter molecule.

Suspensions including the two other polyols were also observed by optical microscopy. The total solubilization previously observed in the case of glycerol is no longer observed even at high temperature ($t_{max} = 160$ °C). A very slight swelling of the granules was only detected in this case. This shows that the ability of propylene glycol and polyethylene glycol to plasticize starch is not as good as that of glycerol. Temperature is not a relevant parameter to lead to plasticization phenomenon in the case of propylene glycol and polyethylene glycol, and as a consequence shear experiments are required.

4. Conclusion

To characterize the sol–gel transition occurring during the gelatinization of starch using glycerol as a plasticizer, dynamic rheology and optical microscopy were used. Dynamic rheology turned out to be a relevant tool to monitor the modifications of starch particles in suspension in glycerol up to the formation of a physical gel. The volume fraction was found to have a substantial influence on the sol–gel transition. An increase of this parameter reduces the gel time and enhances the level of the final plateau. The maximal packing fraction was estimated by fitting the Krieger–Dougherty equation on the experimental zero-shear viscosity plotted as a function of the volume fraction. A value of 0.341 was thus determined.

As expected, the rate of gelation process increases with temperature. By means of isothermal frequency sweep tests, the relaxation exponent was determined 0.73. This value is indicative of a gelation process controlled by the percolation. The influence of temperature was investigated as well. Temperature plays a major role in the gelatinization of starch granule since it greatly influences the diffusion of the plasticizer into the grains. The gelation process being kinetically controlled, an apparent activation energy was estimated ($E_a \approx 110\,\mathrm{kJ\,mol^{-1}}$). The variation of t_{gel} for any composition of glycerol/starch suspension was described using the Dickinson model.

Optical microscopy was used as a complementary tool to monitor the granule growth during the gelatinization process. During isothermal heating, the surface of the granules was continuously observed with a video camera thus allowing us to determine the variation of growth rate as a function of temperature. As in the case of rheological investigations, an apparent activation energy was estimated ($E_a = 100\,\mathrm{kJ\,mol^{-1}}$) and was found to be very close to the one deduced from rheological data ($E_a \approx 110\,\mathrm{kJ\,mol^{-1}}$). Finally, the ability of two polyols (propylene glycol and polyethylene glycol) to act as a plasticizer was estimated and compared with the one of glycerol. Both propylene glycol and polyethylene glycol can act as starch plasticizer. Their gelatinization rate and induction temperature are nevertheless quite different as compared with glycerol. While the increase of induction temperature observed in the case of propylene glycol can be explained by the presence of hydrogen bonding as a result of a reduced number of hydroxyl groups in the molecule, the same phenomenon observed in the case of polyethylene glycol is induced by its high molecular weight as compared to glycerol and propylene glycol thus impeding its diffusion.

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