COMPOSITE MATERIALS CONTAINING BIODEGRADABLE POLYMERS –RHEOLOGICAL BEHAVIOR OF THE STARCH PASTE-

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Abstract
The use of composite materials based on biodegradable polymers in various fields, becomes increasingly frequent. This is due to the significant advantages they offer, including their lightness and strength. However, their employment requires a control of their mechanical behavior. To this end, we will expose in this work, a polysaccharide like a biodegradable polymer and who can be used to work out materials nanocomposites, and the most known polysaccharide and most representative at the present time, it is the corn starch. Then we determine his rheological behavior in experiments (viscometer with coaxial cylinders) and with the use of the various air-gaps, one notes the influence of the size of the air-gap on the behavior like on the rheological parameters of the starch paste. Finally we represent the found results which confirm the work already obtained by other researchers in the field.

1 Introduction

While mixing or not with other natural substrates, raw material of vegetable origin most usually used and which makes it possible moreover to replace materials coming from oil is the starch, the use as a material became a subject of topicality with an aim of reducing the pollution generated by polymers of petrochemical origin. The starch is a raw material of vegetable origin. Most usually used is the corn starch. This one has the advantage of being renewable, biodegradable and available in unlimited quantity.

1.1 Presentation of the starch

The starch and starch are the two names given to the same substance which one extracts, that is to say cereal seeds of corn, corn, rice, the product takes the starch name then, that is to say certain tubers, roots, stems, potatoes, manioc, sagou... etc, it takes the starch name. On the industrial level, the most used raw materials are the corn and the potato. In this work, one chose to work on corn.

1.1.1 Physicochemical properties of the starch grains

The starch, like very produced, of the physical properties and chemical which are clean for him. Several factors come into play:

- Solubility: The starch is insoluble in water and organic solvents. In suspension in water and with a light mechanical agitation one obtains starch milk, unstable suspension but which becomes a thickening colloidal solution commonly called starch paste after the heating from 70°C (Figure 1).

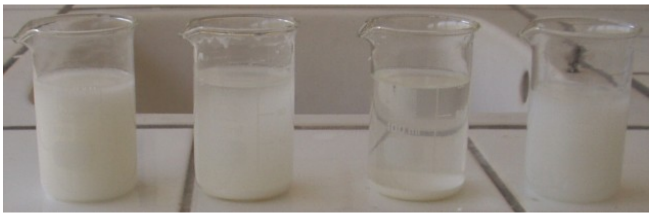

Figure 1. Corn starch to a concentration of 5% in various times: - from left to right - agitation at once, after 15 mn: no homogeneous, after 1 H: biphasic medium, cooks with 95°C: starch paste, [1].

- Temperature: With ambient temperature, the starch in water reacts in a strange way; it forms a no homogeneous mixture, which starts to gel gradually starting from 50°C. Gelation represents the swelling of the grains of native starch in the presence of water, heat and molecular agitation.
- Granular dimension: The size of the starch granules contributes to its viscosity, the speed of gelatinization and the temperature of gelatinization. The larger the granule is, the more viscosity becomes significant.
- Thermal action: It changes the color and the taste of the starch by dextrinisation.
- Chemical action and enzymatic: The acids involve hydrolysis partial of the starch which leads to the dextrin formation. Formed freezing is less thick. This hydrolysis is accelerated by an increase in temperature.

2 Properties rheological of the starch

Within the framework of this study, it is the rheological behavior of the starch pastes which interest us (not very high temperature and water excess) and not that of the starches in a molten state (high temperature and under weak conditions of hydration).

2.1 Rheological behavior of the starch pastes

This behavior could be generally described by curves according to the equation of Ostwald-in Waele, [2], [3].

$$\tau = K \times \left(\dot{\varepsilon}\right)^n \quad \textbf{(1)}$$

where: (τ) is the Shear stress, (K) is the Consistency of a fluid of Ostwald, ($\dot{\varepsilon}$) is the Gradient speed or speed of shearing, (n) is the Index of flow of a fluid of Ostwald.

The index of the behavior of the flow informs us about the variation compared to the behavior Newtonian; it is lower than 1 when the behavior is rheofluidifiant.

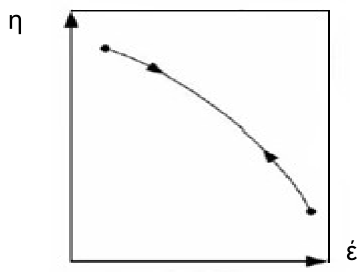

Figure 2. Influences variation the speed of shearing on the viscosity of the starch pastes. Rhéofluidifiant behavior [4].

Figure 2 shows that the native starches are very sensitive to shearing, and in general the result is a reduction in viscosity. The various chemical modifications of the starches improve their resistance to the industrial conditions of treatment. Thus the reticulation reinforces the strength to the high temperatures of the processes of sterilization like to significant shearing, while stabilization reduces the formation of the gel, retro gradation and synaeresis. Generally, the starch pastes have a rhéofluidifiant behavior (Pseudo plastic).

2.2 Properties of the starch pastes

One of the index properties of the starch pastes is the retrogradation, caused by two effects:

- destruction of the inflated starch grains;
- The molecular degradation of the chains of the polymer which is done under certain conditions of temperature and shearing.

If one gives up a starch paste at the ambient temperature, it becomes turbid then it is formed a precipitate or a gel, according to the concentration. This last thus obtained shows a diagram of diffraction to x-rays and redissolves itself only at temperatures higher than 120-130°C, even 160°C.

3 Experimental Study

3.1 Description of the measuring apparatus

The apparatus used for this study is a viscometer of Brookfield, rotational with coaxial cylinders of the model Visco Tester VT5R; it is designed in such manner to provide us the number of revolutions at the same time as well as the couple. The viscosity of the studied substance is also provided by the measuring apparatus.

3.2 Material used

The material used is a natural polymer. The corn starch employed, provided by the starch industry of Maghnia [5], was used for the preparation of the starch paste.

4 Analyze and interpretation of the results

The treatment and the analysis of the experimental results provided by the measuring apparatus for the choice of the model as well as the parameters of the most representative model were done by means of software established for this purpose.

4.1 Variation of the shear stress according to the gradient speed

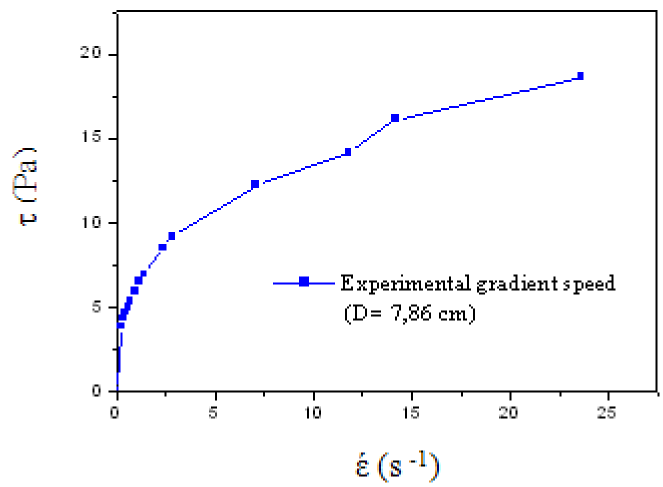

Figure 3. Variation of the shear stress according to the gradient speed –Starch paste of corn with 5% and 95°C in a bécher of Ø = 7,86 cm, [1].

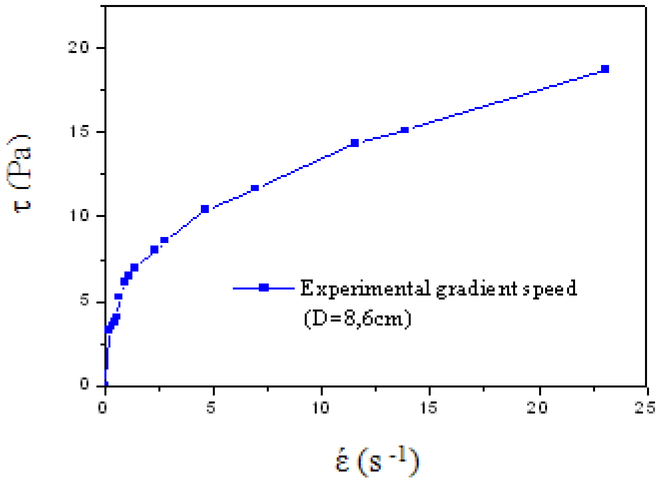

Figure 4. Variation of the shear stress according to the gradient speed –Starch paste of corn with 5% and 95°C in a bécher of Ø = 8,6 cm, [1].

Figures 3 and 4 represent the variation of the shear stress according to the gradient speed of the starch paste of corn to a concentration of 5% and a temperature equal to 95°C, in béchers of various diameters.

4.2 Modeling of the experimental results

To determine the rheological model of the starch paste of corn, one uses software worked out for this purpose. The analysis of the experimental points by this software enabled us to determine the rheological model nearest to the studied solutions.

Figures 5 and 6 represent the superposition of the curves obtained starting from the experimental points of the starch paste of corn and the curve of the most representative model obtained starting from the software, [6].

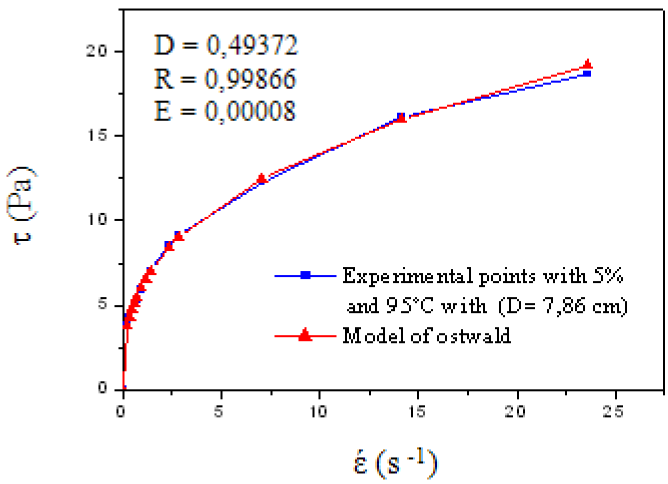

Figure 5. Comparison enters the experimental points and the model of Ostwald –Starch paste of corn with 5% and 95°C in a bécher of Ø = 7,86 cm, [1].

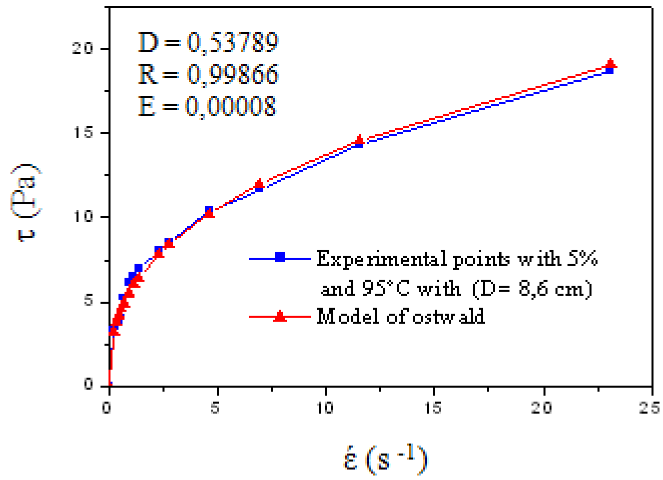

Figure 6. Comparison enters the experimental points and the model of Ostwald –Starch paste of corn with 5% and 95°C in a bécher of Ø = 8,6 cm, [1].

It is clear that the experimental points are almost confused with the points given by the model analyzed as illustrated on figures 5 and 6.
The rheological model of the starch paste of corn nearest to the experimental points is that of Ostwald. This model was already met in [7] and [8].
The variation of the air-gap did not modify the rheological behavior of the starch paste. This behavior is always pseudo plastic.
The model of the fluid of Ostwald is governed by a law of power of the form:

$$\tau = K.\dot{\varepsilon}^{n} \qquad \textbf{(2)}$$

This model with two parameters (n) and (k) correlates the behavior of flow of the starch pastes. They vary according to the size of the air-gap.
4.3 Correction of the gradient speed in a viscometer has coaxial cylinders
According to the manufacturers of the viscometers, this measuring apparatus gives us gradients speed relating to a Newtonian fluid, its noted (έnew).
For a non Newtonian fluid, the gradient speed must be corrected. One establishes a coefficient of correction (ψ). This coefficient multiplied by the value of the experimental gradient speed (έnew) gives us the value of the gradient of v noted corrected itess (έcorr).
Correction of the experimental gradient speed (έnew) Necessity knowledge of the rheological behavior of the studied fluid. The rheological behavior of the starch paste obeys the law of power.

$$\dot{\varepsilon} = f(\tau) = \left(\frac{\tau}{k}\right)^{1/n} \qquad \textbf{(3)}$$

The gradient calibrated airspeed is given by

$$\dot{\varepsilon} = \frac{2\Omega}{n\left[1-\left(\frac{R_1}{R_2}\right)^{2/n}\right]} \qquad \textbf{(4)}$$

Where: (Ω) is the angular velocity of the rotor, (R_1) is the ray of the rotor of the rotary viscometer, (R_2) is the ray of the cup of the rotary viscometer.
Figures 7 and 8 illustrate a comparison between the experimental and corrected gradient speed for the starch paste of corn.

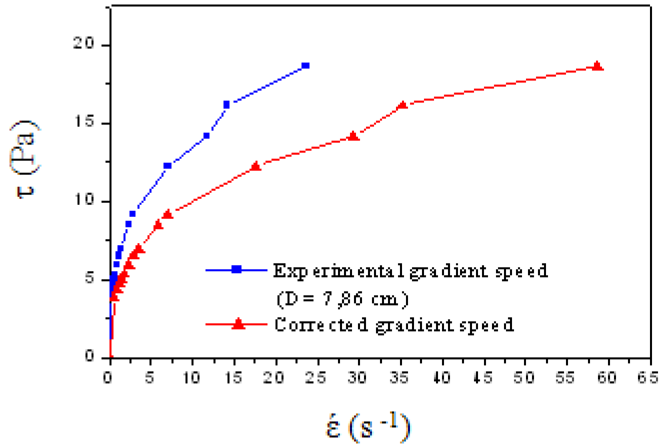

Figure 7. Comparison of the experimental and corrected rhéogramme –Starch paste of corn with 5% with 95°C in a bécher of Ø=7, 86 cm, [1].

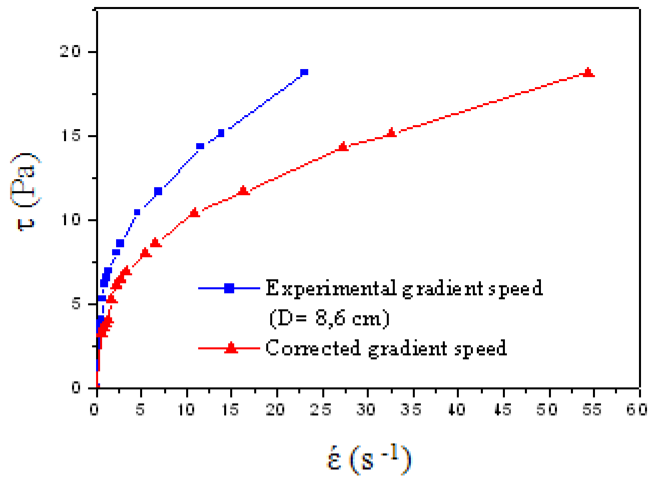

Figure 8. Comparison of the experimental and corrected rhéogramme –Starch paste of corn with 5% with 95°C in a bécher of Ø=8, 6 cm, [1].

According to figures 7 and 8, the difference between the points in the case of the gradient calibrated airspeed and experimental is significant. This variation is more significant with the width of the air-gap and the importance of the value of the gradient speed (έ).

4.4 Theoretical calculation of the gradient speed by the model of Krieger

One uses the method of Krieger and Elrode with only one mobile and according to, [9], [10], [11], [12], the expression of the theoretical gradient speed noted ($\acute{\varepsilon}_K$) is given by:

$$\dot{\varepsilon}_k = \left(1 + C_k\right)\Omega \frac{2\alpha^2}{\alpha^2 - 1} \qquad \textbf{(5)}$$

where: ($\acute{\varepsilon}_k$) is the gradient speed of Krieger, (C_k) is the correction of Krieger, (α) is the report/ratio of the rays (R_1/R_2).

One distinguishes according to figures 9 and 10, the variation enters the two gradients speed such as theoretical ($\acute{\varepsilon}_{th}$) and corrected ($\acute{\varepsilon}_{corr}$) is visible only for the high values.

That is due probably to the sensitivity of the apparatus measuring like to the disturbance of the molecular structure of the substance used under the effect of the gradient speed.

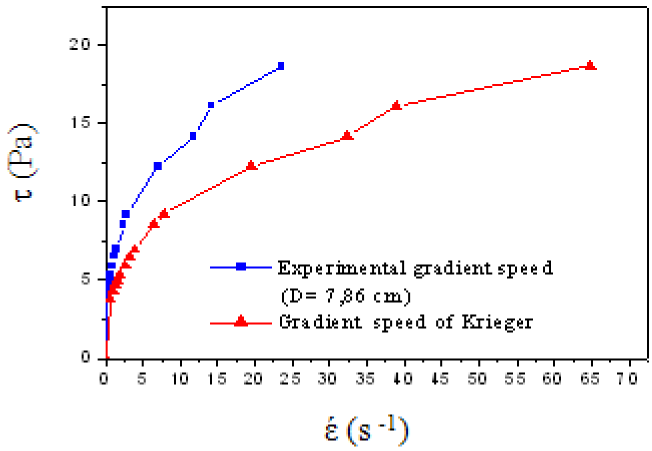

Figure 9. Comparison of the experimental and theoretical rhéogramme –Starch paste of corn with 5% with 95°C in a bécher of Ø=7, 86 cm, [1].

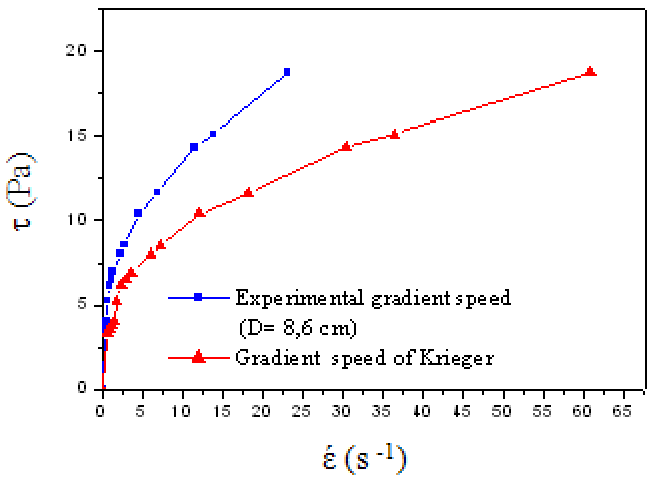

Figure 10. Comparison of the experimental and theoretical rhéogramme –Starch paste of corn with 5% with 95°C in a bécher of Ø=8, 6 cm, [1].

5 Use of the starch of maïs

The corn starch can replace for oil and the other raw materials organics nonrenewable of fossil origin of which, one day, the man will not be able to lay out any more. Although it is present in a vast range of foodstuffs, it is also in the nonfood ones. Here are examples:

5.1 Use in industry

Papers and paperboards, plastics and resins, adhesives and paintings, pharmacy and health, detergents, biocarburants and tire.

5.1 Use in civil engineering

- Concrete and mortar: Research related to the valorization of a by-product resulting from the hydrolysis of the corn starch like additive for the mortars and concretes. It plays the role of agent of cohesion, of retaining of water and retarder additive. It showed that its employment made it possible to ensure a time of handiness prolonged, to limit sweating considerably, to decrease the plastic withdrawal and the permeability and to improve the mechanical resistances to 16 hours without harming those at 28 days [14], [1].
- Plaster: mixed a mixer with starch to improve adhesion enters the plaster and the paperboard for the plasterboards, of the retarders to slow down the time of catch of the plaster.

6 Conclusion

In conclusion, the rheological study of the corn starch as polymeric naturalness makes it possible as well as possible to include/understand its behavior under various conditions.

The rheological behavior of the starch paste to a given concentration is the resultant of the combined effect of three parameters: time, temperature and shearing.

The results obtained starting from a viscometer with coaxial cylinders are valid that for Newtonian fluids. In the case of a nonNewtonian fluid, it is necessary to correct the gradient speed measured directly starting from the measuring apparatus.

In the case of a broad air-gap, the gradient calibrated airspeed and the theoretical gradient speed is identical for a Newtonian behavior, therefore the size of the air-gap does not influence the difference between these two gradients speed. But for a plastic pseudo behavior there is a light difference.

In the case of a plastic pseudo behavior, the error between the gradient experimental speed and the gradient calibrated airspeed are very significant for broad air-gaps. It is increasing with an increasing size of the air-gap. It is about 60% for (α) varies between 2, 98 and 3, 26.

To minimize this error for a plastic pseudo behavior, a solution is generally proposed by the manufacturers of viscometers with coaxial cylinders. This solution consists in imprisoning the substance studied in a very small annular space whose report/ratio of the rays (α) is lower than 1, 15.

According to the use of a coaxial viscometer with various broad air-gaps, the rheological behavior of the starch paste does not change. It is concluded that its behavior does not depend on the size of the air-gap.

REFERENCES

[1] BOUTALEB S., "Etude de la Correction Viscosimètrique d'un Ecoulement Pseudo-plastique", Mémoire de magister, Université de Djillali Liabes, Sidi Bel Abbes, (2008).

[2] TAKACHE H., "Effet du traitement thermique et du cisaillement dans un échangeur tubulaire sur les propriétés rhéologiques d'un système à base d'amidon", Rapport bibliographique, Université de Nantes, site de Gavy, (2006).

[3] NAYOUF M., LOISEL C., DOUBLIER J.L., "Effect of thermomechanical treatment on the Rheological properties of crosslinked waxy corn starch", Journal of Food Engineering, 59, 209-219, (2002).

[4] HUHM K., SCHAULCH S., "Comparative study about commercially available starch for high shear and high temperatures applications in foods", Starch/Stärke, 46, 208-218, (1994).

[5] GROUPE METIDJI., "Amidonnerie de Maghnia", www.groupe.metidji.com.

[6] DRIS M.A., " modèle rhéologique", Logiciel de calcul, USTO, Oran, (1994).

[7] TARA A., "Modification chimique de l'amidon par extrusion reactive", Thèse de doctorat, Universite de Reims Champagne-ardenne, (2005).

[8] KOROLCZUK1 J., EL GARAWANY2 G., T J.P., M3 J.F., "Rhéologie et microstructure de gel d'amidon de maïs", Département Agroalimentaire, ENSA, Rennes, France.

[9] GAGNON M.J., SIMARD G., CHARRETTE A., PÉLOQUIN G., "Characterization of red mud aggregate populations under shear conditions", Proc. Of International Symposium on Ligths Metals, Éditeurs M.Sahoo et T. Lewis, Toronto, (2001).

[10] BENRAHOU K.H., "Caractérisation des écoulements des fluides complexes dans une géométrie de couette", Thèse de doctorat, Université Djillali Liabes, Sidi Bel Abbes, (2006).

[11] MIDOUX N., "Mécanique et rhéologie des fluides en génie chimique ", Lavoisier, (1988).

[13] KRIEGER I.M., ELROD H., "*Shearing rate in the concentric cylinder viscosimeter*", Journal of applied physics, vol 24, (1953).

[14] WOLF JEAN-LUC., "Valorisations des amidons et des amidons modifiés comme adjuvants des mortiers et des bétons ", Thèse de doctorat, CNRS, (1996).