

# Durability of wood polymer composites: 1. Influence of wood on the photochemical properties

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### Durability of wood polymer composites:

#### 1. Influence of wood on the photochemical properties

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#### Abstract:

The photooxidation of wood-based composites (WPC) using thermoplastics (PE, PP) as a continuous phase has been investigated. WPC are increasingly used in applications in which UV exposure has become a concern. The composites were produced by melt blending in a Brabender at 180°C. Characterization of the samples, with the aid of scanning electron microscopy supplemented by microscope photography, showed a good dispersion of wood in the polymeric material. Dispersion was improved by adding polypropylene grafted with maleic anhydride (PP-g-MA). The results clearly displayed that the presence of wood in polymer composites does not change the pathway of photooxidation of the host polymer. However, wood absorbs in the UV-visible domain and can contribute to the degradation initiation through the creation of radicals. The outstanding outcome of this study is the significant improvement of the photostability of WPC made with PPgMA. This opens a door of better long term behaviour of this last formulation in the objective of outdoors applications.

*Keywords*: A polymer-matrix composites (PMCs); A wood; B Durability; D Infrared(IR) spectroscopy. \*Corresponding author Tel : 33 (4) 73 40 71 77, Fax : 33 (4) 73 40 77 00 *e-mail address : luc.gardette@univ-bpclermont.fr* 

#### 1. Introduction

Composites made from blend of thermoplastic and natural fibres have attracted a number of researchers and manufacturers because of their great advantages [1]. Among them, one can quote a reduction of the production cost, a low density of the material, and good mechanical properties combining with renewability. So far, various thermoplastics, including polyethylene and polypropylene, have been used as host material for research and development, both on laboratory and industrial scales [2]. The enthusiasm in this field is explained by the number of potential applications. For example wood - polymer composites (WPC), mostly manufactured through extrusion and injection moulding processes are used in automotive (dashboards or screen-doors of the vehicles) and construction industry (interior floor coverings, profiled for doors and windows, ornamental panels, external shutters, pavements, garage or entrance doors, and so on). However, because they are constituted of organic materials, polymers and wood fibres, WPC are sensitive to UV light and thermal ageing. Then, in applications which demand routine exposure to solar radiations, WPC are likely to undergo degradation that limits their use.

The first key point for the production of acceptable WPC is the compatibility between wood and polymer host matrix. Wood is hydrophilic in nature (high surface tension), which lowers the compatibility with hydrophobic polymeric material (low surface tension) during composite preparation. Scanning the literature, one can find different surface treatments that have been experienced to improve wood/polymer adhesion in composites. Remind that the level of adhesion and/or the dispersion state of wood are the key points for the improvement of mechanical properties of the composites. Indeed, the wood particles which have high strength and modulus -with good adhesion and uniform dispersion- can impart better mechanical properties to the host polymer in order to obtain a composite with better properties than those of the unfilled polymer. Maleic anhydride is the usual choice as a

coupling agent [2]. Thus, the surface tension of wood fibres is reduced approaching that of the molten polymer. From this point, wetting and adhesion are improved via mechanisms such as diffusion and mechanical interlocking between the two entities.

WPC are produced starting from wood (up to 70 %), in the form of pellets, "flour" (fine particles) or fibres, mixed with a polymeric matrix: for instance polyethylene, polypropylene or polyvinylchloride. The unit is supplemented by many additives (antioxidants, pigments, fungicides, stabilizing anti-UV, etc...).

Wood is a composite material consisting mainly of three major polymers: cellulose, hemicellulose and lignin (schemes 1 and 2). It also contains extractives in few percentages (proteins, oses). Contrary to the other components of the fibres which have an amorphous structure, the cellulose has mainly a crystalline structure. The cellulose chains are joined together into micro fibrillates which are arranged into several layers.



Scheme1: Chemical structure of cellulose



Scheme 2: Monomers constitutive of lignin (Alcohol coumarylic, coniferylic and

synapylic).

As mentioned above, WPC are very sensitive to UV-light degradation. It has been shown that lignins are keener to degradation among constituents of the wood [3-8]. The main degradation process of lignin identified by the authors is the demethoxylation of the guaiacyl or syringyl ring. Phenoxy radicals, which are the key intermediates, are formed through different pathways. Phenols present might be photo oxidized into quinines and muconic acids. The explanation given is the abstraction of phenol hydrogen by excited  $\alpha$ -carbonyl or singlet oxygen. Direct oxidation of phenols absorbing near UV light or homolysis of the  $\beta$ -O-4 bond in aryl glycerol- $\beta$ -aryl ethers can then occur. Scission of chemical bonds can also take place leading to a production of radicals. This process is claimed to be responsible for yellowing of wood [6].

The aim of this work is to develop photostable composite materials from polyolefin (polypropylene and polyethylene) and wood flour. A first series of specimen was obtained by blending wood flour and polymeric material. In a second series, polypropylene-grafted-maleic anhydride was added to the previous ingredients. The behaviour of these materials under UV light was studied. The evaluation of mechanical properties of the produced composites through several tests (thickness swelling, hardness and moisture content) was also carried out and will be reported in a forthcoming article.

#### 2. Experimental

#### Materials

The wood flour particles of 425 microns (40-mesh) in size were kindly donated by American Wood fibbers (Schofield, WI) and are constituted predominantly with ponderosa pine, maple, oak, spruce, southern yellow pine, cedar. The wood was oven dried at 100°C for 24 h before processing to remove moisture.

The isotactic polypropylene matrix (PP) has a density of 0.900 g/cm<sup>3</sup> and a melt flow index of 2.5g/10min. High density polyethylene (HDPE) used has a density 0.963g/cm<sup>3</sup> and a melt index of 0.72g/10min. Both polymers were provided by Solvay Co.

Polypropylene grafted with maleic anhydride (PP-g-MA) with an approximate maleic anhydride (MA) content of 3 wt% was purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). All ingredients were used as received.

#### **Compounding and processing**

The composite materials were obtained by melt blending in a chamber of a Brabender mixer AEV 330 at 180°C for 10 min at 90 rpm. For the extraction of volatile and harmful gases, the hood was open. At first, polymer was introduced for 5 min at 170°C and the screw speed fixed at 40 rpm. In a second step the wood granulates and others compatibilizers were introduced. The system was mixed during 10 min at 180°C at 90 rpm. After the processing step, each sample was sandwiched during 1 min between two Teflon papers and pressed at 175°C under a pressure of 200 bars to obtain films with thicknesses between 100 to 200 microns. For each polymer matrix (PP, PE), four formulations were produced with various content of wood (table 1).

#### Table 1

#### Electron and optical microscopy

The state of dispersion of the wood inside the polymeric matrix was analyzed using optical microscopy on samples of 100 to 200  $\mu$ m thick. Scanning Electron Microscopy (SEM) was used to obtain microphotographs of the fracture surfaces of the wood composites. These factures have been performed in liquid nitrogen to avoid any deformation. SEM has been performed using a FEI Quanta 400 microscope working at 30 kV.

The polymer surface was examined with LEICA optical microscope working in a transmission mode. Samples were thin enough that no special preparation of the samples was needed for their observations with the optical microscope.

#### UV-irradiation and chemical characterization

The UV absorption of each sample was measured using a UV-510 Perkin-Elmer spectrophotometer. Irradiation in conditions relevant to outdoor exposure ( $\lambda > 300$  nm) in the presence of air was carried out in a SEPAP 12/24 unit working at a temperature of 60°C. Details on this artificial accelerated photoageing device are given elsewhere [9]. To follow the degradation of the UV-light irradiated specimen, the infrared spectra were recorded with a Nicolet 5SX FTIR-spectrometer, working with OMNIC software. Spectra were obtained using 32 scans and a 4 cm<sup>-1</sup> resolution.

#### **3.** Experimental results

#### 3.1. Characterization of the initial properties of the WPC samples

#### Morphology and dispersion of the composites

Figure 1 shows the SEM micrographs of the fracture surface of the WP composites made from PP, PE and PP with PPgMA.

#### Figure 1

Visual observation reveals a separation between particles and matrix in PP and PE composites probably because of the lack of interfacial adhesion. In composites in which a coupling agent is used, it looks smooth. This could result from the presence of PPgMA that could bind the two phases together due to the OH groups of the wood that react with maleic anhydride to form bonds [2] This provides sufficient adhesion between the components to resist cracks forming as the consequence of the Poisson effect. Note that in all cases, an absence of fibre pull-out, which indicates a weak interfacial adhesion [2, 10, 11]. The actual

images of the wood dispersion acquired display a good dispersion of wood in the polymeric material whatever the host material (Fig 2). However, in PE and PP composites, the wood remains compact at opposite to PP/PPgMA in which the fibres are separated. This good dispersion could be attributed to the fact that some of the OH groups of wood react with maleic anhydride to form linkages and thereby improve the dispersion of wood in the composite [10].

#### Figure 2

#### UV-visible absorption

The WPC samples made with PP and different percentages (from 0 to 50%) of wood were characterized by their UV-visible spectrum before irradiation. Figure 3 shows the curves obtained for thin films (thickness around 100 microns) of WPC with 0%, 5%, 10%, 25% and 50% of wood (WPPC0 to 4). The UV-visible spectrum of a PP film shows the presence of two maxima at 230 nm and 280 nm which correspond to the processing phenolic antioxidant remaining in the processed polymer. In presence of wood, the UV-visible spectra of WPC reveal an increase of absorbance towards the long wavelengths in the visible part of the spectrum. The absorbance increases with the amount of wood, but the presence of the processing antioxidant is still observable even for the highest contents in wood.

#### Figure 3

Very similar observations can be made on the basis of the analysis of the UV-visible absorption spectra of the PE/wood composites.

**3.2.** Influence of UV-irradiation on the chemical structure of PP and PE wood polymer composites

**PP/wood composites (WPPC)** 

Infrared analysis

UV light irradiation of PP in air is known to produce dramatic modifications of the infrared spectra of the exposed samples. The modifications of the IR spectra of all the WPC films upon irradiation in the presence of oxygen are comparable to that of pristine polypropylene, and are mainly characterized by an increase of absorbance in the hydroxyl and carbonyl regions, as observed on figure 4, which shows the IR spectrum of the sample with 5 % of wood.

#### Figure 4

The photooxidation of polypropylene results in the formation of hydroxyl (mainly hydroperoxides and alcohols) and carbonyl groups (mainly ketones, esters and acids) easily detectable by infrared spectroscopy respectively in the 3200-3600 cm<sup>-1</sup> and 1900-1500 cm<sup>-1</sup> domains. The chemical structure of the main oxidation products can be considered as well established and the mechanisms by which oxidation occur is now fairly well understood [12]. In the carbonyl domain the photochemical oxidation of PP leads to the formation of a broad band with several maxima, peaking at 1713, 1735 and 1780 cm<sup>-1</sup>. The photoproducts corresponding to these absorption maxima have been identified formerly [13, 14], and it is agreed that the main absorption at 1713 cm<sup>-1</sup> is that of the carboxylic acids in the dimer form. The formation of nano/microcracks at the surface of the polymer and lead to the degradation of the mechanical properties of the material. The chemical modifications of the polymer measured by the concentration of the oxidation photoproducts can be quantitatively related to the mechanical degradation of the material [15].

#### Rates of photooxidation

Figure 5 shows the variation of the ratio 1713 cm<sup>-1</sup>/ 2722 cm<sup>-1</sup> as a function of irradiation time respectively for PP and PP/wood films with different percentages of wood

flour (WPPC 0 to 4). Because the content of polymer was different for the various samples as a result of the different contents of wood flour, the kinetic curves of oxidation were plotted as the ratio of the absorbance at 1713 cm<sup>-1</sup> versus the absorbance at 2722 cm<sup>-1</sup> ( $v_{(C-H)}$  stretching vibration band characteristic of PP).

Fig. 5 shows that in the case of pristine PP (WPPC0), no increase of absorbance is observed during the first 20 hours of exposure. This is also the case in the domain of hydroxyl not shown here. Oxidation can be detected only after this first period. This induction period results from the disappearance of the processing antioxidant, which is consumed as a sacrificial additive [16].

At opposite, it can be observed on the infrared spectra of all the samples containing wood (WPPC1 to 4) that the absorbance in the carbonyl domain increases within the first 20 hours of irradiation. A careful examination of the hydroxyl domain shows that no increase of absorbance occurs in this last domain for the same irradiation time (see for example Fig. 4 relative to WPPC2). This observation suggests that oxidation is not coming from the PP matrix. A second important point observed in Figure 5 is that, within these first 20 hours, the carbonyl absorbance in the case of PP/wood composites increases with the amount of wood in the samples. These observations indicate that the initial increase of the carbonyl absorbance is related to the oxidation of wood and not that of PP.

After the first period, oxidation of the polymer starts with a rate which is more important for the samples with wood than for the PP one. The rate is slightly increasing with the amount of wood in the composite but a plateau is reached for concentrations above 25% of wood. These results indicate that the presence of wood considerably shortens the durability of the composite.

#### UV-visible analysis

Figure 6 shows the modifications of the UV-visible spectrum of WPPC4 (PP/ (50 % wood) during photooxidation. This figure shows that the absorbance in the visible domain increases with irradiation time. No modifications of the absorption spectrum of pristine PP are expected in this domain of the visible absorption (above 300 nm) [16], even for longer irradiation times. This result suggests that the modifications of the UV-visible absorption can be unambiguously attributed to a photochemical transformation of wood in the polypropylene matrix. The reaction involved in this process has been largely reported in the literature [3, 4, 6]. Considering the chemical composition of wood, lignin is the key structure in wood photodegradation as only lignin absorbs in the UV-visible spectral domain [5-7]. The mechanism of lignin photodegradation is complex, involving different pathways giving the formation of radical species. These free radicals react with oxygen to produce chromophoric groups as carbonyl and carboxyl groups, which also lead to chain cleavage and yellowing. One of the main radicals is a long life guaiacoxy radical, which undergoes transformation into quinoid structures which are the origin of the yellowing of wood [5-7].

Figure 6

#### HDPE/wood composites

#### Rate of oxidation

Photooxidation of WPC films with HDPE as polymer matrix (samples WPEC 0 to 4) was followed by IR analysis. The same conclusions as for WPC with PP (samples WPPC 0 to 4) can be drawn concerning the reaction stoechiometry. The photooxidation of pure HDPE gives an induction time of 30 hours, and in presence of wood the oxidation of the polymer starts earlier (Fig. 7). Moreover, an increase of the rate of oxidation is observed by increasing the percentage of wood. These observations indicate that the presence of wood participates in

the initiation of degradation but does not change the reaction stoechiometry as seen previously.

#### Figure 7

#### WPC made with PP/PPgMA/wood:

Beside the study of composites of wood and PP or HDPE, the photooxidation of composites with wood, PP and a compatibilizing agent (PPgMA) was examined in order to characterize the influence of a compatibilizing agent (PPgMA) on the photodegradation of WPC. Figure 8 shows the modifications of the infrared spectrum of a sample made with 25% of wood resulting from UV light irradiation in the presence of air (WPPG 1). The initial spectrum of a WPPG 1 film shows a broad complex absorption band in the carbonyl domain. This band results of the presence of both wood (25%) and maleic anhydride (3%). During the UV irradiation, absorption bands develop in the carbonyl domain (Fig. 8). Previous studies of the photooxidation of PPgMA samples have shown that no specific photoproducts of maleic anhydride degradation were detected [16]. The modifications observed in Fig. 8 indicate then the formation of oxidation photoproducts that come only from wood and PP, and not from MA. As reported above, in the first 20 hours, the modifications reveal a rapid oxidation of wood. The same behaviour is observed in the case of the other samples not presented here (WPPG 2 to 4).

#### Figure 8

On the basis of the infrared spectra of the various samples, the rates of photooxidation of WPC containing increasing amount of PPgMA (WPPG1 to 4) can be compared. Figure 9 represents the kinetic curves of oxidation for these samples and compares them with the curve obtained in the case of the sample of PP/wood (25%) (WPPC3) extracted from fig. 5. Two sets of curves are given, one for the carbonyl domain (fig.9a) and another one for the

hydroxyl domain (fig.9b). In both cases one can make the same remarks. At first it is clearly observed that the presence of MA as a compatibilizer has for effect to decrease the oxidation rate of PP in the WPC. All the curves presented in figure 9 are below the curve corresponding to the sample that has no compatibilizer. Moreover it can be clearly observed that increasing the amount of PPgMA increases the stability of the polymer. After 80 hours of irradiation, no oxidation can be observed in the case of the samples with PPgMA (WPPG 3 and 4), whereas in the case of WPPC 3, oxidation started after only 20 hours under irradiation. This stabilizing effect resulting from the presence of maleic anhydride has to be considered as rather important in terms of applications of WPC.

#### Figure 9

#### 4. Conclusion

The wood polymer composites produced using PE and PP as the host polymer showed interesting features. The characterization of the samples with the help of electron microscopy supplemented with microscope photographs revealed an acceptable level of dispersion of the wood particle in the polymeric material. Addition of PPgMA in polypropylene composites appreciably improved this dispersion, which might be explained by the formation of linkages between the OH groups of wood and maleic anhydride.

The following of the photooxidation behaviour of the samples highlights that the presence of wood in polymer composites has no influence on the mechanism of photooxidation of the polymer (PP or PE). This means that the same photoproducts are formed as well in WPC and as the pristine polymer, in the same relative concentrations. However, wood absorbs in the UV-visible region, as observed on the spectra of the WPC samples that present a higher absorbance in the UV domain (300-400 nm) than the polymer samples. Wood is not inert under UV-visible light and specific photoproducts coming from the oxidation of wood are detected in the first 20 hours of irradiation.

Under irradiation, ligning that are considered in the literature as the key structures involved in the degradation of wood generate phenoxy radicals, and phenols might be oxidized [3, 4, 5, 19]. The influence of wood in composites expresses itself in the durability of the WPC by the modification of the kinetics of photooxidation. The results show that wood has no marked effect on the oxidation induction time of the polymer, which corresponds to the disappearance of the residual processing antioxidant [17, 18]. However one can clearly observe that the presence of wood results in an increase of the oxidation rate of the polymeric matrix, after the induction period. This effect is more and more accentuated with increasing amounts of wood within the WPC, up to 25%. This can be explained by radicalar species produced by photooxidation of wood that are likely to initiate the oxidation of the polymer once the antioxidant has been consumed within the induction period. Wood acts then as an initiator on the photooxidation of the polymer matrix, PP or PE, in the WPC material. However, by increasing the percentage of wood, the amount of polymer in the composite is lower, and the global effect on the durability of the WPC material might be positive if one considers the level of degradation of the composite and of the pure polymer after the same ageing time.

In PP/PPgMA/wood composites the fibres are separated. This better dispersion has been attributed to the possible reaction of some of the OH groups of wood with maleic anhydride to form linkages and thereby improve the dispersion of wood in the composite. Interestingly this results in an improvement of the photostability of WPC composites made with PPgMA and a better long-term behaviour in the objective of outdoors applications.

The next step of this study will be the analysis of the evolution of the used properties of the WPC material, which have only been characterized before ageing.

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#### **Figure captions**

**Figure 1**: SEM micrographs of WP composites with PE (left) PP (middle) and PP /PPgMA (right). The percentage of wood is 25% in all samples.

Figure 2: Photographs of the composite surfaces: PE/wood (left), PP/wood (middle) and

PP/PPgMA/wood (right).

**Figure 3**: UV-Visible spectra of film of WPC made with PP and wood: the curves go from bottom to the top according to the percentage of wood incorporated in the sample (0, 5, 10, 25, and 50% wood's weight).

Figure 4: IR spectra of a WPPC2 film (PP/wood (5%)) during photooxidation.

Figure 5: Variations of the normalized carbonyl absorbance

 $(\Delta(OD(1713 \text{ cm}^{-1})/OD(2722 \text{ cm}^{-1}))$  as a function of irradiation time for films of PP/wood during photooxidation at  $\lambda > 300$ nm, 60°C (WPPC0 to 4).

**Figure 6**: UV-visible spectra of a WPPC4 film (e~100  $\mu$ m) during photooxidation ( $\lambda > 300$  nm, 60°C)(the curves go from bottom to the top according to the irradiation time 0h, 30h, 60h and 80h).

**Figure 7**: Variations of normalized absorbance ( $\Delta$ (OD (1712 cm<sup>-1</sup>)/OD(720 cm<sup>-1</sup>)) as a function of irradiation time for films of HDPE/wood (WPEC 0 to 4) during photooxidation at  $\lambda > 300$ nm, 60°C.

**Figure 8**: Modifications of the infrared spectra of PP/PPgMA/wood (WPPG 1) under photooxidation at  $\lambda > 300$ nm, 60°C (differences of spectra in the carbonyl domain 10h-0h, 20h-0h,...80h-0h).

Figure 9: Variations of a) normalized carbonyl absorbance

 $(\Delta(OD(1718 \text{ cm}^{-1})/OD(2722 \text{ cm}^{-1}))$  and b) normalized hydroxyl absorbance

 $(\Delta(OD (3400 \text{ cm}^{-1})/OD(2722 \text{ cm}^{-1}))$  as a function of irradiation time for films of PP/PPgMA/wood (25% of wood) during photooxidation at  $\lambda > 300$ nm, 60°C (WPPG1 to 4)and film of PP/wood (WPPC3).

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Sample	<b>PP</b> (%)	Wood (%)
WPPC0	100	
WPPC1	95	5
WPPC2	90	10
WPPC3	75	25
WPPC4	50	50

Sample	HDPE (%)	Wood (%)
WPEC0	100	0
WPEC1	95	5
WPEC2	90	10
WPEC3	75	25
WPEC4	50	50

Sample	<b>PP</b> (%)	PPgMA(%)	Wood (%)	
WPPG <sub>1</sub>	70	5	25	
WPPG <sub>2</sub>	65	10	25	
WPPG <sub>3</sub>	60	15	25	
WPPG <sub>4</sub>	55	20	25	

Table1: Composition of the wood/polymer composites (percentage is in weight)

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Figure 1: SEM micrographs of WP composites with PE (left) PP (middle) and PP /PPgMA (right). The percentage of wood is 25% in weight in all samples.



Figure 2: Photographs of the composite surfaces; PE/wood (left), PP/wood (middle) and PP/PPgMA/wood (right).





Figure 3: UV-Visible spectra of film of WPC made with PP and wood: the curves go from bottom to the top according to the percentage of wood incorporated in the sample (0, 5, 10, 25, and 50°/° wood's weight)



Figure 4: IR spectra of a WPPC2 film (PP/wood (5%)) during photooxidation



Figure 5 : Variations of the normalized carbonyl absorbance ( $\Delta$ (OD (1713 cm<sup>-1</sup>)/OD(2722 cm<sup>-1</sup>)) as a function of irradiation time for films of PP/wood during photooxidation at  $\lambda > 300$ nm, 60°C (WPPC0 to 4).

0



Figure 6: UV-visible spectra of a WPPC4 film (e~100  $\mu$ m) during photooxidation ( $\lambda$  > 300 nm, 60°C)(the curves go from bottom to the top according to the irradiation time 0h, 30h, 60h and 80h)

South South



Figure 7: Variations of normalized absorbance ( $\Delta(OD (1712 \text{ cm}^{-1})/OD(720 \text{ cm}^{-1}))$ ) as a function of irradiation time for films of HDPE/wood (WPEC 0 to 4) during photooxidation at

 $\lambda > 300nm, 60^{\circ}C.$ 

Look



Figure 8: Modifications of the infrared spectra of PP/PPgMA/wood (WPPG 1) under photooxidation at  $\lambda > 300$ nm,  $60^{\circ}C$  (differences of spectra in the carbonyl domain 10h-0h, 20h-0h,...80h-0h)

CEPT

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Figure 9: Variations of a) normalized carbonyl absorbance ( $\Delta$ (OD (1718 cm<sup>-1</sup>)/OD(2722cm<sup>-1</sup>)) and b) normalized hydroxyl absorbance( $\Delta$ (OD (3400 cm<sup>-1</sup>)/OD(2722 cm<sup>-1</sup>)) as a function of irradiation time for films of PP/PPgMA/wood (25% of wood) during photooxidation at  $\lambda > 300$ nm, 60°C (WPPG1 to 4)and film of PP/wood (WPPC3).