Crystallization of polypropylene in the presence of biomass-based fillers of different compositions

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ABSTRACT

Natural fillers composed of cellulose, lignin and fillers with a varying lignin/cellulose ratio (flax, jute, curauà fibers and miscanthus stem fragments) were used to prepare composites with polypropylene using the same procedure, with or without a maleic anhydride—grafted polypropylene (MA-*g*-PP) coupling agent. A clear acceleration of the crystallization kinetics was observed in the presence of miscanthus stem fragments. For non-coupled composites, the size and aspect ratio of fragments had no significant influence onto the crystallization kinetics of polypropylene. The presence of the MA-*g*-PP coupling agent increased even more the kinetics. A clear effect of the nature of the polymers present in the filler was observed. There is a direct relationship between the values of the Avrami kinetic constant *k* for the six fillers and their lignin content, the more effective to enhance crystallization kinetics being pure cellulose. Lignin has no effect onto the crystallization kinetics of polypropylene.

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1. Introduction

Composites made of a natural, renewable filler and a polymer matrix have been widely studied and they are more and more used due to their renewable character, good mechanical properties and lightness. There are numerous papers describing their preparation and properties depending upon the processing method, polymer matrix, compatibilization agents and type of natural filler. When plant-based, these natural fillers can have many aspects and compositions, from lignocellulosic pieces like for wood or plant stems to very fine nanocellulosic fibers. When the matrix is a polyolefin like polypropylene, there is a very low compatibility between the polymer matrix and the hydrophilic fillers which is leading to poor mechanical properties. This phenomenon was recognized and conveniently targeted a long time ago. Currently, the most popular method for improving the interface quality is the use of maleic anhydride moieties, able to form covalent links with the hydroxyl groups present at the surface of the lignocellulosic filler [1].

Many types of natural fillers can be used. "Natural plant-based fillers or fibers" are a class of materials with a very wide dispersion of properties and characteristics since all ligno-cellulosic plants and trees have structures, composition and traits which are highly depending on plant species, genotype and tissues. A plant may have stems, leaves and fruits which have each a specific biochemical composition and structure related to their function in the plant. The mechanical strength of plant is given by fibers made of cellulose chains arranged in different manners, surrounded by other components like species- and tissue-dependent hemi-celluloses and lignins. When willing to reinforce polypropylene, one has to use elongated fillers, usually (and misleadingly) called fibers.

There are many ways to extract elongated fillers from plants. They can come from organs having no structural role like cotton hairs, from cell structures of various nature as in wood, or from inner tissues situated below the outside bark skin of plants (as bast fibers extracted from plants like flax, hemp, or ramie). They can also be extracted from leaves as in the case of curauá and banana. Fruits can also provide fiber-like pieces like in coir, where fibers are extracted from the husk of coconut. Another option is to break stems into elongated fragments as in the case of bamboo, straw or miscanthus. In some cases, as for bast or pulp fibers, enzymatic, physical and/or chemical treatments are applied. In other cases, strong mechanical treatments are used, as for obtaining nano-fibrillated cellulose. Stem fragments are obtained after a mild mechanical treatment. As said above, these elongated fillers are in nearly all scientific articles called "fibers". Taking bamboo as an example, a bamboo fiber can come from the full stem broken into

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pieces [2] or wall cell cellulose fibers extracted by a pulping process [3]. These two "fibers" are very different in all aspects: aspect ratio, length, diameter, composition, surface chemical properties, and histological structure. These parameters should have an effect on the way any polymer, in our case polypropylene, will interact with these fillers. This should affect composite properties, and could have an influence on polypropylene crystallization.

Although there are a large number of articles dealing with plant-based filler-polypropylene composites, very few are studying the crystallization of the matrix. Among the physical phenomena which have been investigated, crystallization should have a special place, since it partly controls the properties of the matrix and of the interface, since the filler may have an effect on crystallization kinetics, degree of crystallinity, crystalline morphology and crystal type. The first papers dealing with the crystallization of polypropylene in the presence of natural fillers are more than 20 years old. However, the picture of the papers published up to now is somehow full of contradictions.

It has been reported that the crystallization rate is higher in the presence of bamboo stem fragments than without. This phenomenon was attributed by the authors [2] to the nucleating effect of the filler. Bamboo fragments, however, did not induce trans-crystallinity. On the contrary, the use of maleated polypropylene did not change the kinetics but it strongly promoted trans-crystallization. In fact, although fiber surface morphology and composition can inhibit transcrystallization [4—7], several papers have reported that natural fibers (such as jute, flax, sisal, or kenaf) can induce transcrystallinity in PP [8—12].

The effect of chemical treatments on the capacity to induce transcrystallinity is also common object of debate [7,10—13]. In this aspect, some controversial results have been reported, and whilst some works report that the rate of growth was higher for composites coupled with MA-g-PP [11,14], others reported that treated fibers had no effect [8]. Similarly, it has been reported that the addition of flax fibers (a bast fiber) increased the crystallization kinetics due to an increased nucleation, an effect that was even greater when fibers were treated with maleic anhydride [8]. However, the result was different when using kenaf (another bast fiber) as crystallization slowed down when maleated polypropylene was added [15]. The effect of fiber surface composition is not clear either. Gray [5] reported that the presence of lignin or hemicellulose might inhibit transcrystallization. More recent works have reported that the removal of low molecular constituents (wax and lignin) reduced the nucleation ability of wood, a difference that might be due to the fact that whilst cellulose I produces trans-crystallization, cellulose II does not [4]. In addition, it has been reported that the absence of cellulose seemed to be unfavorable for the growth of transcrystallinity [4]. In many papers, the thermal results were analyzed using Avrami approach. Polymer crystallization results from a nucleation and growth process. According to Avrami-Evans theory, there exists in a molten polymer a number N_0 of potential nuclei, able to only decrease by activation or absorption. Each potential nucleus present in a non-transformed area can be activated (nucleation) to be transformed (growth) in a semi crystalline entity that grow in all available direction until it impinges on another one. The activation frequency q(t) is the probability for a random nucleus to be activated. q(t) and the growth rate G(T depend on crystallization temperature). Avrami Evans theory has the following three hypotheses, a uniform repartition of potential nuclei in the volume, a constant G(T)/q(T) ratio (isokinetic hypothesis) and: a constant material volume (isovolumic hypothesis).

Differential scanning calorimetry can follow the crystallization process as a function of time via the apparition of an exothermic peak. The integration of this peak gives access to the enthalpy of crystallization and then after calculations to the overall kinetic of

transformation. The transformed fraction α(t) at a time t is equal to the ratio of the enthalpy at a given time t by the total crystallization enthalpy:

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}}$$

In isothermal condition, Avrami's approach is described as [16,17]

$$\alpha(t) = 1 - exp[-kt^n]$$

where n is Avrami's coefficient (a coefficient dependent on the nucleation mode and on the growing geometry of semi-crystalline entities) and k is the rate constant, depending on nucleation mode, growing geometry and temperature.

Pracella et al. [18] reported an Avrami coefficient for neat PP between 2.5 and 2.7, depending upon crystallization temperatures. In their work, they reported that hemp fibers (a bast fiber) have the capability to act as nucleating agents, promoting trans-crystallization. In addition, fibers increased the crystallization kinetics when increasing the amount of maleic anhydride bonded on the fibers. As for all other cases, nucleation occurred at the fiber wall surface, with hemp fibers not inducing the crystallization of β phase. The Avrami exponent of PP increased from about 3 for the pure PP to around 4 for PP/hemp composites. Recently, Zhou et al. [19] investigated the formation of the transcrystalline regions induced by ramie fibers. Three cases were investigated, neat fiber, neat fiber pulled and fibers treated with dopamine. Their results showed there was no transcrystallinity when neat fiber was used. However, when the fiber was pulled, transcrystallinity occurred, first in α and then in β form. Dopamine-treated fibers induced transcrystallinity, but only in the α form. In other works, it was reported that the presence of bamboo fragments induced a small fraction of polypropylene to crystallize in the β form [2].

As it can be seen from these examples, there is no rational picture regarding the way lignocellulosic "fibers" act on polypropylene. A general reason for such a disparity of results lies on the many parameters that can affect nucleation, from chemical composition, to surface roughness, geometry and size of fibers [20,21]. In the papers reporting PP crystallization, other reasons for these inconsistent results are (1) that none of these studies used the same polymer matrix, which may account for part of these differences, (2) the way compatibilization is treated (even if most methods are based on the addition of maleic anhydride, the compatibilizer can be added as a third component, used directly as the matrix or grafted onto the fiber), (3) that the "fibers" used are of different nature and structures, showing different tissues and compositions at the "fiber" surface.

Using a single matrix and well-characterized biomass-based fillers such as miscanthus stem fragments, jute, flax, cotton, curauà and lignin, we studied the crystallization of polypropylene varying the size of miscanthus stem fragments and their preparation method under isothermal and non-isothermal crystallization. The nucleating abilities of the fillers at different crystallization temperatures, cooling rates and in the presence of a coupling agent were evaluated.

2. Materials and methods

2.1. Materials

A general purpose injection grade homopolymer polypropylene PPH5060 (Melting point = 164 °C, MVI = 6.0 g/10 min at 230°C/ 2.16 kg, M_w = 320000 Da, M_n = 46000 Da) provided by Total, and a polypropylene specially compounded by Addiplast to minimize the