Effect of Wood Content on The Thermal Behavior and on The Molecular Dynamics of Wood/Plastic Composites

Gisele C. X. Valle,[1] Maria I. B. Tavares,[1] Leandro Luetkmeyer,[1] Giovanni C. Stael[2]*

Summary: In the last decades, the growing environmental awareness has resulted in a renewed interest in the use of natural materials for different applications. In this context, the use of wood in plastic to obtain composites has grown significantly. In the present work, heartwood and sapwood from Angelim Pedra (*Hymenolobiun petraeum*) were used to prepare PVC/wood composites. To study the composites with different wood types and filler contents the molecular dynamic was investigated through low field NMR by poton spin- lattice relaxation time measurements (T_1H) and the thermal behavior was characterized by means of differential scanning calorimetry (DSC) focusing the glass transition temperature and thermogravimetric analyses (TGA) observing the changes in the thermal stability. It was found that increasing addition of wood flour (sapwood and heartwood) caused a small but progressive improvement of the decomposition temperature of the composites, whereas the glass transition temperature remains practically unchanged. In the molecular dynamic behavior, a gradual decrease in T_1H values was observed with increasing sapwood and heartwood content, indicating that the composites became less rigid. The distribution curves of the domains showed a better interaction and phase dispersion between the composite components with higher filler content.

Keywords: composites; NMR; PVC; thermal properties

Introduction

Wood is a natural polymeric composite, made up mainly of cellulose, hemicellulose, lignin, and a small amount of extractives with approximately 45%, 22%, 25% and 8% of composition, respectively.[1–3]

The use of wood as reinforcing filler in polymer composite has made significant gains in popularity due to their many advantages including economic, technical and ecological aspects. Their main benefits are: low cost, low density, high relative strength and stiffness, flexibility during processing with no mechanical harm to the equipment and because it is from natural renewable source, biodegradable and it provides a solution to environmental pollution by finding new uses for waste wood.[4,5]

To produce wood plastic composites (WPCs) both thermosets and thermoplastics polymers are attractive as matrix materials, however, thermoplastics offer advantages over thermosets: low processing cost, design flexibility and ease of molding complex parts are some examples.[4] The most commonly used thermoplastics are polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC), representing 83%, 7% and 9% respectively of the whole markets in North America.[6,7] PVC is in particularly one of the most important commercial thermoplastic polymers and is

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[1] Instituto de Macromoléculas Professora Eloisa Mano – Universidade Federal do Rio de Janeiro (IMA/UFRJ). Centro de Tecnologia, Bloco J, Ilha do Fundão. PO Box: 68525, CEP 21945-970, Rio de Janeiro, RJ- Brazil
E-mail: gisele@ima.ufrj.br
[2] Observatório Nacional – MCT, Rua Gal. José Cristino, 77, CEP 20921-400, São Cristóvão, Rio de Janeiro, RJ- Brazil

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used in large amounts (it is a second polymer in consumption), representing a great technical and economic importance.[8,9]

Potential applications of wood thermoplastic composites include automotive, the building industry and furniture.[10] PVC-based wood composites are widely used in building construction applications, such as window/door profiles, decking, railing and siding because they offer good mechanical properties, chemical and water resistance, rot-proof ability, stain and paint-ability, as well as a long lifetime (UV resistance, free from maintenance). Furthermore, PVC/wood composites can be cut, sawed, nailed, screwed, and processed by the conventional wood working equipment.[6,7]

In this work, composites were prepared using PVC as matrix and heartwood or sapwood from Angelim Pedra (*Hymenolobiun petraeum*) as filler. Angelim Pedra tree is found in the north of Mato Grosso (Brazil) and it is much exploited in construction, furniture and carpentry generating an expressive amount of waste flour wood, which must be used by ambient reason.[11,12]

With the objective to investigate and compare the influence of the two wood types with different filler contents in the molecular dynamic and thermal behavior of PVC/wood composites, the proton spin-lattice relaxation time, the decomposition temperature and the glass transition temperature were evaluated.

Experimental Part

Materials

Matrix polymer

The polymer used in this study was a poly(vinyl chloride) (Norvic® SP 800) supplied by Braskem S/A, from Brazil. To prepare the PVC matrix some additives are need to achieve its processability and/or performance. The additives used were: stabilizer (Naftosafe® CZ-4004), impact modifier (KaneAce®B52) and processing aids (MMA-co-EA K120).

Reinforcing Filler

Heartwood and sapwood from Angelim Pedra were triturated and bolted in a mesh size 40–80. Subsequently, they were exposed to the heat treatment in an oven at 80 °C during 48h to minimize the moisture content before mixing with PVC. This treatment is important because during processing of natural filler with thermoplastic matrix, the moisture content can lead to poor processability, generating porous products.[4] Three different wood proportions (10, 25 and 40 phr (parts per hundred of resin)) were used to prepare the composites, this corresponding to 8.1, 18.1 and 26.1 per cent weight fraction (wt%), respectively. For a cost benefit, no chemical treatment was applied to the woods used in this study.

Sample Preparation

The samples were prepared in a Haake Rheocord 9000 fixed with 165 °C and 50 rpm. The PVC compound (polymer, stabilizer, processing aids and impact modifier) was prepared in 8 min without interruption. The preparation of the composites was made in two steps. The PVC compound ingredients were mixing for 5 min and immediately the filler was added and the mixing was continued for 3 min. The ingredients to prepare PVC compound and composites and their respective proportions are listed in Table 1.

Characterization of the Molecular Dynamic Behavior

Low field NMR MARAN ultra 23, operating at 23 MHz (for protons) and equipped with an 18 mm variable temperature probe,

Table 1.
PVC compound and PVC/wood composites formulations.

Ingredients	Proportion (phr)
PVC	**100**
Stabilizer	**4**
Processing aids	**1**
Impact modifier	**8**
Heartwood	**varied**
Sapwood	**varied**

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was used for the relaxation measurements. T_1H was determined directly by the traditional inversion recovery pulse sequence (180°- τ - 90°), the 90° pulse (4.6μs) was calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.1 to 10,000 ms, with 4 scans for each point and 5s of recycle delay. The static and solid state experiments were performed at 27 °C. The relaxation values and relative intensities were obtained by fitting the exponential data with the aid of the program WINFIT. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the software WINDXP.

Characterization of the Thermal Behavior

To know and understand the thermal behavior of the composites, DSC and TGA were performed. TGA (TA Instruments Q 500) was used to determine the decomposition temperature under the following conditions: the samples were heated up to 700 °C at a rate of 10 °C/min, in nitrogen atmosphere. DSC (DSC7, Perkin- Elmer) was used to determine the glass transition temperature (*T*g) with heating up to a temperature of 150 °C at a rate of 20 °C/min, under nitrogen atmosphere. The glass transition temperature was determined from the onset of the DSC-curve.

Table 2.
T_1H values obtained from low field NMR.

Composites	T_1H (ms)
PVC Compound	**320.1**
PVC/Sapwood 10 phr	**242.7**
PVC/ Sapwood 25 phr	**174.2**
PVC/ Sapwood 40 phr	**150.4**
PVC/Heartwood 10 phr	**266.2**
PVC/ Heartwood 25 phr	**198.2**
PVC/ Heartwood 40 phr	**159.8**

Results and Discussion

Molecular Dynamic

Inversion-recovery pulse sequence is an important NMR technique employed to supply the spin-lattice relaxation time that provide detailed information on mobility at the molecular level for differents materials, as for example, polymeric composites. The proton spin-lattice relaxation time is a parameter that reflects the influence of sample heterogeneity, inter- and intramolecular interactions and the chemical nature of the samples. The relaxation process can give information on molecular dynamics for solid samples, if T_1H values increase the molecular mobility decrease and vice versa.

The Table 2 shows the T_1H values found for the different composites. Three measurements were conducted for each sample, and the results were averaged to obtain the relaxation parameter, with 2% of standart deviation.

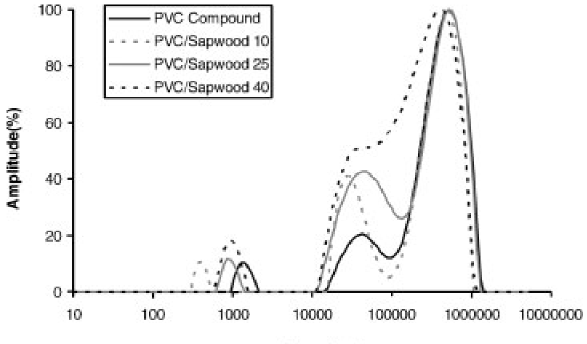

Figure 1.
Distribution curves of domains obtained for the PVC/Sapwood composites.

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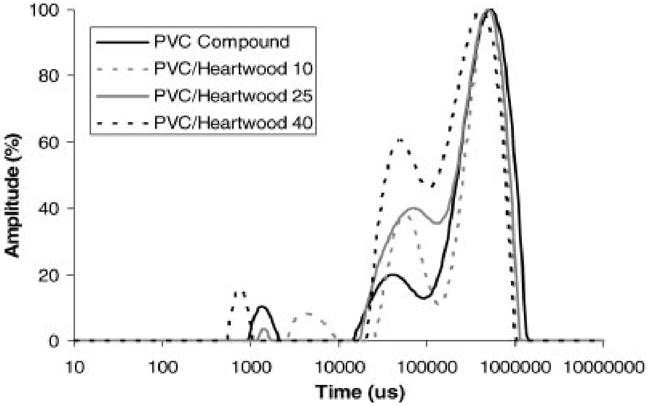

Figure 2.
Distribution curves of domains obtained for the PVC/Heartwood composites.

According to results obtained it was possible to observe that the increase of the wood addition promotes a gradual decrease in the T_1H values of the PVC/sapwood and PVC/heartwood composites, indicating that the molecular mobility was increased due to the material molecular reorganization. This result shows that the composites became progressively less rigid with the increase of filler quantity.

Comparing the T_1H values obtained for the composites with different wood types it was possible to verify that the PVC/heartwood composites (higher values) present higher rigidity than PVC/sapwood composites, with the same wood proportion. This result suggests that the sapwood presents a structure that is more flexible than heartwood filler, which, probably, promotes differences in the chemical arrangements and packing in the composites. It could also come from the components interaction.

The distribution curves of the domains presented in the composites were obtained as it was described in the experimental part. Figure 1 shows the distribution curves of domain for the PVC/sapwood composites and Figure 2 for PVC/heartwood composites; comparing both Figures they show a similar behavior. It can be observed that

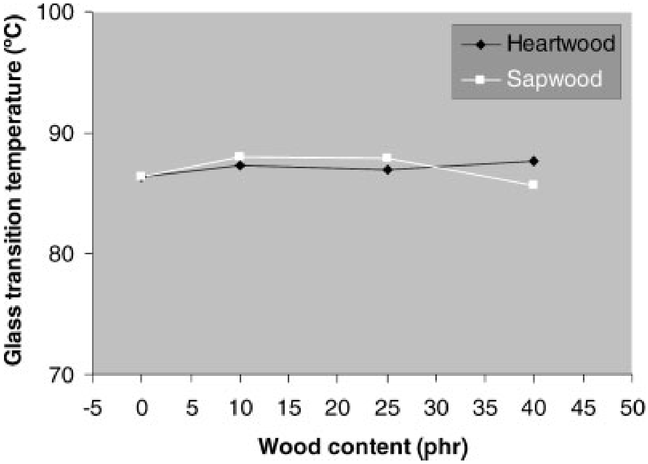

Figure 3.
Change in glass transition temperature as a function of wood content.

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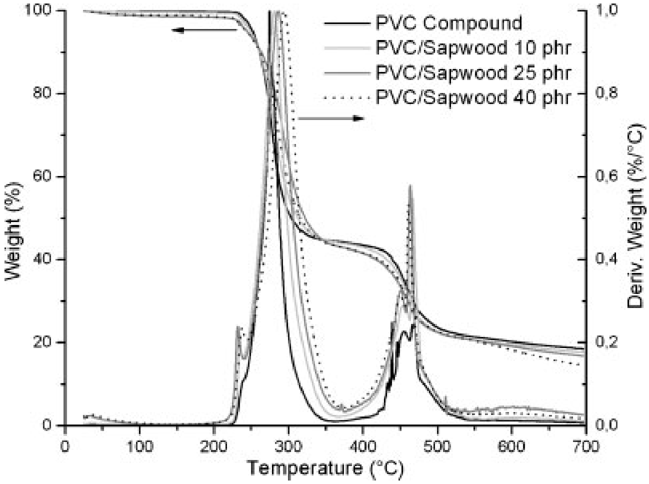

Figure 4.
TGA and DTG curves of the PVC compound and PVC/Sapwood composites.

with the increase of both wood types, the systems formed showed good interaction and phase dispersion between the composites components, since an overlapped of domains peaks was found.

Thermal Behavior

Essential statements regarding the thermal stability of composite materials can be successfully obtained from TGA and DSC analyses. Information about the decomposition and glass transition temperatures are fundamental to determine important parameters such as processing conditions and application of the final product.

The Figure 3 shows the glass transition temperature (*T*g) found for PVC compound (unfilled polymer) and different studieds composites. Each of the data reported an average of three runs. The variation of values was ±0.6 °C.

The analysed samples present onset value between 85.7 and 88 °C. This result shows that DSC-studies of the glass-

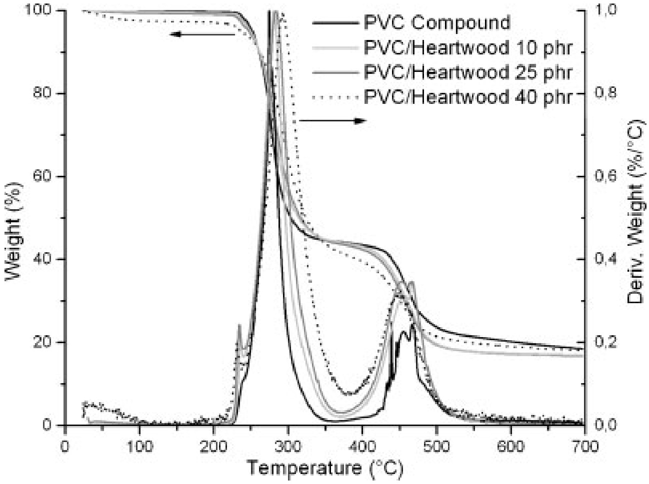

Figure 5.
TGA and DTG curves of the PVC compound and PVC/Heartwood composites.

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transition temperature showed no significant influence of the composition on *T*g in the concentration range that was studied.

The TGA and DTG graphs of the PVC/sapwood composites and PVC/heartwood composites are showed in Figure 4 and 5, respectively.

From the TGA results, it was observed that the thermal degradation of the analyzed samples occurs in two distinct steps. The composites showed a slightly initial decrease of weigth below 100 °C due to loss of moisture present in the sapwood and heartwood. Evaluating the thermal decomposition temperature (TDT) calculated from the first derivative of TGA curves, it was seen that the increasing wood addition improves gradually the thermal stability of the composites. The TDT of the PVC/sapwood composites increase 6.5, 11.9 and 19.5 °C and for the PVC/heartwood composites this enhacement was of 5.9, 9.4 and 18.1 °C for the composites with 10, 25 and 40 phr of wood, respectively comparing to the unfilled PVC.

Conclusion

In the present work, the effect of sapwood and heartwood of Angelim Pedra with different filler content on the properties of PVC/wood composites was examined, and the following can be noted: The decomposition temperature was gradually improved with the increasing sapwood and heartwood addition, showing that the thermal stability of the different composites was increased. From the molecular dynamic behavior, it was found that the T_1H values decrease with the increase of wood content, it indicates that the composites present good adhesion between components. The distribution curves of domains showed a good interaction and phase dispersion between the composite components.

From the results of this study it can be concluded that the use of granulated sapwood and heartwood from Angelim Pedra, generated by the industry as waste, can be used in the preparation of new materials, such as PVC composites, resulting in an enhancement in the thermal stability and good interaction between composites components.

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