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# Treated Olive Husk flour in a PVC-Based Composite Material: Recycling Effect on Physico-Mechanical and Rheological Properties

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**Abstract**

***The work is directed to study the recycling effects on the olive husk flour reinforced polyvinylchloride composites with and without maleic anhydride-grafted polyvinyl chloride used as compatibilizer. To improve the fiber-matrix adhesion, olive husk flour was chemically treated by benzoylation treatment. The material was characterized after each extrusion using tensile tests, Rheological measurements, scanning electron microscopy (SEM), and Size Exclusion Chromatography (SEC). Results indicated that generally after four cycles, the recycled composites had considerably higher modulus as compared with the original composites which were attributed to changes in physical and chemical properties of the composites induced by the recycling process. This effect was enhanced for the compatibilized samples. Increase of the modulus strength of the poly (vinyl chloride) (PVC) matrix is detected due to the molecular chain cross-linking resulting from degradation.***

***Keywords:*** *Poly (vinyl chloride), Benzoylation treatment, Olive Husk flour, Recycling, Physico-Mechanical properties.*

## I. Introduction

In recent decades, the increase in world population and the need to adopt better living conditions have led to a dramatic increase in the consumption of polymers, mainly plastics, resulting in the generation of waste in large quantities. To reduce the environmental problems caused by the accumulation of this waste, it is in our interest to recycle it [1].

Several research works have focused on the effect of recycling on composites based on polypropylene, polyethylene and vegetable fibres [2]

Petchwattam et al [3] carried out a study on the recycling of composites based on polyvinyl chloride and wood flour (WF), their work is composed of two parts, the first focuses on the recycling of the mixture of industrial waste from PVC/WF composites and PVC pellets reinforced with WF. The second part consists in recycling the PVC/WF composites (seven extrusion cycles), according to their results they found that the recycling reduced the molecular weight of the PVC matrix, they explained this reduction by the scission of chains molecule by shear stress during the recycling process. On the other hand, the results of the mechanical tests have shown that PVC/WF composites can be recycled again as composites without critically affecting their mechanical performance.

Hammiche et al [4] studied the effect of mechanical recycling on the properties of PVC/Alfa composites. They prepared three formulations, Virgin PVC, Composite loaded with 20% of alfa in the presence and in the absence of 5% of PVC-g-MA.

The composites produced underwent four extrusion cycles. According to their results, they found that the mechanical properties of composites increase with the number of recycling cycles. Indeed, the tensile strength and the Young's modulus in the studied formulations increased considerably. These are clearly revealed by scanning electron microscopy (SEM). After recycling, the morphology of the composite materials indicates that the alfa fiber particles are uniformly dispersed and embedded in the polymer matrix. They also observed that the maximum degradation rate is shifted to a slightly higher region in the case of composites compared to virgin PVC, due to the higher thermal stability of composites.

This work is devoted to the study of the effect of mechanical recycling on the properties of PVC/Olive husk flour composites. Four formulations were prepared, virgin PVC, the composite loaded with 20% untreated olive husk flour and treated by benzoylation and also the composite loaded with 20% olive husk flour in the presence of 5% PVC-g-MA.

A series of four extrusion cycles was carried out on the four formulations using an internal mixer equipped with two counter-rotating screws.

## II.Material and methods

Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

### II.1 Material

The used Polyvinyl chloride (PVC), type SE-1200, has K-Wert value of 70.20 to 72.00, viscosity value of 0.99-1.030 and a density of 0.481-0.561

The main additives of PVC were summarized in table 1.

**Table 1:** Additives of PVC SE-1200

| Additives | Names | Value (%) |
|---|---|---|
| Plasticizer | Dioctyl Phthalate (DOP) | 30 |
| Stabilizer | Ca/Zn | 4 |
| Lubricant | Stearic Acid | 0.5 |

The filler used was olive husk flour; it was obtained after olives processing for oil in the region of Bejaia (Algeria). The olive husk has sustained several pre-treatments, namely washing with hot water to eliminate pulp, drying under ambient conditions for 48 h, grinding, and sieving to have a grain size of ≤100 μm [5].

The reagents used for benzoylation of olive husk flour are sodium hydroxide (MW=40) and benzoyl chloride (MW=140.56) which are supplied by BIOCHEN CHERMOPHARMA.

PVC-g-MA was synthesized at the laboratory of organic materials A. Mira University of Bejaia, Algeria by Hammiche et al [6]. The addition of a coupling agent aims for interfacial adhesion improvement.

### II.2 Methods

**Chemical modification of olive husk flour by benzoylation**

This modification was carried out according to the following experimental protocol: 35g of olive husk flour were soaked in an 18% NaOH solution for 30min, followed by filtration and washing with distilled water. The treated flour was then suspended in a 10% NaOH solution with 50ml of benzoyl chloride with stirring for 15min, the contents are kept at room temperature for 15min, then the mixture was filtered, washed and dried at room temperature, the isolated flour was then soaked in ethanol (96%) for one hour to remove excess benzoyl chloride and finally, the mixture was filtered, washed and dried in an oven at 60°C for 24 hours.

**Preparation of composites**

To study the effect of recycling on composite materials, composites were prepared in two steps. The first step consists of mixing the different constituents in an internal mixer. The second is to grind them then mold them by compression at 180°C with a pressure of 30bar to obtain films with an average thickness of 150 μm. The same processed samples are recycled four times in the internal mixer. These are characterized after each transformation cycle.

The mixtures are made using a Brabender type mixer, Plasticorder W 50 EHT. The PVC-g-MA compatibilizers and the olive husk flour treated and untreated are first steamed at 60°C for 24 hours. The various constituents are mixed manually then introduced into the Brabender for 5 min, at a temperature of 180° C. and a rotation speed of 50 rpm.

Mass compositions of the various formulations are given in Table 2.

**Table 2:** Mass composition of the different formulations

| | PVC compound (%) | OHF (%) | OHFT (%) | PVC-g-MA (%) |
|---|---|---|---|---|
| PVC | 100 | 0 | 0 | 0 |
| PVC/OHF | 80 | 20 | 0 | 0 |
| PVC/OHFT | 80 | 0 | 20 | 0 |
| PVC/PVC-g-MA/OHF | 75 | 20 | 0 | 5 |

**Tensile test**

The tensile tests of formulations PVC, PVC/OHF, PVC/OHFT and PVC/PVC-g-MA/OHF composites were carried out on an MTS synergy RT1000 type tensile machine at ambient temperature (23° C.) and a displacement speed of 2 mm/min. in this study, the results presented are the average of five trials for each sample.

**Rheological measurements**

The rheological behavior of virgin PVC and composites obtained was studied in dynamic mode using a dynamic rotational shear rheometer (Rheometer AntonPaar MCR 301). The jaws are of plane/plane geometry with a diameter of 25mm in oscillatory mode at 175°C, which makes it possible to evaluate the viscoelastic properties such as the storage and loss moduli, and the complex viscosity. The strain imposed is 2%. It is determined so as to remain in the linear domain during the amplitude sweep. The samples were prepared by compression in a mold at 180°C in the form of a disc approximately 1.5mm thick. The elastic modulus and the complex viscosity have been measured in the linear domain, for frequencies ranging from 100 to 0.01Hz.

**Morphological characterization**

The morphological analysis of virgin PVC and composites was carried out using a brand name scanning electron microscope (SEM) (Joel JSM 6460LV). The samples to be analyzed were prepared by fracturing after immersing them in liquid nitrogen.

**Size Exclusion Chromatography (SEC)**

The analysis was carried out by a device of the shimadzu RID 10 A type. The sample to be analyzed is dissolved in tetrahydrofuran, the samples are put in solution with stirring for 12 hours, and before injection the solutions are filtered on a dynaguard filter of porosity 0.20 µm.

## III.Results and discussion

**Tensile test**

Mechanical property is a characteristic property of a material that describes its behavior when subjected to one or more mechanical stresses, the most common measures are: Young's modulus, tensile strength and elongation at break. Figure 1 illustrates the evolution of tensile strength, Young's modulus and elongation at break as a function of the number of transformation cycles of the polyvinyl chloride matrix, treated and untreated PVC/OHF composites and PVC/PVC-g-MA/OHF. In the first processing cycle, a significant increase in Young's modulus is recorded with the addition of flour. However, this increase is more remarkable in the presence of PVC-g-MA. On the other hand, we observed a decrease in the tensile strength of the composites compared to virgin PVC.

The increase in the strength of virgin PVC is less marked with recycling, there is a slight decrease in strength in the first cycle then an increase in this property in the fourth cycle, and this is probably due to the crosslinking of PVC induced by the artwork.

The increase in strength at break of PVC/OHF, PVC/OHFT and PVC/PVC-g-MA/OHF composites is recorded, going from 5.4MPa, 9.1MPa, and 9.4MPa, respectively in the first cycle to 9MPa, 13.6MPa and 12.1MPa and this is due to better flour dispersion in the matrix due to the reduction in melt viscosity [7].

contrary to virgin PVC, the Young's modulus of the composites show a strong increase induced not only by the reduction in the dimension of the flours caused by the grinding but also by their good dispersion and therefore an improvement in the interfacial adhesion between the matrix and the reinforcement especially in the presence of PVC-g-MA and at the third cycle of transformation.

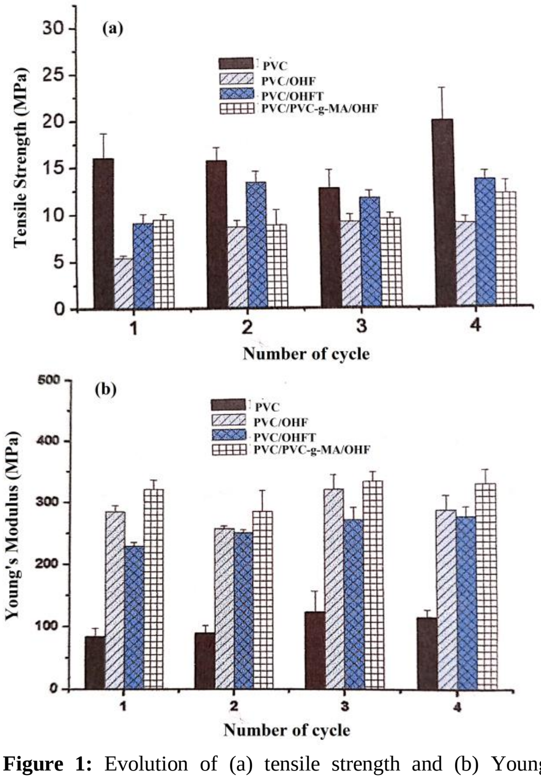


**Figure 1:** Evolution of (a) tensile strength and (b) Young's modulus as a function of the number of transformation cycles of the polyvinyl chloride matrix, treated and untreated PVC/OHF composites and PVC/PVC-g-MA/OHF

Pillin et al [8] conducted a study on the effects of extrusion cycles on the mechanical properties of polylactic acid (PLA). They found that the number of extrusion cycles has no influence on the tensile modulus; they assumed that this value remains constant because the potential decrease in the molecular weight of PLA is compensated by an increase in its crystallinity. On the other hand, the recycling effect on the tensile strength of PLA is very significant, leading to a great reduction in this characteristic; it goes from 66 MPa to 25 MPa after 7 cycles. This strong decrease is attributed to a lower cohesion in the material, probably due to a decrease in the molecular pods and therefore the resistance of the entanglement between the chains. They also observed the decrease in the strain at break from 6% to 0.8%. This phenomenon may be a consequence of both the decrease in chain length and the increase in the degree of crystallinity, both of which favour the propagation of cracks above the elastic domain. Similarly Kaci et al [9] have carried out a study on the effects of repeated extrusion cycles on the structure and properties of PP/wood flour composites in the presence and absence of the terpolymer of butyl acrylate glycidyl ethylene methacrylate (EBAGMA) used as a compatibilizer agent. They compared the variation of the modulus according to the number of cycles of the composites PP/WF, PP/WF/EBAGMA and virgin PP. They found that the tensile modulus for virgin PP is about 1270MPa and this value increases by about 15% in compatible PP/WF composite materials. They attributed this increase to the effect of the grafting of the EBAGMA terpolymer on the PP chains. They also observed that the tensile modulus for composite materials is not affected by repeated extrusion cycles. On the other hand, the effect of reprocessing on the tensile modulus of PP is drastic causing a strong reduction in this characteristic of about 40% between the second and the third cycle. This is probably due to the decrease in molecular weight, due to the phenomenon of chain scission, induced by recycling. They also observed that the tensile strength of virgin PP is around 34MPa. On the other hand, the increase in the number of transformation cycles induces a significant drop in the breaking stress of virgin PP to reach 9 MPa after the third cycle. The addition of 20% by weight of WF to the polymer leads to a reduction in the initial value of the breaking stress to about 20 MPa due to the poor interfacial adhesion between the matrix and the flour. When the compatibilizer is added to the PP/WF composites, the breaking stress is slightly increased from 20 to 24MPa. This improvement is generally attributed to better interfacial adhesion and the reinforcing effect of the flour. Both for the non-compatible composite samples and those compatible with EBAGMA, they observed a very slight decrease in the breaking stress (about 5%).

The recycling process which can induce the decrease in molecular weight in the polymer matrix does not significantly affect in the mechanical properties of the composites.

It is observed that the elongation at break (Figure 2) of the PVC matrix is less affected by recycling; it is around 208% in the first transformation cycle and 198% in the fourth transformation cycle. The addition of olive husk flour to the PVC matrix significantly reduces the elongation at break and this is due to the rigidity induced by the vegetable flour. Generally, the addition of the lignocellulosic filler causes a significant reduction in the ductility of the composite [10]. Recycling causes a decrease in this elongation until the third transformation cycle probably caused by the good dispersion of the flour in the polymer matrix as well as better adhesion between the two constituents, causing a decrease in elongation especially in the presence of PVC-g-MA. According to Bourmaud et al [11], the increase in the fracture strain of the composite is attributed to the loosening of the reinforcement particles from the matrix due to their poor adhesion. Hamad et al [12] have found that the elongation at break of the poly (lactic acid)/polystyrene mixture decreases by a factor of 0.61 after two processing cycles and by a factor of 0.73 after four processing cycles. This phenomenon may be a consequence of both the reduction in the molecular chain length and the increase in the degree of crystallinity, which both favour the propagation of cracks above the elastic domain.

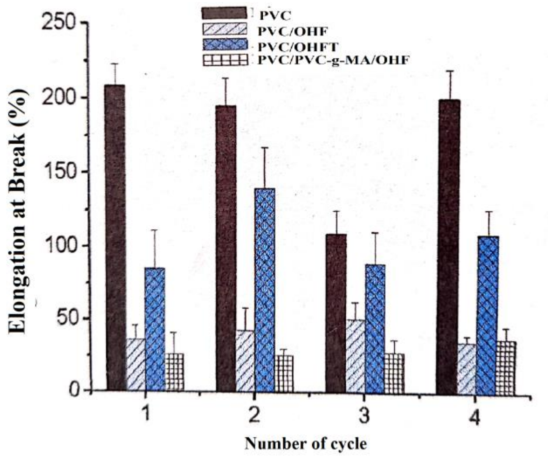


**Figure 2:** Evolution of elongation at break as a function of the number of transformation cycles of the polyvinyl chloride matrix, treated and untreated PVC/OHF composites and PVC/PVC-g-MA/OHF

**Rheological measurements**

The rheological measurements are carried out with the aim of evaluating the effect of the number of transformation cycles on the viscoelastic properties and on the state of dispersion of the flour.

Figures 3 and 4 show the evolution of the elastic modulus as a function of the formation of the PVC, PCV/OHF, PVC/OHFT, and PVC/PVC-g-MA/OHF formulations after recycling, carried out at a frequency of 1Hz at 180°C.

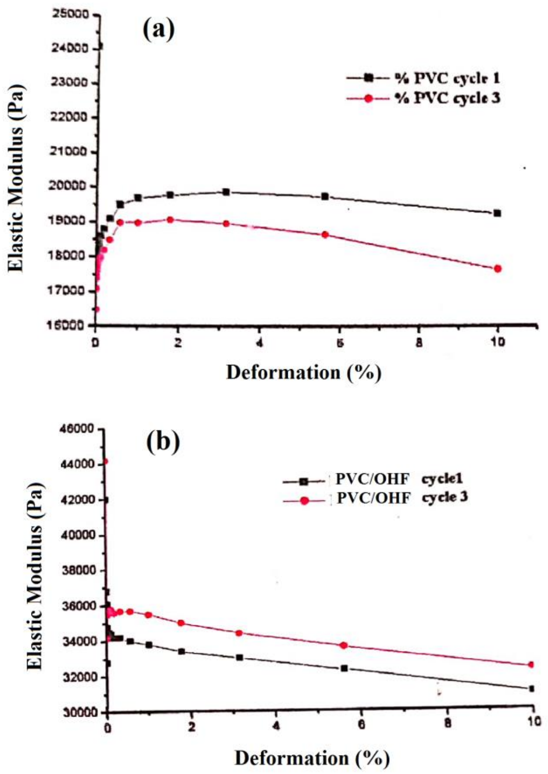


**Figure 3**: Evolution of the elastic modulus as a function of the formation of the PVC and PCV/OHF formulations after recycling

The linear viscoelastic domain extends only at a strain of 0.5%. The linear viscoelastic properties are therefore determined for all the formulations at this strain of 0.5%. It is observed that the addition of flour causes a reduction in the linear viscoelasticity range of the composites. The network structure comes from the entanglements present in the amorphous phase as well as from the order characterizing the semi-crystalline phase of PVC. This network structure maintains a large deformation, but in the composite a new microstructure is formed. This does not resist large deformation compared to the virgin matrix.

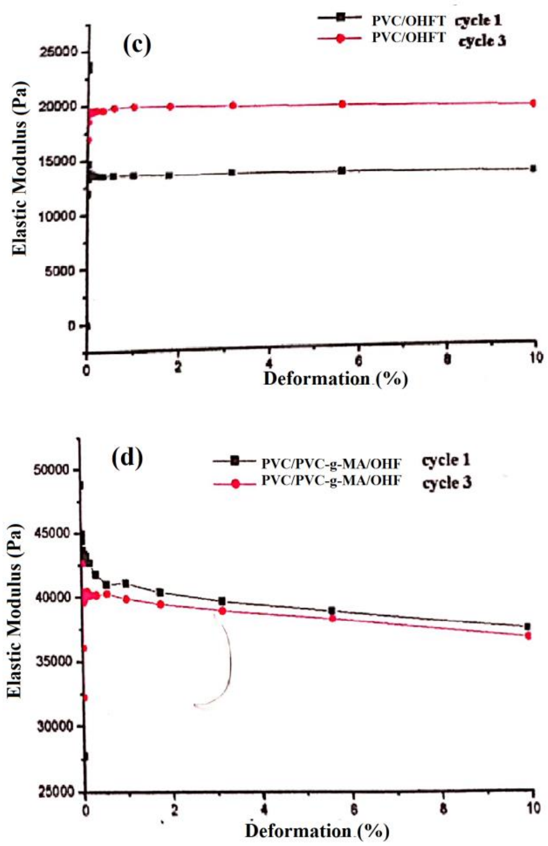


**Figure 4:** Evolution of the elastic modulus as a function of the formation of PVC/OHFT and PVC/PVC-g-MA/OHF formulations after recycling

Figures 5 and 6 present the evolution of the elastic, viscous modulus and the complex viscosity as a function of the frequency of the PVC matrix and the composites in the 1st and 3rd transformation cycle. Polyvinyl chloride show a mainly viscous elastic behavior, it can be concluded that PVC behaves as a homogeneous melt only above a critical temperature while below this temperature it exhibits rheological characteristics unknown to others, molten polymers but typical for cross-linked polymer systems [13].

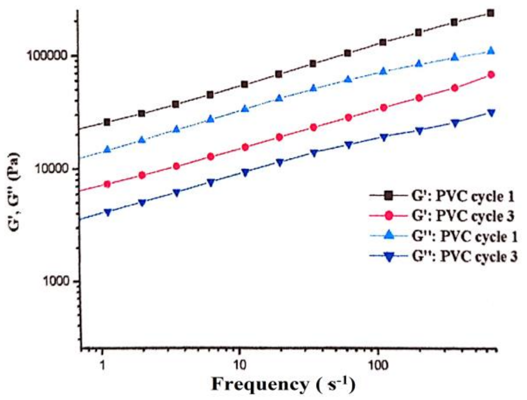

**Figure 5**: Evolution of the elastic, viscous modulus as a function of the frequency of the PVC matrix in the 1st and 3rd transformation cycle.

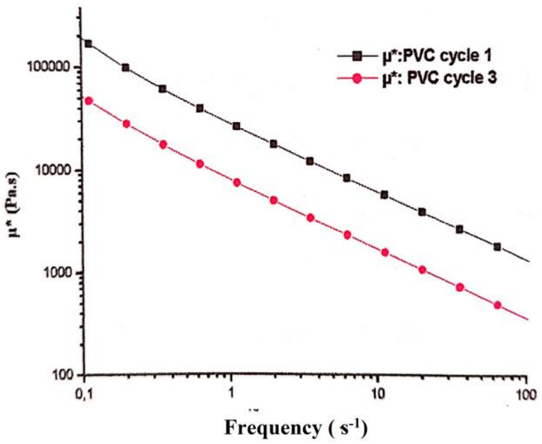


**Figure 6:** Evolution of complex viscosity as a function of the frequency of the PVC matrix in the 1st and 3rd transformation cycle.

After recycling, a decrease in the elastic and viscous modulus and in the complex viscosity of the PVC is recorded. The viscosity of polymers depends on both the weight average molar mass Mw and the molar mass distribution of the material. The decrease in the complex viscosity is therefore linked to the decrease in the average molecular mass in weight Mw due to the chain scission reactions. According to Gonzalez et al [14] this occurs in the case of thermomechanical aging of polyvinyl chloride on the chains with the highest molecular masses and preferentially in the centre of the macromolecules.

Figure 7 represents the evolution of the complex viscosity as a function of the frequency of the composites between the 1st and the 3rd transformation cycles. According to the results, an increase in the complex viscosity of the untreated PVC/OHF and PVC/OHF composites is observed in the presence of the compatibilizer agent PVC-g-MA after recycling. This is interpreted as the result of a strong interaction between the matrix indicating an improvement in the state of dispersion [15].

However, for flour composites treated by benzoylation, a decrease in viscosity is recorded, and this can be attributed to chain scission which leads to a reduction in molecular weight [16].

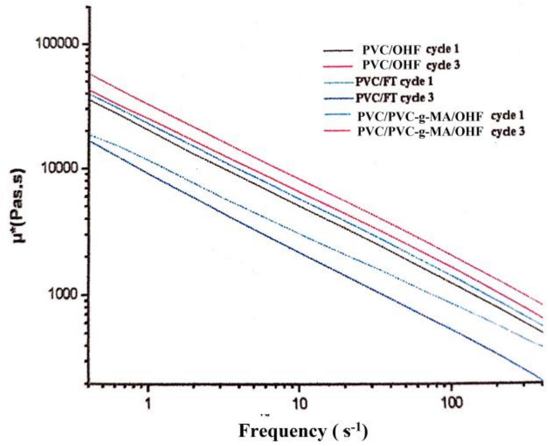


**Figure 7:** Evolution of the complex viscosity as a function of the frequency of the composites between the 1st and the 3th transformation cycles.

## Size Exclusion Chromatography (SEC)

The average molecular weights Mw and the molecular weight distributions (polydispersity index) Ip of PVC and the composites with and without PVC-g-MA at the first and third processing cycle are shown in Figure 8 and 9, respectively. It turns out that the masses molecular weight increases after mechanical recycling. An increase in the polydispersity index is also observed. Indeed, after four cycles we can observe an increase in Mw. The degradation of the polymer matrix is accelerated especially in the presence of olive husk flour leading to dehydrochlorination, formation of unsaturation and then crosslinking of the chains of our materials. Consequently, the length of the molecular chains of the polymer increases and the matrix shows better mechanical properties which in turn increase the mechanical properties of the composite [17] leading to dehydrochlorination, formation of unsaturation and then crosslinking of the chains.

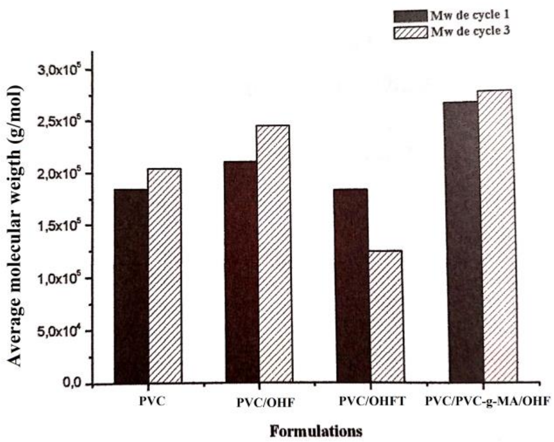

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**Figure 8:** Average molecular weights Mw of PVC and the composites with and without PVC-g-MA at the 1st and 3rd processing cycle

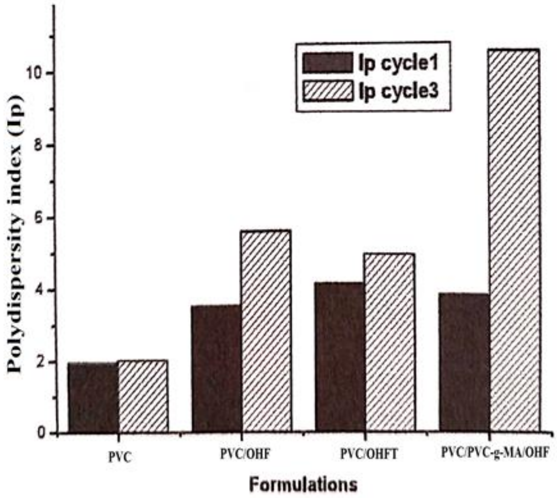


**Figure9:** molecular weight distributions (polydispersity index) Ip of PVC and the composites with and without PVC-g-MA at the 1st and 3rd processing cycle

## Morphological characterization

Figure 8 represents the pictures obtained by SEM of the PVC/OHF, PVC/OHFT, and PVC/PVC-g-MA/OHF composites at 1st cycle and at the 3rd transformation cycle. The results of the first cycle (figure 10 (a)) reveal that the flour is completely stripped from the matrix, which shows that the adhesion is very weak between the matrix and the untreated olive husk flour, the benzoylation and the coupling improve the adhesion between the PVC and OHF, we observe the decrease in the number and the size of the cavities for the composites treated by benzoylation (figure 10 (c)) [18]. In the fourth transformation cycle, we notice the reduction in diameter of the flours compared to the first cycle, confirming the fibrillation. This also explains the increase in the modulus of recycled composites caused by the decrease in the form factor after recycling [19].

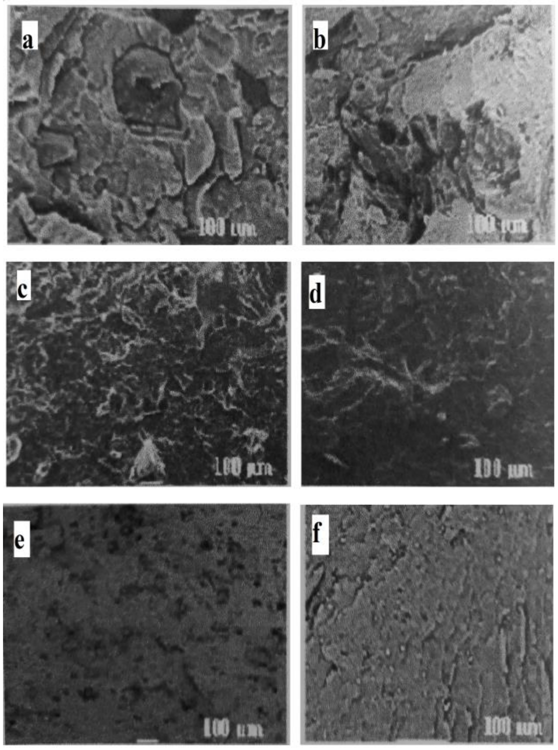


**Figure 10:** pictures obtained by SEM of the PVC/OHF, PVC/OHFT, and PVC/PVC-g-MA/OHF composites at the 1st cycle and at the 3rd transformation cycle

## IV.Conclusions

In conclusion, the aim of this work is to study the mechanical and rheological properties of PVC/OHF composites treated and untreated by benzoylation and with the coupling agent PVC-g-MA as a function of the mechanical recycling number. The results showed that generally the mechanical properties of the composites increase with the number of recycling. Indeed, the tensile strength and the Young's modulus in the studied formulations increased considerably. Recycling has caused chain scissions which are manifested by a decrease in viscoelastic properties for flour composites treated by benzoylation.

### *Conflict of interest*

The authors declare that they have no conflict for financial interests or personal relationships that how can influence the work reported in this paper.

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