Preparation and Characterization of PVC/Natural Filler Composites

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Summary: The main purpose of the present work is to use a renewable material obtained from fruit seed to prepare a reinforced polymer composite with poly(vinyl chloride) (PVC). The characterization of the composites was based on the determination of the molecular motion and of mechanical and thermal properties. The thermal properties were characterized through thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The mechanical properties were characterized through tensile tests. The molecular dynamic behavior of the polymer matrix was studied by proton spin-lattice relaxation, using low field nuclear magnetic resonance (NMR). It is shown that the thermal properties do not depend on the filler content, although mechanical properties are improved with the addition of filler. Despite that, no strong interaction between the filler and the PVC matrix could be detected.

Keywords: composites; low field NMR; mechanical and thermal properties; natural filler; PVC

Introduction

Composite are usually developed to improve the properties of the individual components.[1] Generally, composite materials are composed of two phases: the matrix (or continuous phase) and the dispersed phase. Final composite properties are functions of the morphology and homogeneity of the constituent phases, their relative amounts and the geometry of dispersed phase.[2] Reinforcement of polymer matrices was initially achieved with man-made fibers, such as glass, carbon and aramid resins, to take advantage of their high tensile moduli.[3] Over the last few years, significant amount of work has been carried out to allow for use of natural fillers extracted from vegetable source.[4,5] Natural fillers present numerous advantages, as they present low density, are biodegradable, are nontoxic, are not abrasive, among many other useful and advantageous properties.[6–9] Sisal, coconut fiber (coir), henequen, jute, palm, bamboo and wood are examples of fillers commonly used in thermosetting and thermoplastic composites.[10–17] Particularly, cumbaru pits can be used for preparation of new composites. The cumbaru tree belongs to the *Fabaceae* family and is commonly found in Brazil.[18–21]

Among the many polymers that have been used as matrices for preparation of composites, PVC is certainly one of the commonest one.[8,22] Besides, PVC is one of the most important commodity polymers, finds many technical applications and is of enormous economic importance.[23,24]

Based on the previous discussions, the main objective of the present study was to investigate the effect of the addition of a cumbaru filler on the mechanical and thermal properties of the PVC composites. Besides, the molecular dynamic behavior of the matrix in the presence of the filler was also investigated with the help of NMR techniques.

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Experimental Part

Materials

Poly(vinyl chloride) (Norvic® SP 800 100 phr,) and stabilizer (Naftosafe® CZ-4004, 4 phr) were supplied by Braskem. Impact modifier (KaneAce®B52, 8 phr) and processing additives (MMA-co-EA K120, 1 phr) were supplied by Vulcan Material Plástico.

The filler was extracted from cumbaru pits. Pits were separated from the fruit, washed with current water, grinded and bolted, resulting in a filler with mesh size 30–200. Afterwards, the material containing 8.6% of water was treated in an oven at 80 °C for 48 h to reduce the moisture content before blending with PVC. Thermal treatment was necessary because the moisture content can lead to poor processability during the composite preparation, generating porous products.[8] No chemical treatment was applied to the natural filler. Filler ratios used for preparation of the composites were 10, 25 and 40 phr.

Sample Preparation

Samples were prepared in a Haake Rheocord 9000 at 165 °C and 50 rpm. The PVC compound (polymer, stabilizer, processing additives and impact modifier) was prepared by mixing for 8 min. Composites were prepared in two steps: compound ingredients were initially mixed for 5 min and then the filler was added and additionally mixed for 3 min.

Mechanical Tests

Samples were conditioned at 23 ± 3°C and 50 ± 5% of relative humidity for 48 h and then molded by compression into sheets at 180 °C and pressure of 4 MPa for 10 min. Then, samples were cooled for 10 min under the same pressure. Tensile experiments were performed in an Instron Universal Testing Machine 4204, at room temperature and according to ASTM D638 (type V). At least ten specimens were tested for each sample and the average values were saved for quantitative analyses.

Characterization of the Thermal Behavior

TG (TA Instruments Q500) was used to determine the characteristic decomposition temperature. Samples (12-28 mg) were loaded in platinum pans and heated to 700 °C with heating rate of 10 °C/min and precision of ±2 °C. The N_2 flow rate was kept equal to 60 ml/min.

DSC (DSC7, Perkin-Elmer) was used to determine the glass transition temperatures (Tg), obtained from the second heating scan. Samples of 5–6 mg were initially placed in aluminum pans and runs were then conducted in the temperature range of 40–150 °C with heating rate of 20 °C/min and precision of ±2 °C. The N_2 flow rate was kept equal to 20 ml/min.

Characterization of the Molecular Dynamic Behavior

Low field NMR measurements were carried out in a Maran Ultra 23 spectrometer (Resonance, Oxford-UK) at 27 °C. The spin-lattice relaxation time (T1H) values were determined directly by the traditional inversion-recovery pulse sequence, using a range of τ varying from 10 to 106 μs (20 τ values), with 4 transients for each τ value, applying 5s of recycle delay.

Results

Mechanical Properties

One can observe in Figure 1 that the tensile modulus increases with the increase of filler content. As the modulus is strongly affected by the characteristics of the incorporated filler and less affected by polymer-filler adhesion, this indicates that the modulus of the cumbaru filler is larger than that of the PVC matrix. One can also observe the decrease of tensile strength (Figure 2) and elongation at break (Figure 3). The decrease of tensile strength is probably due to the increase of interfacial defects, as one might already expect. The decrease of elongation at break is due to the adhesion between the filler and the matrix, as one might also expect.

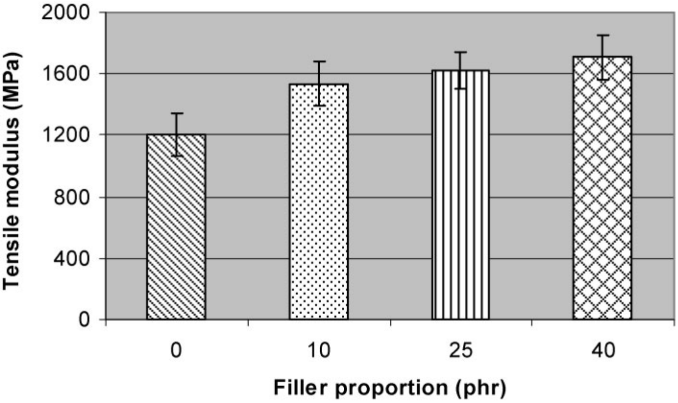

Figure 1.
Influence of filler content on tensile modulus of PVC compound and composites.

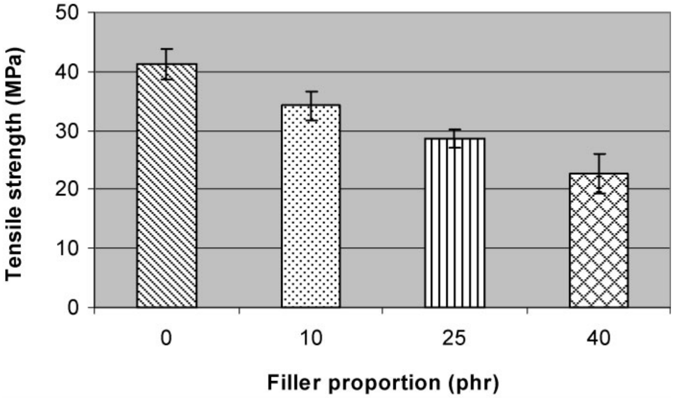

Figure 2.
Effect of filler content on tensile strength of PVC compound and composites.

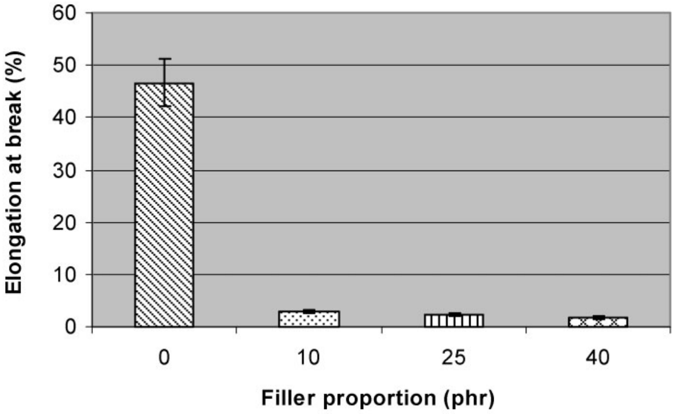

Figure 3.
Influence of filler content on the elongation at break of PVC compound and composites.

Thermal Properties

Most polymer composites present worse mechanical and physical properties after thermal treatment, due to thermal stress during the manufacturing of the filler reinforced composite materials. Fundamental information regarding the thermal stability of the composites materials can be obtained from TG and DSC analyses.[25] Typical TG and DTG curves (Figures 4 and 5) revealed that the thermal degradation of the analyzed materials comprises two stages.

Although the temperature at maximum degradation rate of the first stage shows a slightly increase in the decomposition temperature with the increase of filler content (Figure 4), the onset values obtained by TG (T_1 e T_2 as can be seen in Table 1) show that the filler addition did not cause significant change on the thermal stability of the composites.

Figure 6 shows the DSC curves and the results suggest that the addition of the cumbaru filler did not cause a significant change in the Tg values in the analyzed

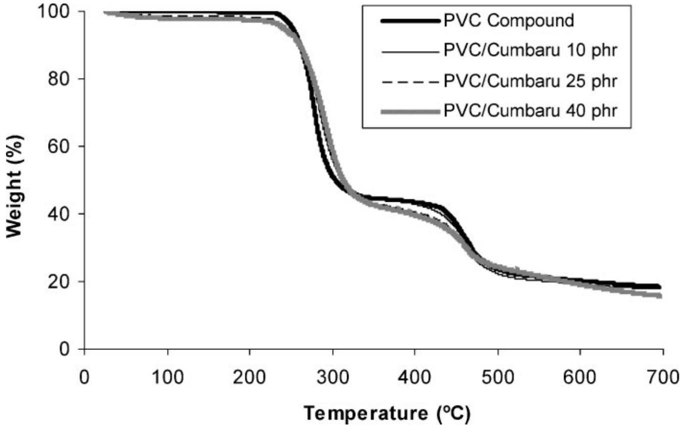

Figure 4.
TGA curves of PVC compound and composites.

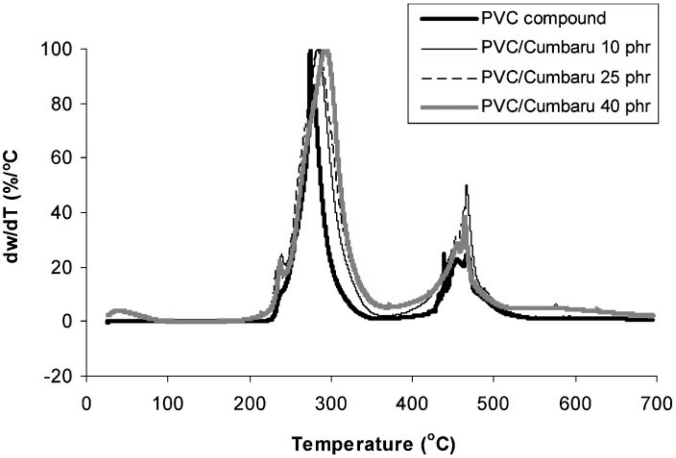

Figure 5.
DTG curves of PVC compound and composites.

Table 1.
Temperatures at the maximum degradation rate of the first and second degradation stages (T1 and T2 respectively) obtained from DTG curves and Tg values obtained from DSC thermograms of PVC compound and composites.

Samples	T_1 (°C)	T_2 (°C)	Tg (°C)
PVC compound	274.4	456.6	86.4
PVC/Cumbaru 10 phr	283.5	466.5	84.3
PVC/Cumbaru 25 phr	284.4	463.6	85.9
PVC/Cumbaru 40 phr	292.5	463.3	84.9

range (Table 1). Therefore, results obtained through thermal analyses can be regarded as good, as the addition of the filler did not prejudice the thermal properties of the composites.

Molecular Dynamic Behavior

Knowledge about the dynamic molecular behavior is important to evaluate the final properties of the materials and their potential applications. Information about the dynamic molecular behavior can be supplied by solid state nuclear magnetic resonance spectroscopy, through determination of the spin-lattice relaxation time (T_1H). Generally, the increase of T_1H values indicates that the sample becomes more rigid, due to the reinforcement and/or interaction forces. Besides, a single value of T_1H indicates that the sample is homogeneous at the T_1H measurement scale.[26]

Table 2.
T_1H values obtained from low field NMR for PVC compound and composites.

Composites	T_1 H (μs)	%
PVC Compound	5×10^3	5
	50×10^3	16
	481×10^3	79
PVC/Cumbaru 10 phr	2×10^3	5
	38×10^3	20
	435×10^3	75
PVC/Cumbaru 25 phr	2×10^3	6
	48×10^3	26
	423×10^3	68
PVC/Cumbaru 40 phr	192×10^3	100

T_1H values found for this system (Table 2) show that a single parameter value is determined when cumbaru filler content increases. T_1H values are normally controlled by the rigid domains, which control the relaxation process. Analysis of the distribution of domains (Figure 7) shows that domains tend when the filler content reaches 40 phr. Therefore, it can be concluded that this system presents homogeneous distribution, as also supported by independent studies.[26] It must be pointed out that T_1H values of rigid domains decrease with the increase of the filler

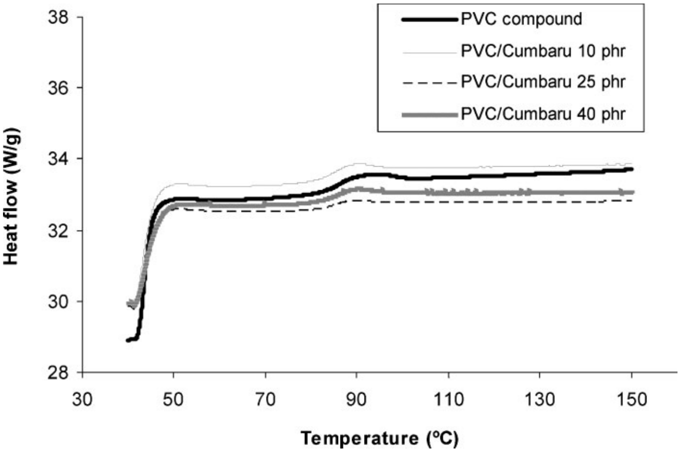

Figure 6.
DSC thermograms of PVC compound and composites.

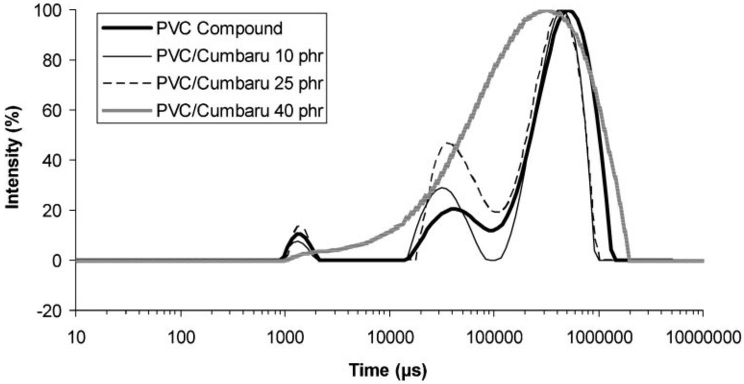

Figure 7.
Distribution curves obtained by low field NMR of PVC compound and composites.

content, indicating the reduction of the rigidity at the molecular level. This can be explained in terms of the polymer-polymer chains separation, due to the breakage of polymer interactions and creation of new interactions between polymer chains and filler. Results obtained through low field NMR are in accordance with the previous mechanical analyses, showing that there is no strong interaction in the molecular level; consequently, lower compatibility was observed with the increase of the filler content.

Conclusion

Composites were prepared with PVC and a cumbaru filler. It was found that the increase of cumbaru filler content did not cause any significant change on the thermal properties. Relaxation analyses of the molecular dynamic behavior showed the homogeneous distribution of motion within the individual components and the reduction of the material rigidity at the molecular level. These results were in agreement with results provided by independent mechanical tests and showed that there is no strong interaction in the molecular level.

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