EVALUATION OF THE REINFORCEMENT EFFECT ON WHEAT GLUTEN/NATURAL FIBER BIOCOMPOSITES

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Abstract

An addition of 0-20% hemp or wood fiber in the wheat gluten-based matrix resulted in an increase in the tensile strength and Young's modulus of composite. No significant difference in mechanical properties was observed between materials containing different fiber type. Fiber addition reduced the water absorption, except at high hemp fiber content. The glass transition temperature (T_g) of composite was determined by DMTA which allowed to describe the effect of fiber addition on the material properties by 2 mechanisms: reinforcement and anti-plasticization. At low fiber content, fiber addition increased Young's modulus but no change in T_g was observed, indicating a pure reinforcing effect. Inversely, at high fiber content a matrix T_g increase was observed, indicating a decrease in matrix glycerol content, called anti-plasticizing effect, thus reducing the processability.

1. Introduction

Increase in petroleum prices and emergence of environmental concerns lead to a growing interest in the design of innovative biodegradable materials based on agro-polymers [1]. Wheat gluten can be consider as an interesting raw material for a production of biomaterials, since it has unique viscoelastic properties, a low water sensibility as well as a thermoplastic behaviour [2].

To improve the functional properties of the materials, fillers are widely used. Natural fibers present many advantages as fillers : they have good mechanical properties, they are inexpensive, they have a low density, they are non-abrasive during processing and they are fully biodegradable [3]. Natural fibers are mainly composed of cellulose and lignin, which is located at the fiber surface and acts as a joint between fibres [4]. Thus, it might play a role of compatibilizer, and improve the adhesion between the matrix and fibers.

To prepare agropolymer based materials, plasticizer is required to reduce the glass transition temperature. This plasticization allows gluten to be processed at the desired temperature without protein degradation. However, the plasticizer greatly effects on the material mechanical properties [5] [6]. Thus, the optimum plasticizer content should be added to obtain both a good processability and high material properties.

The objective of this work is to study the effect of fiber addition and fiber type on the processability and properties of gluten-based material in order to have a comprehensive understanding of the physical principles that governs the reinforcing effect of fibers in gluten matrix.

2. Experimental

Commercial vital wheat gluten was obtained from Amylum Group (Aalst, Belgium). Anhydrous glycerol was purchased from Sigma-Aldrich (Steinheim, Germany).

Hemp fiber was provided by Les Chanvrières de l'Aube (France). Wood fiber (industrial paper fiber), a mixture of 90 spruce/10 poplar, was provided by the STORA de Corbéhem factory (France).

2.1 Sample preparation

Composites were prepared by mixing in a mixer at 30°C for 15min., then thermomolding at 130°C, under the pressure of 150 bars for 15 min. It consisted of 70gluten/30glycerol wt./wt. as a matrix, and 0-20% fiber as a reinforcing agent. In this paper, all percentages are given in weight basis (%wt).

2.2 Mechanical properties at high deformation

Tensile tests were performed on a Rheo TAXT2 rheometer (Champlan, France) at elongation speed

of 1 mm/s. Samples were preconditioned at 25°C and 53% relative humidity over a saturated salt solution of $Mg(NO_3)_2$.

Stress values (MPa) were calculated by dividing the measured force values (N) by the initial cross-sectional area of the specimen (mm^2). Strain values were expressed in percentage of the initial length of the elongating part of the specimen. Young's modulus was determined as the slope of the linear regression performed on the first points of the stress-strain curve.

2.3 Water swelling

Samples of 24 mm. in diameter were placed in controlled atmosphere with 0% relative humidity (RH) until their weight was constant (W_i). Then, they were immersed in water at 25°C for 1 week. The swelling samples were weighed (W_w). Then they were dried to 0% RH (W_f).

$$\text{Water absorption (\%)} = \frac{(W_w - W_f)x100}{W_i} \qquad (1)$$

2.4 Mechanical properties at low deformation

Samples ($10\times3\times1$ mm^3) were analyzed with a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific, Piscataway, USA) equipped with a cryogenic system fed with liquid nitrogen. A tensile test was performed with a temperature ramp from –50 to 150°C at a heating rate of 3°C.min^{-1}. A variable sinusoidal mechanical stress was applied to the sample (frequency = 1 Hz) to produce a sinusoidal strain amplitude of 0.05%, which is in the linear domain of viscoelasticity. During analysis, the storage modulus (E'), the loss modulus (E") and tan δ (= E"/E') were recorded and plotted against temperature for further evaluation of thermal transition. The glass transition temperature was identified to the tan δ peak.

3. Results and discussion

3.1 Mechanical properties

To investigate whether lignin can act as a compatibilizer to improve the adhesion between gluten and fiber, hemp (3% lignin) and wood fiber (24% lignin) [7] were used.

The tensile strength increases significantly with the fiber content, while the elongation at break decreases (Fig.1). This evolution is characteristic of a reinforcing effect, which is classically observed for the reinforcement of synthetic polymer materials, with synthetic [8] or natural [9] fibers.

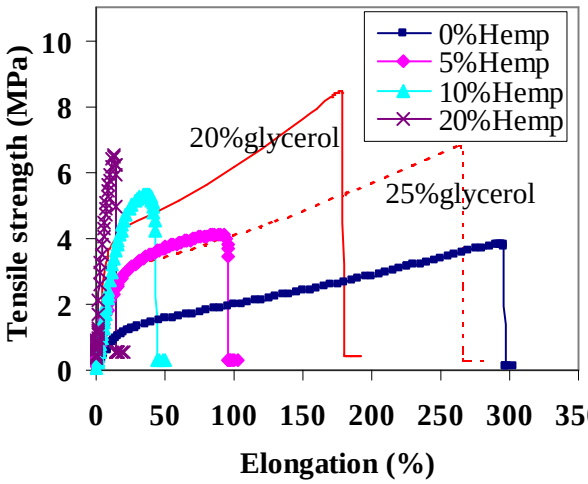

Fig. 1 Mechanical properties of composites plasticized with 30% glycerol containing 0-20% hemp fiber and materials plasticized with 20% and 25% glycerol.

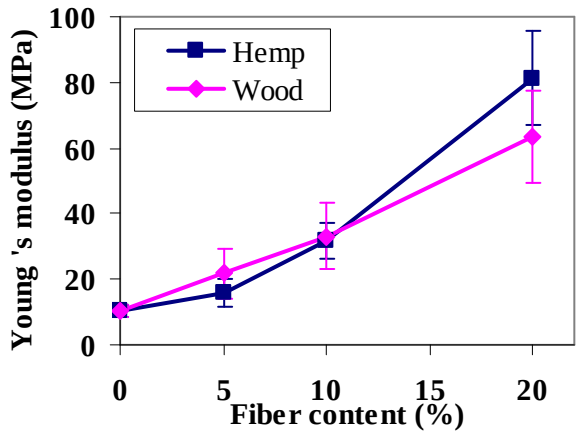

Fig. 2 Young's modulus of composites containing 0-20% hemp and wood fiber.

It is clearly observed that the fiber addition improves significantly Young's modulus (Fig.2), which increases about 6-8 times by adding 20%fiber in the material. However, no significant difference in mechanical properties was observed between the materials containing hemp and wood fibers (data not shown).

We added on Fig. 1 the mechanical properties of materials prepared with various plasticizer content, but without fibers. A decrease in plasticizer content displays the same effect on mechanical properties as fiber addition, but the importance of the variations is quite different. For a same tensile strength increase, the decrease of the elongation at breack is quite lower if plasticizer content is decreased instead of adding natural fibers, whatever their type.

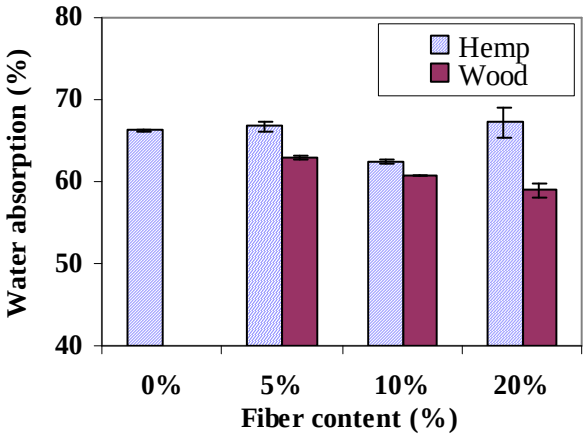

Fig. 3 Water absorption of composites with hemp and wood fiber.

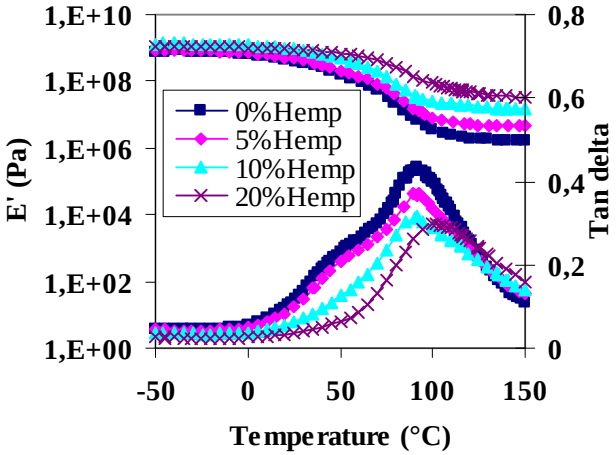

Fig.4 E' and tan δ of composites containing 0-20% hemp fiber.

3.2 Water absorption

The addition of fibers tends to reduce the material water absorption. Concerning this aspects of the composite properties, there is a clear effect of the fiber type.

Water absorption is continuously reduced by wood fiber addition. These fibers are more efficient in reducing water absorption than hemp fibers, which can be correlated with their lignin content. Indeed, lignin (a polyphenolic polymer) is well known to be water resistant [10], and its content in wood fibers is significantly higher than in hemp fibers (approximately 24% against 3%) [11].

Concerning hemp fiber addition, the effect on water absorption is more complex: it decreases from 5 to 10% fiber, and then increases, so that materials with 20% hemp fiber absorb more water than the reference. At high fiber content, we visually observe a bad dispersion of the hemp fibers in the matrix. They formed agglomerates and we assumed that this new structure introduces voids in the matrix. When the composites are immersed in water, these voids are filled of water, explaining the higher water absorption.

3.3 Glass transition measurments

In order to investigate the effect of fiber on the material processability, the glass transition temperature (T_g) was determined by DMTA measurements. During glass transition, the elastic modulus decreases during the transformation of the product from a vitreous state into a rubber one. In this study, glass transition is identified as the maximum of tanδ. The storage modulus and tan δ evolution of composite containing hemp fiber as a function of the temperature is shown in Fig.4.

Table 1 T_g of composites reinforced with hemp and wood fiber.

Fiber (%)	T_g (°C)	
	Hemp	Wood
0	90.2	90.2
5	91.6	90.8
10	90.1	94.7
20	100.2	109.6

No effect of the fiber addition on T_g is observed until 20% hemp fiber content and 10% in case of wood fiber (Table 1). At high fiber content, the T_g increases. The T_g is known to be highly sensitive to the plasticizer content: as plasticizer is added to wheat gluten, the mixture glass transition temperature decreases [12]. However, T_g is not really sensitive to the protein cross-linking level [13].

Therefore, it can be thought that the T_g increases at high fiber content could result from a glycerol absorption by fibers, thus reducing the plasticizer content in the composite matrix.

Fig. 5 presents a comparison between the effect of the fiber addition and the effect of a plasticizer content decrease on T_g. The T_g of a gluten plasticized mixture without fiber increases dramatically as the glycerol content decreases. A decrease in 5% of the glycerol content increases about 10°C of T_g, from 90°C for a material with 30% glycerol to 98°C for a material with 25% glycerol. Contrary to a decrease in plasticizer, there is no change in T_g of composite containing 5-10% hemp fiber plasticized with glycerol (in a glycerol/gluten mass ratio of 30/70), and a little change of Tg in the case of 10% wood fiber addition.

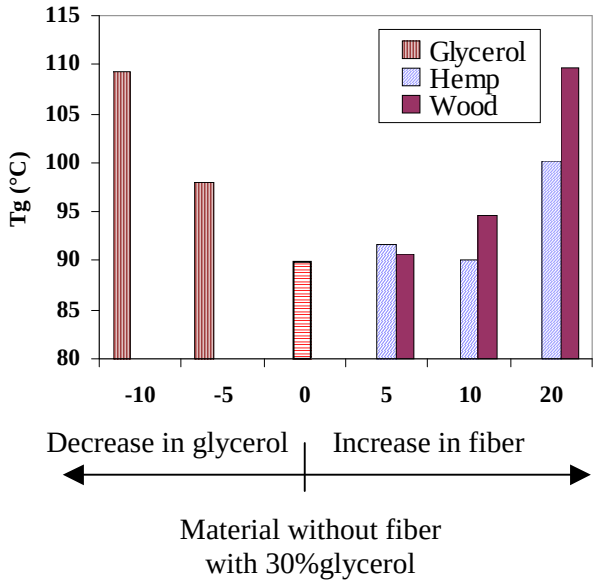

Fig.5 Effect of the fiber addition and a decrease in glycerol content on T_g.

Considering the composites mechanical properties previously presented in Fig.1, it is observed that the tensile strength and the Young's modulus of the composite containing 10% fiber are very similar with those of a plasticized gluten blend containing 25% glycerol. However, the composite processability is quite easier than the one of the plasticized gluten, since its glass transition temperature is lower. Therefore, it can be concluded that the addition of 5-10% fiber is a better way to improve the mechanical properties without affecting the processibility compared to a decrease in the plasticizer content.

However, at high content it shows that there is a competition for plasticizer absorption between fibers and gluten matrix.

It can be concluded that the machanical propertie evolution due to the fiber addition could be attributed, depending on the fiber content, to two phenomena. The first one is a reinforcing effect: at low fiber content, Young's modulus increases as the fiber content increases, but no change of the matrix T_g is observed. The second one is an anti-plasticizing effect: at high fiber content, Young's modulus and T_g increase with the fiber content, but the glycerol content in the matrix decreases.

4. Conclusion

The addition of natural fiber in gluten-based matrix resulted in an improvement of mechanical properties of composite which can be characterised in 2 mecanisms: a reinforcing effect and an anti-plasticizing effect.

At low fiber content, an increase in mechanical properties could be a result of the reinforcing effect. Therefore, at this fiber content, the fiber addition is a good way to improve the mechanical properties, and the water resistance without decreasing the processibility.

Inversely, at high fiber content, the mechanical properties evolution could be attributed to an anti-plasticizing effect which is a result of glycerol absorption by fibers, thus decreasing the glycerol in composite matrix.

Moreover, it can be observed the fiber lignin content significantly affected the water absorption, as wood fibers with high lignin content have a major decrease effect on water absorption.

Reference

[1] Redl, A., et al., *Extrusion of wheat gluten plasticized with glycerol: influence of process conditions on flow behavior, rheological properties, and molecular size distribution.* Cereal Chem., 1999. **76**(3): p. 361-370.

[2] Cuq, B., N. Gontard, and S. Guilbert, *Proteins as agricultural polymers for packaging production.* Cereal Chem., 1998. **75**(1): p. 1-9.

[3] Nabi Saheb, D. and J.P. Jog, *Natural fiber polymer composites: A review.* Adv. in Pol. Tech., 1999. **18**(4): p. 351-363.

[4] Thielemans, W. and R.P. Wool, *Butyrated kraft lignin as compatibilizing agent for natural fiber reinforced thermoset composites.* Composites Part A: Applied Science and Manufacturing, 2004. **35**(3): p. 327-338.

[5] Zhang, J., P. Mungara, and J. Jane, *Mechanical and thermal properties of extruded soy protein sheets.* Polymer, 2001. **42**(6): p. 2569-2578.

[6] Averous, L., et al., *Properties of thermoplastic blends: starch-polycaprolactone.* Polymer, 2000. **41**(11): p. 4157-4167.

[7] Tserki, V., et al., *A study of the effect of acetylation and propionylation surface treatments on natural fibres.* Composites Part A: Applied Science and Manufacturing ACMC/SAMPE Conference on Marine Composites (MarComp) 2003, 2005. **36**(8): p. 1110-1118.

[8] Ota, W.N., S.C. Amico, and K.G. Satyanarayana, *Studies on the combined effect of injection temperature and fiber content on the properties of polypropylene-glass fiber composites.* Composites Science and Technology, 2005. **65**(6): p. 873-881.

[9] Mutje, P., et al., *Full exploitation of Cannabis sativa as reinforcement/filler of thermoplastic composite materials.* Composites Part A: Applied Science and Manufacturing, 2006. **In Press, Corrected Proof**.

[10] Whetten, R.W., MacKay, J.J. and Sederoff, R.R., *Recent Advances in Understanding Lignin Biosynthesis.* Annu. Rev. Plant Physiol. Plant Mol. Biol., 1998. **49**: p. 585–609.
[11] Espert, A., F. Vilaplana, and S. Karlsson, *Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties.* Composites Part A: Applied Science and Manufacturing, 2004. **35**(11): p. 1267-1276.
[12] Pommet, M., et al., *Intrinsic influence of various plasticizers on functional properties and reactivity of wheat gluten thermoplastic materials.* Journal of Cereal Science, 2005. **42**(1): p. 81-91.
[13] Micard, V., et al., *Thermal properties of raw and processed wheat gluten in relation with protein aggregation.* Polymer, 2001. **42**(2): p. 477-485.