Ecocomposites developed for the valorization of postconsumer plastics and waste cellulose fibers: water uptake

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Abstract

Water absorption of ecocomposites obtained from waste plastics and residual cellulose was studied in order to increase the recyclability of these wastes by improving the properties of the recycled materials in a cost-effective way. Water absorption is very detrimental because it causes loss of dimensional stability and hydrolytic degradation, which results in loss of properties and reduction of the service life. The composites were obtained from a recycled agricultural plastic (RAP), a high-density polyethylene (rHDPE) from the urban solid waste and waste cellulose fibers (WCF). Fourier transform infrared spectroscopy and gravimetric measurements were used to study the absorption and characterize the absorbed water. The amount of absorbed water depends on the cellulose content and can be reduced by increasing the coupling agent content or by using blends of RAP and rHDPE, instead of pure RAP, as matrices for the ecocomposites. The spectroscopic analysis reveals the presence of water in three different states in the hydrated composites: water bound to cellulose, liquid water and water unbound or very weakly bound. The whole water absorption process cannot be accurately described by a Fickian model; however, this model gives a good description of the absorption of the absorption of the early stages of the process.

1. Introduction

In Europe, including the EU-28 countries, Norway and Switzerland, the collected plastic waste reached 25.8 Mt in 2014. Out of these, 30.8 % were sent to landfill, 39.5 % were sent to energy recovery and only 29.7 % were mechanically recycled [1], although it is well known that mechanical recycling is a very interesting alternative for waste plastics because it saves energy, raw materials and emissions and also generates jobs. Among the technical and economic factors that contribute to explain the low percentage of mechanical recycling, we can highlight the high costs of collection, sorting and cleaning of some waste plastics and the variable (and sometimes reduced) quality of the recycled materials [2], due to the presence of plastics of different formulation, with different levels of impurities and degradation, in the waste streams.

The poor performance of the recycled plastics is a very important issue because it compromises the demand for these materials in the market, which is one of the key factors determining the final destination of waste [3]. Therefore, the development of cost-effective processes for improving the properties of the recycled plastics is required in order to increase the recyclability of the waste plastics. Furthermore, the development of recycled plastics with better properties will help to meet the EU targets for 2025 and 2030 regarding solid waste treatment, contained in the new directives about circular economy [4].

Different alternatives are used to obtain recycled plastics with improved properties, including the blending with virgin plastics, the use of additives for the re-gradation or the incorporation of reinforcements to make composites with enhanced mechanical properties. When the reinforcement comes from natural sources, such as cellulose-based fibers, the ecocomposites obtained have additional environmental advantages. In previous works we have shown that it is possible to obtain composite materials with good properties by compounding recycled agricultural plastic with residual cellulose fibers [5,6]. The mechanical properties of these ecocomposites were improved by adding a postconsumer polyethylene coming from urban solid waste (rHDPE) [7].

The use of cellulosic fibers as reinforcement also shows some disadvantages, such as the increased water uptake, due to the hydrophilic nature of cellulose. High water absorption is very detrimental for the material because it causes loss of dimensional stability and hydrolytic degradation of the fiber-matrix interface, which ultimately results in loss of properties and reduction of the service life [8-12]. The absorption of water also raises the risk of microbial degradation. Therefore, the absorption of water (and how to minimize it) must be studied when developing a new ecocomposite in order to validate the suitability of the material for its use [13].

In this work, the development of ecocomposites for the valorization of waste plastics and residual cellulose is analyzed, with special focus on the issue of water absorption. The goals were to understand the absorption process and to increase the recyclability of these wastes by improving the properties of the recycled materials in a cost-effective way. The matrix of the composites was a blend of recycled agricultural plastic (RAP), whose major component is low-density polyethylene (LDPE), and a post-consumer plastic coming from urban solid waste, mainly composed of high-density polyethylene (rHDPE). The residual cellulose fibers (WCF) used as reinforcement were a by-product obtained in the manufacturing of Kraft cellulose pulp. The state of the absorbed water was characterized using Fourier Transform Infrared (FTIR) spectroscopy. The water uptake was measured by gravimetry and FTIR spectroscopy. A Fickian model was used to study the absorption.

The results have allowed to observe the different types of water present in the hydrated material, to analyze the kinetics of the absorption and to understand the effect of the different components of the composite on the water absorption.

2. Materials and methods

The recycled agricultural plastic (RAP), obtained by recycling greenhouse and other agricultural films used in the south and east of Spain, was kindly supplied by Befesa Plásticos (Spain), in pellet form, as ALFATEN 200TM. It was characterized in a previous work [5]. The main component was low-density polyethylene, with minor amounts of ethylene-vinyl acetate (EVA) copolymer, impurities and additives. rHDPE was supplied by TERSA (Spain) as flakes obtained from bottles and other containers found in urban solid waste and was previously pelletized in order to obtain a homogenous material and to facilitate its dosing during melt compounding. The main component was high-density polyethylene, with minor amounts of polypropylene (ca. 7.5 wt %) [7]. Residual cellulose fibers (WCF), kindly supplied by ENCE-Navia (Spain), were unbleached Eucaliptus Globulus cellulose fibers obtained as a by-product in the manufacturing of Kraft cellulose pulp. Licocene PE MA 4351 GR, a maleic anhydride-modified polyethylene (MAPE) with acid number = 43, supplied by Clariant Ibérica (Spain), was used as coupling agent. Two different concentrations of MAPE (1.5 and 3 wt %) were evaluated. A 0.3 wt % of Irganox B900 (Ciba, Spain) was used as antioxidant.

Two different polymer matrices and three cellulose levels were studied. The proportion of rHDPE in the matrix was 0 or 40 wt %. The WCF contents in the composites were 25, 30 or 35 wt %, with regard to the total weight of composite material. Composites were compounded in a corotating

intermeshing twin screw extruder, mod. ZE25 (Berstorff, Germany). The temperature profile, from hopper to die was 155-152-149-146-143-140-137-155/170 °C in all cases. The temperature of the last zone varied between 155 and 170 °C depending on the content of cellulose and MAPE. The residual cellulose was previously dried at 105 °C for 3 h in an air-circulating oven and the moisture content was lower than 1 wt %. The ecocomposite pellets were dried at the same temperature before the injection.

The test specimens for the gravimetric water absorption tests were cut into 2.5 x 2.0 x 0.4 cm specimens from standard samples obtained, according to the ISO 3167 standard, in an injection molding machine, mod. METEOR 120/45 (Mateu & Solé, Spain). After vacuum drying at 80 °C for 1 day, each specimen was dipped in a flask containing 100 ml of deionized water at constant temperature. After selected immersion periods, the specimens were removed, gently wiped with tissue paper to remove surface water and weighed, at room temperature, in a laboratory balance with a precision of 0.1 mg. The percentage of absorbed water at any time *t*, M_t , was determined using the following expression:

$$M_t(\%) = \frac{W_t - W_0}{W_0} \times 100 \tag{1}$$

where W_0 and W_t denote, respectively, the weight of the specimens before and after the immersion.

Films for the FTIR study were molded by compression in a IQAP-LAP hot-plate press at 185 °C and immersed in deionized water. After carefully removing surface water, the infrared spectra were recorded in transmission mode using a Nicolet iS10 spectrometer. Each spectrum was recorded at a resolution of 4 cm^{-1} with 16 scans.

3. Results and discussion

3.1. Water absorption

Water absorption may be very high in composite materials reinforced with lignocellulosic fibers, due to the hydrophilic nature of the cellulosic materials and the possible existence of microvoids and microcracks, mainly located at the fiber-matrix interface. The structure of the interface depends on the composition of the material and can be significantly altered using coupling agents or surface-modified celluloses. Taking into account that the water absorption leads to a significant reduction in the properties and useful life of the material, it can be concluded that it is important to study the effect of the composition of the composite on the water uptake.

The water absorption has been studied in this work by means of gravimetric measurements and FTIR spectroscopy. The gravimetric absorption curves corresponding to composite materials prepared with different amounts of WCF are shown in Fig. 1 In the three materials shown the amount of coupling agent is the same, 1.5 wt %. It can be seen that, as might be expected, the amount of absorbed water increases with the cellulose content. If materials with 25 and 35 wt % of cellulose are compared after 1900 h (79 days) of immersion in distilled water at 25 °C, it is observed that the amount of water absorbed by the composite with 35 wt % of cellulose is 50 % higher. The same behavior was observed in materials prepared with other mixtures of recycled plastics and different coupling agent contents. In addition, similar results have been reported by authors who have studied very different polymer-cellulose systems [8-10]. These results indicate that a significant part of the absorbed water is associated with cellulose, either as water bound to cellulose by hydrogen bonds, or as water contained in microvoids and microcracks in the fiber-matrix interface. The results of the characterization of the water present in the material by FTIR spectroscopy are presented below.



Fig. 1 Water uptake at 25 °C in composites of RAP with 1.5 wt % of MAPE and 25, 30 or 35 wt % of WCF

Fig. 2 shows that the water uptake can be reduced by the use of MAPE as a coupling agent. MAPE is soluble in the plastic matrix and can be joined by the maleic groups to the surface hydroxyl groups of the cellulose, forming ester bonds [14]. This reduces the concentration of surface OH groups available to absorb water and also the number of defects in the interface. This result, which is similar to those observed in all the materials studied in this work, coincides with the results reported by other authors [8]. Fig. 2 also shows that, while the addition of 1.5 wt % MAPE causes a significant reduction in water absorption, only slight improvement is obtained when the amount of coupling agent is increased to 3 wt %.



Fig. 2 Water uptake at 25 °C in composites of RAP with 30 wt % of WCF and different coupling agent contents

In this work, the use of a blend of RAP and rHDPE (60 wt % of RAP; 40 wt % of rHDPE) as matrix for the ecocomposites was also studied. It can be seen in Fig. 3 that the water absorption can also be reduced if a mixture of rHDPE and RAP, instead of RAP alone, is employed as the matrix of the composite. This result has been explained as a consequence of the higher crystallinity of HDPE compared to LDPE, the major component in RAP, since the crystalline phases show lower water permeability. Furthermore, the substitution of a portion of RAP reduces the EVA content in the final composite. EVA is a copolymer with polar groups found in RAP but not in rHDPE [7].

This result is important because it reveals that it is possible to reduce the undesirable water absorption by using mixtures of different residues, which is cheaper than the use of coupling agents. In a previous work we have shown that the incorporation of rHDPE increases the strength and stiffness of the composites obtained from RAP and WCF, without compromising impact strength and processability [7]. The improved mechanical properties and water absorption can increase the recyclability of the polymer and cellulose wastes used in this work.



Fig. 3 Effect of the matrix composition on the water uptake at 25 °C of composites with 30 wt % of WCF and no coupling agent

In order to reduce water uptake, it is important to understand the nature of the absorption processes. Traditionally, the absorption of water in many polymers and composites has been described using Fickian models, that is, the absorption has been considered as a reversible process where the water transport is controlled by a concentration gradient and a plateau state is finally reached. However, the absorption in the complex materials studied in this work may be rather different, due to the presence of microvoids and microcracks located at the fiber-matrix interfaces that can play a main role in the water transport, and also to the hydrolytic degradation in the hydrated material. These two factors are not considered in the Fickian model.



Fig. 4 Water absorption data for the composite of RAP with 30 wt % of WCF and 1.5 wt % of MAPE. The line shows the fitting of the data using Eq. 2

In Fig. 4 the experimental results are compared with the prediction of a Fickian model. If the sample is considered a plane sheet with constant diffusion coefficient and the absorption is considered to take place under unidirectional flow, a numerical solution to the Fick's second law is given by Eq. 2 [15]:

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 Dt}{h^2}\right)$$
(2)

where M_t is the water absorbed at time t, M_{∞} is the water content at equilibrium (saturation mass), D is the apparent diffusion coefficient, h is the thickness of the sample and n is the number of terms of the solution used in the calculation. The best value of n was determined to be 10, since no additional improvements were observed with greater values of n.

The fitting of the whole set of experimental values, not only for short absorption times, allows to evaluate the validity of the model. Fig. 4 shows that the Fickian model can not accurately describe the entire set of experimental data (similar results were obtained with all the materials studied). The main difference is that the model predicts a final plateau, while the experimental values grow continuously, probably due to the hydrolytic degradation caused by the absorbed water, with breakage of ester bonds and weakening of the fiber-matrix interface, which facilitates the swelling and the subsequent absorption of water.

3.2. Characterization of the absorbed water

In addition to knowing the nature of the absorption processes, it would also be important to know the state of the absorbed water inside the material. It should be noted that the nature of the water absorbed in polymers and composites is a complex subject, because there may be water bound through different types of hydrogen bond, in addition to free, unbound water. In this work the state of absorbed water has been studied by FTIR spectroscopy.

Fig. 5 shows the FTIR spectra recorded in the composite of RAP:rHDPE (60:40) with 35 wt % of WCF and 1.5 wt % of MAPE, before and after 3 h of immersion at 25 °C. The behavior of all the studied materials was the same. The spectrum of the hydrated material show two main differences at 3400 and 1640 cm⁻¹ that can be assigned to O-H stretching and H-O-H bending vibration modes, respectively. These bands reveal the presence of absorbed water in the hydrated material and provide information about the state of the absorbed water.



Fig. 5 FTIR spectra of the composite of RAP:rHDPE (60:40) with 35 wt % of WCF and 1.5 wt % of MAPE, before and after 3 h of immersion



Fig. 6 FTIR spectrum and deconvolution of the water absorbed in the composite of RAP:rHDPE (60:40) with 35 wt % of WCF and 1.5 wt % of MAPE, after 24 h of immersion at 25 °C

The FTIR spectrum of the absorbed water can be obtained by subtracting the spectrum of the dried material to the spectrum of the hydrated material. Fig. 6 shows the result of this subtraction in the ecocomposite obtained after 24 h of immersion at 25 °C, in the area between 3000 and 3800 cm⁻¹. The spectrum reveals the presence of three absorption bands, centered at 3176, 3422 and 3582 cm⁻¹ respectively, which can be separated by deconvolution. The three bands can be assigned to O-H stretching modes and indicate the presence of at least three different water types in the hydrated material. The peak at 3176 cm⁻¹ can be attributed to water strongly bound by hydrogen bonds to OH groups of the cellulose. At the other end of the range, the band centered at 3582 cm⁻¹ can be assigned to unbound or very weakly bound water molecules, so we might call it "free water" [16]. Finally, the band centered at 3422 cm⁻¹, which does not usually appear in pure polymers, can be assigned to liquid water, since the IR spectrum of the liquid water has a very similar OH-absorption band [17].

The presence of three types of water in the hydrated materials, revealed by the FTIR spectra, can explain some of the results of the water absorption gravimetric studies presented above. The bound water is water strongly attached to the cellulose and allows explaining that the amount of water absorbed by the ecocomposites grows with the cellulose content. On the other hand, the presence of liquid water can only be explained if it is considered that this type of water is located in microvoids and microcracks in the materials. The absorption of water through these defects of the structure may be a contributing factor to explain the non-Fickian behavior of the water absorption.



Fig. 7 Time evolution of the bands centered at 3582 and 3176 cm-1. The data correspond to the composite of RAP:rHDPE (60:40) with 35 wt % of WCF and 1.5 wt % of MAPE, at 25 °C

Finally, the data obtained by deconvolution of the absorbed water spectra allows a separate study of the temporal evolution of the different types of water. The experimental values of the evolution (at short immersion times) of the bands assigned to the bound water and the "free water", together with the data obtained by fitting with the Fickian model of equation 2, are shown in Fig.7. The data corresponding to the liquid water band are not shown, as it presents erratic behavior with large differences from one sample to another. However, the good fit obtained for the bands of bound water and "free water" indicates that the absorption of these types of water can be adequately described by a Fickian model, at least during the first stages of the immersion, in which hydrolytic degradation of the material is not yet important.

4. Conclusions

The absorption curves reveal that water uptake depends on the cellulose content. Absorption can be reduced by increasing the coupling agent content. A second and more cost-effective alternative for reducing absorption is based on the use of blends of RAP and rHDPE, instead of pure RAP, as matrices for the ecocomposites. The analysis of the absorption curves reveals that the water absorption cannot be accurately described by a Fickian model, due to the existence of microvoids and microcracks and the hydrolytic degradation of the material. Hydrolytic degradation prevents absorption reaching a saturated state in these ecocomposites because it weakens the fiber-matrix interface, thus favoring the subsequent water absorption. The FTIR spectra measured during the hydration reveal the presence in the composites of water in three different states: water heavily bound to cellulose, "free water" (unbound or very weakly bound water) and an intermediate kind of water, which can be described as liquid water. The absorption of "free water" and bound water in the early stages of the process can be accurately described using a Fickian model.

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