



HAL
open science

Influence of the wood fibre filler on the internal recycling of poly(vinyl chloride)-based composites

Laurent Augier, Gianluca Sperone, Carlos Vaca-Garcia, Marie-Elisabeth Borredon

► **To cite this version:**

Laurent Augier, Gianluca Sperone, Carlos Vaca-Garcia, Marie-Elisabeth Borredon. Influence of the wood fibre filler on the internal recycling of poly(vinyl chloride)-based composites. *Polymer Degradation and Stability*, 2007, 92 (7), pp.1169-1176. <10.1016/j.polymdegradstab.2007.04.010>. <hal-02072802>

HAL Id: hal-02072802

<https://hal.science/hal-02072802v1>

Submitted on 19 Mar 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization







Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: <http://oatao.univ-toulouse.fr/23252>

Official URL: <https://doi.org/10.1016/j.polymdegradstab.2007.04.010>

To cite this version:

Augier, Laurent  and Sperone, Gianluca  and Vaca-Garcia, Carlos  and Borredon, Marie-Elisabeth  *Influence of the wood fibre filler on the internal recycling of poly(vinyl chloride)-based composites.* (2007) *Polymer Degradation and Stability*, 92 (7). 1169-1176. ISSN 0141-3910

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Influence of the wood fibre filler on the internal recycling of poly(vinyl chloride)-based composites

Laurent Augier*, Gianluca Sperone, Carlos Vaca-Garcia, Marie-Elisabeth Borredon

Laboratory of Agro-Industrial Chemistry, UMR 1010 INRA/INP-ENSIACET, 118, route de Narbonne, 31077 Toulouse, France

Abstract

The recycling of internal waste of poly(vinyl chloride) (PVC) and wood fibre-reinforced PVC composite was investigated and compared. Twenty extrusion-milling cycles were performed and the mechanical and thermal properties evaluated. This comparison provided evidence of the influence of the vegetable fibres on the thermo-mechanical degradation of the composite material. Up to five cycles, the composite properties remained stable. But after 10 cycles and especially at 20 cycles, the flexural strength increased, whereas the other mechanical properties remained almost constant. At the same time, a decrease of the degradation temperature revealed a deterioration of the molecular structure. The PVC properties remained constant, whereas a great increase in the impact strength was observed after 20 cycles without deterioration of the molecular structure. The different behaviours between the composite and the PVC were explained by the influence of the fibres, which accelerated the PVC degradation, characterized by dehydrochlorination followed by crosslinking reactions.

Keywords: Wood polymer composite; Poly(vinyl chloride); Pine fibres; Thermo-mechanical degradation; Internal recycling

1. Introduction

Among wood plastic composites, the market for PVC-based wood polymer composites (WPC) will be the most active, with a growth perspective of 200% from 2002 to 2010 [1]. It is therefore important to improve our knowledge on these WPC and abundant studies have already contributed to their fabrication and properties.

The addition of vegetable fibres to PVC without coupling agent notably decreases the strain at break and the maximum tensile strength and generally increases the elastic modulus. This leads to a brittle composite material: the impact strength strongly decreases [2–4]. The optimized addition of coupling agents such as silanes or polymethylene polyphenyl isocyanate increases the maximum stress strength and the elastic modulus of the composite in comparison with the unfilled polymer [5–8]. The composite impact strength also increases with the

addition of impact modifiers and can reach values higher than neat PVC preserving the other mechanical properties [9]. In all cases, thermal properties are affected by the addition of vegetable fillers: the composite degradation temperature decreases as the filler amount increases [3,4]. Artificial accelerated weathering has shown that the photodegradation also increases with the amount of fibres [10]. Nevertheless, the addition of UV screeners such as rutile titanium dioxide stabilizes the composite [11]. The addition of wood fibres makes the material more susceptible to moisture uptake and as a consequence, after hydrothermal ageing or accelerated freeze–thaw cycling exposure in the presence of water, the thermal and mechanical (maximum strength and elastic modulus) properties are lowered [12,13].

As far as recycling of PVC-based WPC is concerned, no information is available. Investigations have, however, been carried out on composites based on polypropylene, polyethylene and other thermoplastics. Most of these studies have considered composites made with recycled post-consumer polymers and “fresh” vegetable fillers.

* Corresponding author.

E-mail address: laurent.augier@gmail.com (L. Augier).

In this case, the mechanical properties of the composite are better than those of the recycled matrix and are improved by an adapted formulation: systematic use of coupling agents and vegetable reinforcement near 30% [14–17]. Moreover, the addition of coupling agent improves the adhesion not only between the matrix and the fibre but also between the various immiscible polymeric phases in the case of the heterogeneous matrix [18,19].

In spite of its practical importance, research on the recycling of the entire WPC is practically non-existent. The recycling of a WPC can be of two kinds:

- internal recycling, which consists in re-using the waste originating in the manufacturing process (pre-use),
- end-life (post-consumption) recycling, much more complex because of the availability and heterogeneity of the product.

Balatinecz and Sain [20] have studied the internal recycling of polyethylene- and polypropylene-based WPC (eight cycles of milling and injection moulding). Mechanical properties did not show any significant change during processing cycles. A slight decrease was observed for flexural strength and flexural modulus of PE-based composites. The study of the influence of coupling agent for PP-based composites showed that MAPP was the most efficient one. Maldas and Kokta [21] have investigated the recycling of polystyrene-based WPC during three cycles under various conditions of weathering between the cycles. As for Winandy et al. [22], their research was focused on general considerations of the end-life product recycling.

To our knowledge, no information has been published on the internal or end-life recycling of PVC-based WPC. Therefore, the main objective of this study was to investigate the internal waste recycling possibilities of PVC-based WPC and to reveal the influence of the wood fibres on the thermo-mechanical degradation of such a material.

Another objective of this study was to provide some practical information to the WPC industry about the internal recycling of PVC-based WPC.

2. Experimental

2.1. Materials

Two types of materials were studied: a PVC-based polymer and a PVC/wood fibres composite.

The polymer formulation (**P**) was provided by an industrial partner. It was a classic commercial PVC formulation used in the plastic industry. It contained additives such as titanium dioxide, calcium carbonate, impact modifier and a Pb-based stabilizer (Table 1).

The composite formulation (**C**) was prepared in the laboratory. The PVC-based matrix contained an impact modifier and a Ca/Zn stabilizer. The matrix was reinforced by 40% of pine fibres (250–450 μm). No coupling agent was used (Table 1).

Table 1
Compositions of the studied formulations

	Polymer formulation (P), %	Composite formulation (C), %
PVC K-wert grade 66	82.3	51.7
Impact modifier	4.4	4.3
Calcium carbonate	4.3	n.a.
Titanium dioxide	4.0	n.a.
Stabilizer	5.0	4.0
Dry pine fibres	n.a.	40.0

P and **C** formulations showed some differences. Being a commercial formulation, **P** was used as received from the industrial partner. The same formulation was not used for the composite **C** for several reasons. First, as the study focused on the thermo-mechanical degradation of the material, titanium dioxide was voluntarily excluded from the **C** formulation as it does not play any role in thermo-mechanical stabilization and its addition would have increased the complexity of the formulation. Second, calcium carbonate was used as mineral filler of **P** formulation but was not employed in the **C** formulation as pine fibres were already used as fillers. Last, Pb-based stabilizers are still authorized in the French industry but their use decreases and non-toxic stabilizers were preferred such as Ca/Zn-based ones. In order to fit with eventual future standards or European directives, it has been preferred to use Ca/Zn stabilizer. The authors are aware that the mechanism of stabilization between Pb-based and Ca/Zn-based compounds is different in PVC and that comparison would have been difficult in the case of two polymer matrices. However, we consider that the effect of the vegetable fibres' reinforcement has a much more major impact on PVC degradation than the difference between stabilizers.

2.2. Methods

2.2.1. Internal recycling simulation

The fibres were oven dried at 100 °C for 4 h to achieve moisture content lower than 1%. The starting materials (16 kg of **P** or **C**) were manually mixed for 5 min at room temperature and then melt-blended in a single-screw extruder (the technical characteristics are given in Section 2.2.2). The obtained compound was ground with an ELECTRA hammer mill having a 2 mm screen. The extrusion-grinding operation was repeated 20 times. Particular attention was paid to minimize pollution with material coming from the previous cycle. The contamination did not exceed 2%.

After 1, 2, 3, 5, 10 and 20 cycles, a sample of 2.5 kg of the milled material was taken out for analysis and to mould specimens by hot-injection. The following measurements were carried out on **P** and **C** samples.

2.2.2. Rheological testing

A HAAKE Rheomex PolyLab single-screw extruder (screw *L/D* ratio = 25 and screw compression factor = 2:1) with a capillary die was employed to compound the blend and to measure the rheological parameters of the melt materials.

The temperatures of the different sections of the extruder were set to 165–170–175–175 °C from the hopper to the die zone. Power law fluid theory was used to investigate the melt rheological behaviour:

$$\eta = k\dot{\gamma}^{n-1}$$

- η : viscosity (Pa·s),
- $\dot{\gamma}$: shear rate (s^{-1}),
- k : consistency,
- n : softening index.

2.2.3. Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed on a Perkin–Elmer Pyris 1 DSC instrument under nitrogen from 50 to 250 °C at 10 °C min^{-1} . Open aluminium sample pans were used.

Thermogravimetric analysis (TGA) measurements were also performed on a thermobalance Perkin–Elmer Diamond TG/DTA under air flow, from 50 to 400 °C at 10 °C min^{-1} . Open aluminium sample pans were used. The degradation temperature is expressed as the onset temperature of the mass loss.

2.2.4. Mechanical testing

For each test, 10 samples were measured. They were first conditioned at 25 °C and 60% relative humidity for at least one week. The specimens (80 × 10 × 4 mm) were obtained by injection moulding in a Fanuc Roboshot S-2000i 100A injection moulding press at 1000 and 1800 bars (**P** specimens and **C** ones, respectively) and 175 °C (nozzle temperature). All the evaluations were made at 20 °C.

Flexural properties were measured with a three-point bending system on a Tinius-Olsen H5KT testing machine according to ISO 178 standard. The crosshead displacement rate was 2 mm min^{-1} .

The impact properties of the unnotched samples were determined with a Frank universal resilience test pendulum.

2.2.5. Evaluation of the fibre/matrix interfacial adhesion

The impact test fracture surfaces of some specimens were analysed in a Leo 435VP scanning electron microscope (SEM) to examine the adhesion at the interface between the wood fibres and the matrix. The samples were not metallized as 0.5 mbar partial pressure was used. The electron high tension (EHT) was 15 kV and the working distance (WD) was 12 mm. The micrographs resulted from the backscattered electron signal.

2.2.6. Wood fibres' size measurements

Small quantities of the composite dust were let to stand in tetrahydrofuran (HPLC grade) for one week in order to dissolve the polymer matrix. The wood fibres were separated from the dissolved matrix by filtration and air dried. Their size and aspect ratio were measured by image analysis with a high definition scanner. The measured fibre size was

expressed as the diameter of a circle whose area is equivalent to that of the fibre. The measured aspect ratio was defined as the ratio between the maximal length and the minimal width of the fibre. The number of fibres measured for the calculations varied from 1500 to 5000.

2.2.7. PVC molecular weight measurements

A small quantity of the **P** and **C** samples dust was dissolved in tetrahydrofuran (THF) for one week. The weight of the samples was calculated so that the polymer concentration in the solutions was 1% in volume. For the **C** samples, the fibres and the matrix were separated by decantation. The dissolved matrix was analysed in a size exclusion chromatograph fitted with a Mixed D column (Dionex), and a differential diffractometer detector from Precision Instruments. HPLC grade tetrahydrofuran was used as mobile phase and the test temperature was 25 °C. Polystyrene standards were used to calibrate the apparatus.

2.2.8. PVC spectroscopic analysis

In order to analyse the matrix degradation, infrared and ultraviolet spectroscopic analyses were carried out. Infrared spectroscopy was performed on a Jasco FT/IR-460 Plus spectrometer between 400 and 4000 cm^{-1} . The resolution was 2 cm^{-1} and each sample was scanned 64 times. The transmittance spectra of the matrix were obtained on KBr pellets after casting of the dissolved matrix. The concentration of the matrix in the THF solution was 10% (volume).

UV spectra were measured with a Hewlett–Packard 8452A spectrophotometer between 200 and 700 nm. The resolution was 2 nm. A 1% (volume) solution of the dissolved matrix in THF was analysed in a 10 mm width quartz cell. Ten measurements were realized for each spectrum. A blank spectrum was subtracted from the measured one: for the polymer, the blank was a pellet on which pure THF was “cast”. For the composite, the blank corresponded to a pellet on which was cast a solution obtained by letting the wood fibres stand in THF for one week. This precaution should avoid any signal due to extractable molecules from the wood.

3. Results

3.1. Rheological testing

The apparent viscosity of the **C** melt formulation was about twice that of the **P** melt formulation (Fig. 1). The rheological measurements of the **C** melt formulation did not show any particular tendency versus the number of cycles. On the contrary, the apparent viscosity of the **P** formulation decreased slightly after five cycles and remained constant. The softening index (n) previously defined in the equation of the power law fluid theory was between 0.56 and 0.64 for **C** formulation, and between 0.58 and 0.65 for **P**. The consistency (k) varied from 250 to 400 for the composite (**C**) and from 230 to 350 for the polymer (**P**).

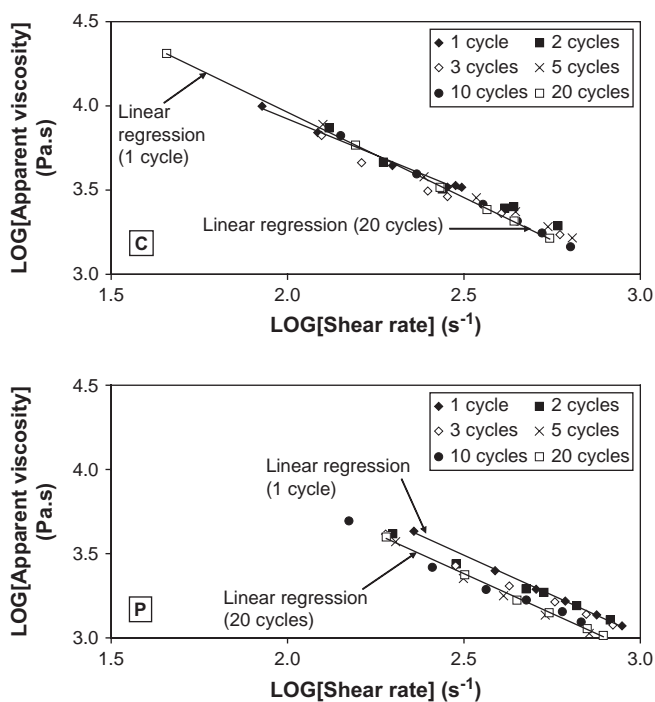


Fig. 1. Evolution of the apparent viscosity versus the shear rate for the composite (C) and the polymer (P).

3.2. Degradation temperature

As shown in Table 2, the onset degradation temperature of the **P** samples remained almost constant between 282 °C for the first cycle and 277 °C after 20 cycles. The degradation temperature of the **C** samples decreased slightly between the first and the second cycles (−5.5 °C) and remained constant until the 10th cycle. It decreased again after 10 cycles (−7.5 °C) reaching 244.5 °C for the 20th cycle.

3.3. Mechanical testing

The flexural modulus remained practically constant for both materials (Fig. 2a). As expected, the flexural modulus of the **C** samples was about twice that of the polymer.

Table 2
Degradation and PVC glass transition temperatures versus the number of extrusion cycles for the polymer formulation (**P**) and the polymer contained in the composite formulation (**C**)

Number of cycles	Degradation temperature (°C)		PVC glass transition temperature (°C)	
	Polymer (P)	Composite (C)	Polymer (P)	Composite (C)
1	281.5	256.5	84.4	71.9
2	278.5	251.0	84.7	73.3
3	278.5	252.5	83.3	70.7
5	278.5	253.0	84.0	69.7
10	277.5	252.0	83.5	69.9
20	276.5	244.5	82.8	84.0

The degradation temperature was measured by TGA (error = ± 0.5 °C) and the PVC glass temperature by DSC (error = ± 0.3 °C).

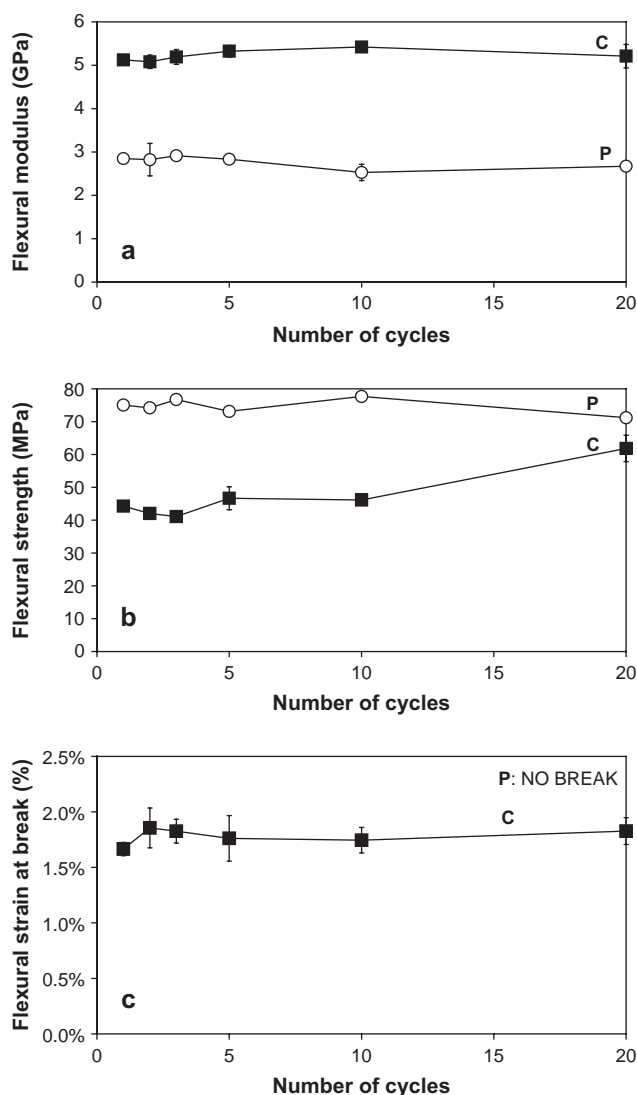


Fig. 2. Evolution of the flexural properties versus the number of cycles for the polymer (**P**) and the composite (**C**). (a) Flexural modulus; (b) flexural strength; (c) flexural strain at break.

The same constant behaviour was noted for the strain at break (Fig. 2c) of the **C** samples, which remained under 2%: the vegetable fibres' reinforcement strongly decreased the strain at break. The **P** samples did not break during the test.

The flexural strength was nearly constant during the first 10 cycles for both **P** and **C** samples (Fig. 2b). Between the 10th and the 20th cycles, the flexural strength of the composite material increased, whereas that of polymers remained constant. After 20 cycles, the polymer strength decreased by 5% and that of composites increased by 40%.

3.4. Impact properties

As shown in Fig. 3, the evolution of the composite impact strength was almost constant. The resilience of the **P** samples was constant until 10 cycles and then increased. During the test of the polymer specimens (**P**) after 20 cycles, five of them, i.e., half of the samples, did not break and the five other

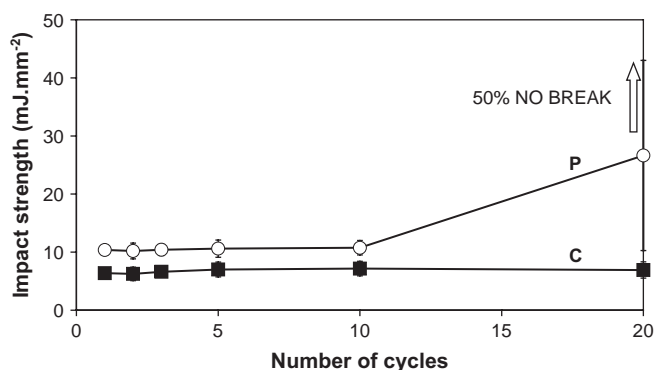


Fig. 3. Impact strength versus the number of cycles. **P**: polymer; **C**: composite.

measurements showed a large scattering. Nevertheless, it is important to note that as the five other samples did not break, their impact strength was above the average value represented on the figure.

3.5. SEM observation

Fig. 4 presents the micrographs of the impact fracture surface of the composite after 1, 5, 10 and 20 cycles. The interfacial adhesion between the fibres and the matrix was weak from the first cycle. This is clearly illustrated by the presence of debonding areas (shown with arrows). Poor dispersion of the fibres can also be observed. The same remark can be

made after five cycles. After 10 cycles, the fibre size decreased slightly and debonding areas were still present. The fibres size decreased again between 10 and 20 cycles and their dispersion within the matrix seemed to improve.

4. Discussion

The mechanical and thermal properties of both materials were almost constant until five cycles of extrusion and milling. The enhancement of the mechanical properties of the **C** samples and the loss of thermal stability after 10 cycles contrasted with the apparent stability of the mechanical and thermal properties of the **P** samples after 20 cycles. This difference may be explained by physical or chemical changes in the blends.

For the **P** samples, the thermal degradation of PVC should lead to a first step of dehydrochlorination of the backbone which was followed by a second step of crosslinking [23–26]. These two steps should increase the molecular weight (M_w) of the PVC as the number of cycles increases.

As far as the **C** samples are concerned, it is also expected that the matrix will be damaged and then crosslinked for the same reasons, but it can also be expected that the fibres will be broken leading to a smaller particle size and consequently to a better dispersion in the polymer matrix (Fig. 4). These two phenomena should lead to an improvement of the flexural and impact strengths.

To explain the difference of behaviour between the two materials, we have chosen to analyse not only the fibre size of the

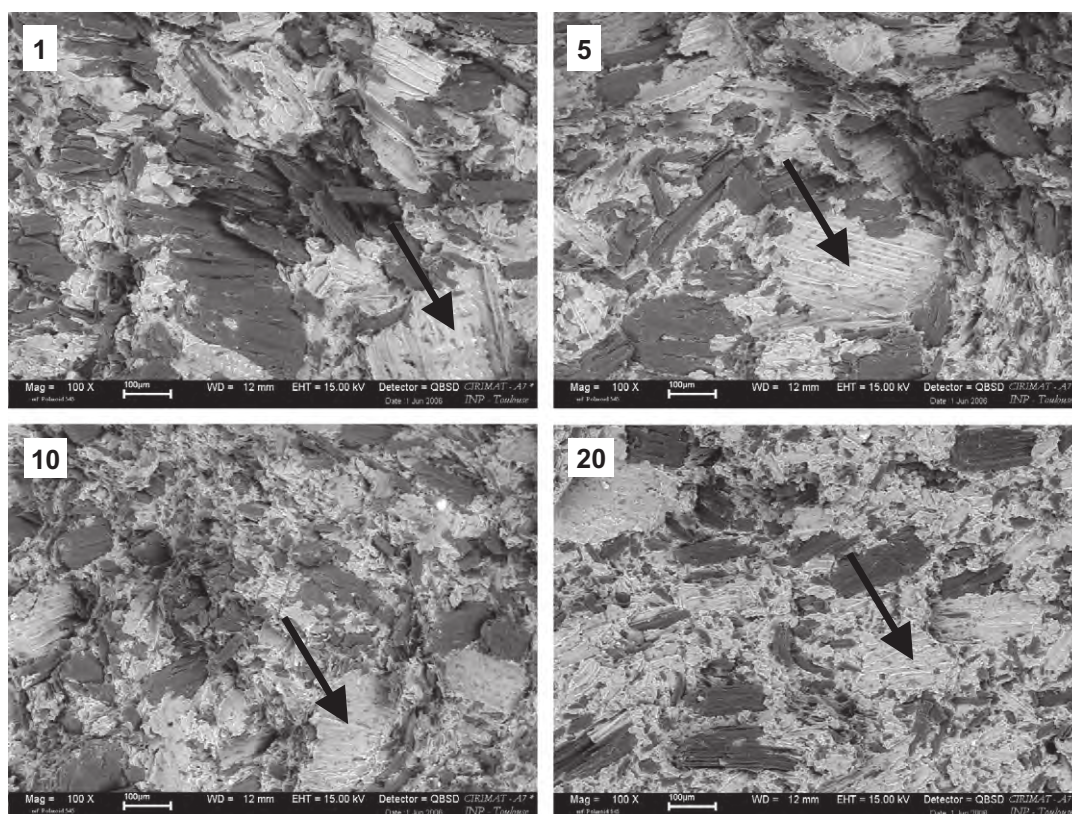


Fig. 4. Micrographs (100 \times) of the impact test fracture surface of the composite samples (**C**) after 1, 5, 10 and 20 cycles. Black arrows highlight the debonding zones.

composite samples but also the changes in the PVC macromolecular chain with the number of cycles for both materials.

4.1. Fibre thermo-mechanical degradation

The fibre size and the aspect ratio were analysed by image analysis after dissolution in tetrahydrofuran of the composite powder, filtration of the fibres and drying.

As shown in Fig. 5, the mechanical processing broke down the fibres especially during the first cycle. A significant decrease in the fibre size was noted between the first and the fifth cycles. The percentile 50 line, representing the fibre size reached by half of the fibres, decreased from 350 μm to less than 100 μm . After five cycles, no significant decrease in the average particle size was noted. Hence, the mechanical processing decreased the average particle size and widened the size distribution. No change was observed for the aspect ratio of the fibres which varied from 1.84 ± 0.66 for the unprocessed fibres to 1.74 ± 0.44 after 20 cycles.

4.2. Matrix thermo-mechanical degradation

The PVC chain length was analysed by size exclusion chromatography after dissolution of the matrix in THF and separation of the fibres. This analysis was also completed by DSC.

No significant change was observed in the PVC chain length of the polymer samples (Fig. 6). In contrast, a clear shift of the elution peak to higher molecular weights was observed for the composite formulation after 20 cycles. A broadening of the peak was also observed leading to a greater polydispersity index. More evidence for the increase in M_w was provided by DSC analysis: the PVC glass transition temperature was constant for the polymer formulation until 20 cycles but for the composite, an increase of 20% of the PVC glass transition temperature was observed between 10 and 20 cycles (Table 2).

Spectroscopic measurements have also been carried out to obtain information about the chemical changes on the PVC chain.

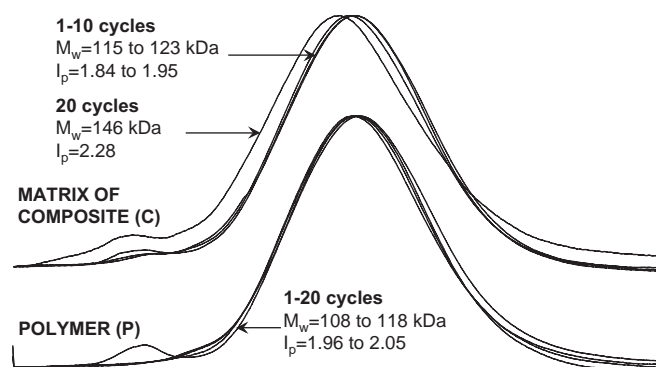


Fig. 6. Exclusion size chromatography elution charts of the dissolved matrices in THF after 1, 5, 10 and 20 cycles.

As shown in Fig. 7, no significant change was observed in the infrared spectra of the PVC during the thermo-mechanical ageing. We observed a small increase of the carbonyl concentration (peak at around 1735 cm^{-1}) for both formulations that was earlier for the **C** samples than for the **P** samples (Fig. 8). The carbonyl index was defined as the ratio of the specific area of the carbonyl peak (at around 1735 cm^{-1}) and the area of the C–H peak relative to the PVC backbone at 1431 cm^{-1} . No signal from unsaturation was observed in infrared spectroscopy (that usually appears at around 1600 cm^{-1}).

A complementary analysis was made by ultraviolet spectroscopy. The spectra of the dissolved matrices (from the **C** and from the **P** samples) are shown in Fig. 9. No change

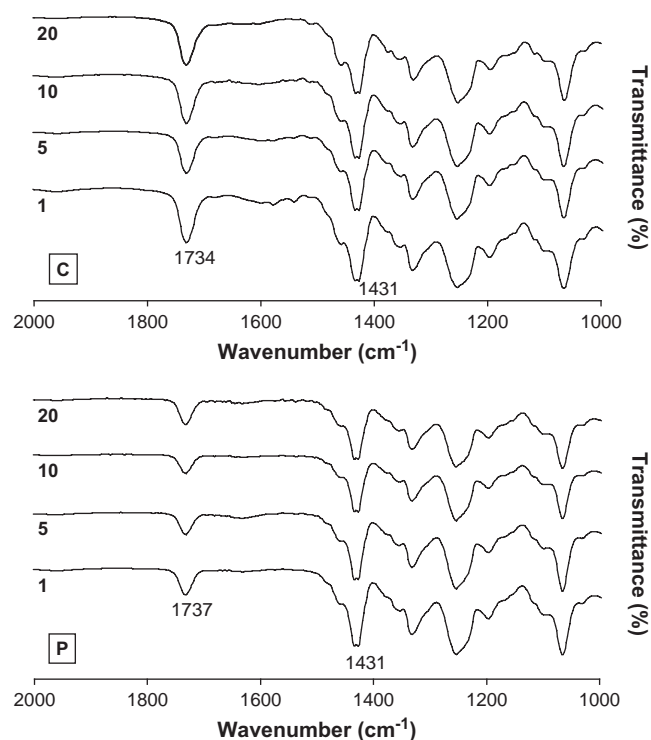


Fig. 7. FTIR spectra of the dissolved samples in THF after filtration of the fibres at 1, 5, 10 and 20 cycles of extrusion and milling. **C**: composite samples; **P**: polymer samples. Both samples were analysed after casting of the solution (1% matrix) on a KBr pellet and drying.

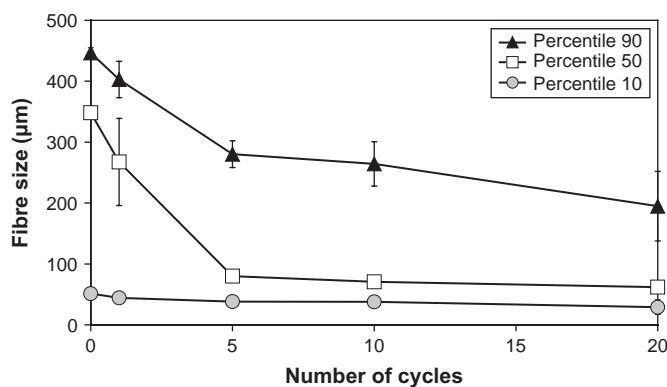


Fig. 5. Evolution of the wood fibres size distribution versus the number of cycles after dissolution of the composite matrix in THF, filtration of the fibres and drying.

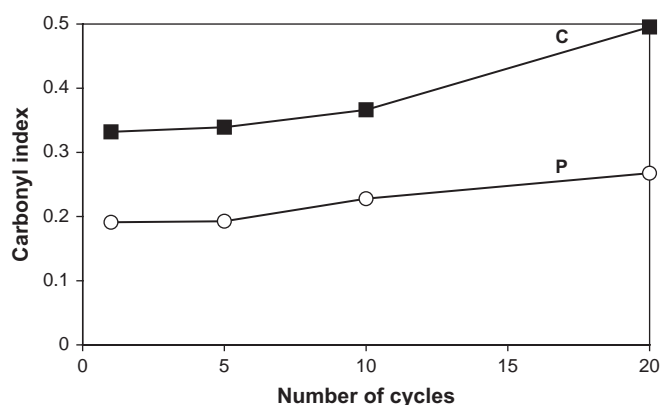


Fig. 8. Evolution of the carbonyl index versus the number of cycles for the composite (C) and the polymer (P). The carbonyl index was defined as the ratio between the specific area of the carbonyl peak (at around 1735 cm^{-1}) and the area of the C–H peak relative to the PVC backbone at 1431 cm^{-1} .

occurred on the UV spectra of the P samples' matrix, whereas significant changes were observed in the UV spectra of the C samples' matrix. The huge peak centred at 300–320 nm corresponds to the UV absorption wavelength of PVC but may also be due to the impurities that were still present in the solution. The formation of conjugated double bonds on the PVC chain of the C samples is illustrated by the presence of several maxima on the spectra. According to previous

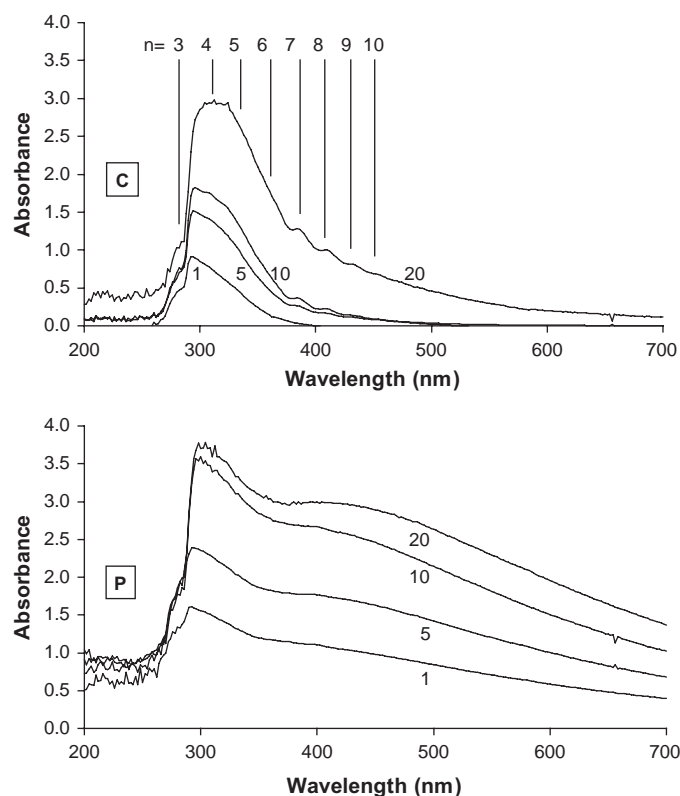


Fig. 9. UV spectra of the dissolved samples in THF after filtration of the fibres at 1, 5, 10 and 20 cycles. C: composite samples; P: polymer samples. Both samples were analysed in solution (1% matrix) in a 1 cm width quartz cell. For the C samples, n represents the polyene sequence length.

studies [23,26–29], each peak corresponds to a specific sequence length that it is possible to calculate. Sequences corresponding to 10 double bonds were found after five cycles. The concentration of each sequences increased as the number of cycles increased (as shown by the growth of absorption). These results (Fig. 9) agreed with those of Li et al. [23] and Daniels and Rees [27]. However, it was not fault-free to calculate the concentration of each sequence because the system was too complex (presence of many additives) and the error might be considerable. Nevertheless, UV spectroscopy demonstrated that thermo-mechanical degradation of PVC took place for the C samples leading to dehydrochlorination and crosslinking.

5. Conclusions

The influence of vegetable fibre reinforcement on the thermo-mechanical degradation of PVC due to recycling can be stated as follows: even if vegetable fibres seem to accelerate the matrix degradation, they also contribute to the stability and to the increasing of the mechanical properties of the composite. However, their influence is not direct: they accelerate the degradation of the polymer matrix leading to dehydrochlorination, formation of unsaturation and then crosslinking. As a consequence, the polymer chain length increases and the matrix shows better mechanical properties, which enhance the entire mechanical properties of the composite.

Moreover, the decrease of the fibres size does not influence the mechanical properties of the composite. And in this study, the mechanical properties' increase cannot depend on the wood fibres aspect ratio as this latter remains constant.

From a technical and industrial point of view, no significant change appears until five cycles. It should be therefore possible to recycle the composite internal waste five times, without adding fresh material. In practice, it is known that the internal waste part does not exceed 20% of the entire blend. So, it is reasonable to think that such recycling procedure would not have any consequence for the mechanical properties of the re-extruded composite.

Acknowledgment

The authors thank the French Agency for the Environment and Energy Management (ADEME) for financial support.

References

- [1] Jiang H, Kamdem DP. *J Vinyl Addit Technol* 2004;10(2):59–69.
- [2] Maldas D, Kokta BV, Daneault C. *J Vinyl Addit Technol* 1989;1(2):90–9.
- [3] Sombatsompop N, Chaochanchaikul K, Phromchirasuk C, Thongsang S. *Polym Int* 2003;52:1847–55.
- [4] Djidjelli H, Martinez-Vega JJ, Farenc J, Benachour D. *Macromol Mater Eng* 2002;287(9):611–8.
- [5] Kokta BV, Maldas D, Daneault C, Béland P. *J Vinyl Addit Technol* 1990;12(3):146–53.
- [6] Kokta BV, Maldas D, Daneault C, Béland P. *Polym Plast Technol Eng* 1990;29(1-2):87–118.
- [7] Matuana LM, Balatinecz JJ, Park CB. *Polym Eng Sci* 1998;38(5):765–73.

- [8] Matuana LM, Woodhams RT, Balatinecz JJ, Park CB. *Polym Compos* 1998;19(4):446–55.
- [9] Mengeloglu F, Matuana LM, King JA. *J Vinyl Addit Technol* 2000;6(3):153–7.
- [10] Matuana LM, Kamdem DP. *Polym Eng Sci* 2002;42(8):1657–66.
- [11] Matuana LM, Kamdem DM, Zhang J. *J Appl Polym Sci* 2001;80:1943–50.
- [12] Djidjelli H, Kaci M, Martinez-Vega JJ, Benachour D. *Polym Int* 2004;53:1760–5.
- [13] Pilarski JM, Matuana LM. *J Vinyl Addit Technol* 2005;11(1):1–8.
- [14] Dintcheva NT, La Mantia FP, Trotta F, Luda MP, Camino G, Paci M, et al. *Polym Adv Technol* 2001;12:552–60.
- [15] Dintcheva NT, La Mantia FP. *Polym Adv Technol* 1999;10:607–14.
- [16] Maldas D, Kokta BV. *J Thermoplast Compos* 1995;14(5):420–34.
- [17] Maldas D, Kokta BV. *J Reinf Plast Compos* 1995;14(5):458–70.
- [18] Hedenberg P, Gatenholm P. *J Appl Polym Sci* 1995;56(6):641–51.
- [19] Maldas D, Kokta BV. *Int J Polym Mater* 1994;26:69–78.
- [20] Balatinecz JJ, Sain MM. *Macromol Symp* 1998;135:167–73.
- [21] Maldas D, Kokta BV. *Polym Compos* 1990;11(2):77–83.
- [22] Winandy JE, Stark NM, Clemons CM. *Proceedings of the fifth Global Wood and Natural Fibre Composites Symposium*. Kassel (Germany); 2004.
- [23] Li D, Zhou D, Zhao D. *Polym Degrad Stab* 1988;22:31–41.
- [24] Yanborisov VM, Minsker KS, Zaikov GE, Zaikov VG. *J Vinyl Addit Technol* 2002;8(3):176–9.
- [25] Anthony GM. *Polym Degrad Stab* 1999;64:353–7.
- [26] Bacaloglu R. *Polym Degrad Stab* 1994;45:301–13.
- [27] Daniels VD, Rees NH. *J Polym Sci Polym Chem* 1974;12:2115–22.
- [28] Anders H, Zimmermann H, Behnisch J. *Teubner-Texte Physik Prog Polym Spectrosc* 1986;6:137–41.
- [29] Braun D, Sonderhof D. *Polym Bull* 1985;14:39–43.