Biopolymer Applications Journal Nadira BELLILI et al. Vol 4, N°2, 2025, pp. 05-09
e-ISSN : 2800-1729

Effect of physical treatment on the performance of thermoplastic matrix composites with natural fillers

Nadira BELLILI[1, 2*]; Badrina DAIRI[1, 2]; Nadjia RABEHI[1]
[1]*Department of Process Engineering, University of 20Aout – 1955, Skikda, Algeria.*
[2]*Department of Process Engineering, Faculty of Technology, Laboratory of Advanced Polymer Materials (LMPA), A. Mira University , Bejaia, Algeria.*
Corresponding author: n.bellili@univ-skikda.dz*
Received: 27 March, 2025; Accepted: 28 May, 2025; Published: 4 July, 2025

Abstract
Date stone flour was, valorized for use as a reinforcement in the manufacture of polyvinyl chloride matrix composites. Gamma irradiation was, used to improve PVC/FND interfacial adhesion. A reduction in the hydrophilic character of the filler after treatment was, demonstrated by the decrease in the water absorption rate of irradiated DSF -reinforced composites, and this was, confirmed by the good dispersion of the treated filler in the matrix, observed by optical microscopy. As a result, better mechanical properties were, obtained.
Keywords: *Date stone flour, Polyvinyl chloride, Gamma irradiation, Polymer matrix composite.*

I. Introduction

Polyvinyl chloride (PVC) is a thermoplastic polymer with good resistance to moisture and fire. Worldwide demand for PVC exceeds 35 million tonnes a year. In terms of tonnage and consumption, it ranks second only to polyethylene in the plastics industry. It is, used to manufacture a wide range of products with different properties at relatively low cost [1, 2].

In recent decades, lignocellulosic natural fiber/polymer composites have attracted the attention of many researchers because of their environmental adaptability and biodegradability [3 - 6].

The valorization of natural wastes such as date pits by using them in the preparation of thermoplastic matrix composite materials provides a highly interesting alternative to environmental problems and the probable depletion of fossil resources. Date pits are generally, removed from dates before consumption, and rather than being discarded, they can be processed into a form of flour and used in a variety of culinary applications, including as an ingredient in pastry recipes due to its richness in dietary fiber, antioxidants and some minerals such as calcium and potassium.

Date pit fiber is attracting increasing attention from researchers. However, the majority of research has focused on the use of these pits in the form of activated carbon, a livestock feed supplement, and in traditional medicine. For their antimicrobial and antiviral properties, they are, used in the preparation of citric acid and proteins.

This material is an inexhaustible biomass available in Algeria, where production is approximately 1,100,000 tons per year. It is, the abundance of this waste that motivated the choice of date kernel flour as a filler in the manufacture of composite materials.

However, the preparation of composite materials based on cellulosic fillers is, hampered by the highly hydrophilic character of the fibers, which is, associated with poor interfacial compatibility with hydrophobic polymer matrices, as well as a loss of mechanical properties after moisture absorption. In this study, the filler used was, modified by physical treatment such as gamma irradiation and the effect of different doses of gamma radiation (10,15 and 20 kGy) on the mechanical, physical and morphological properties of polyvinyl chloride (PVC)/date stone flour (DSF) composites was investigated.

II. Material and methods

Manufactured type 3000H PVC was, used to prepare the formulations. The various additives (plasticizer, thermal stabilizer, lubricant) and the filler used are, mixed until the mixture becomes homogeneous. The natural filler used is date stone flour (DSF). The torrefied and crushed date stones were, brought in from the wilaya of BISKRA. Sheets 0.5 mm thick of F0 and untreated F20 (20% filler) blends, and treated with

Table.1: Physicochemical properties of polyvinyl chloride

Properties	Measurement methods	Units	Values
Viscosity	ASTM D 1243	CSt 1 CSt = 10^{-6} m²/s	0, 89-1,03
Color			White
Density	ASTM D 1885	g/cm^3	0,481-0,561
Particle size <40µm	ASTM D 1921	%	Max.0, 5
Volatility	CIRES 03.05	%	Max.0, 3

Biopolymer Applications Journal *Nadira BELLILI et al. Vol 4, N°2, 2025, pp. 05-09*
e-ISSN : 2800-1729

γ-radiation at doses of 10, 15 and 20 kGy (noted: F20, F20T10kGy, F20T15kGy and F20T20kGy respectively) were prepared using a calender. The temperature along the two-roll mixer was, maintained at 160°C, for a residence time of 15 min. The sheets were, then cut into the appropriate shape for characterization.
The properties of the PVC/DSF composites produced are then determined by measuring mechanical properties, water absorption rate, and optical microscope analysis.
For tensile tests, the specimens used in accordance with the dumbbell standard have the dimensions reported in Table 2.

Table 2. Dimensions of the test pieces

Total length, min(L3)		Width (b)	Distance between marks (L0)
Specimen (method B)	115	6	25

This test allows the values of elongation and breaking stress to be, recorded and Young's modulus to be, deduced using a JJ-TEST tensile testing machine.
The water absorption of the composites was, analyzed by immersing the samples in distilled water at room temperature, with periodic monitoring of the specimen weight increase every 24 hours.
The water absorption of the composites was calculated using the following equation:

$$Water\ absorption\ rate\ (\%)\ = \frac{(m_0 - m)}{m_0} \times 100$$

The surface condition of the composites and the dispersion of the DSF in the PVC matrix were visualized using optical microscopy from mark OPTIKA Microscopies ITALY with a magnification of HC4x0.1 160/0.17.

III. Results and discussion

A. Mechanical properties

The effect of loading and gamma irradiation on the mechanical properties of irradiated and non-irradiated composites was, followed by the change in Young's modulus, stress and elongation at break.
The variation in Young's modulus of the various PVC/DSF samples, untreated and treated with gamma irradiation are, shown in Figure 1.

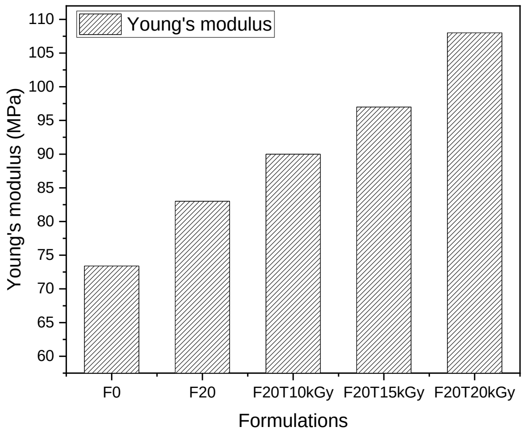

Figure 1. Tensile modulus of PVC matrix and its composites reinforced with unirradiated and irradiated DSF at various doses of gamma radiation

Figure 1, shows that the presence of date stone flour in the PVC matrix increases Young's modulus compared with virgin PVC. The majority of research studies have found an increase in composite stiffness accompanied by an increase in Young's modulus due to the use of a rigid filler [7-9].
Similar results were, reported by DJIDJELI et al. [10] and SAPUANA et al. [11], where they attributed this behavior to the rigid phase of dispersed olive pomace flour, which imparts high stiffness to the polymer matrix. Composites reinforced with the irradiated filler showed high modulus compared with untreated composites. The irradiation process increases the adhesion between DSF particles and PVC matrix by decreasing the hydrophobicity of the DSF particles; this is consistent with the results derived from the water, absorption rate measurements.
Young's modulus increased with increasing irradiation dose. Similar observations have been made by other researchers regarding the effect of gamma irradiation on the elimination of moisture from composites and the improvement of their mechanical properties [12- 14].
The variation in stress and elongation at break before and after incorporation of untreated and treated filler at different irradiation doses are, shown in Figure 2. and Figure 3.
A decrease in stress and elongation at break is, observed for composites filled with untreated DSF compared to those filled with untreated PVC. These results are in agreement with many other works, such as BELLILI et al [7] and DAIRI et al. [9].
This loss, in stress, and strain is due to poor interfacial adhesion between the PVC and date stone flour, and can also, be explained by poor filler dispersion, and consequently the formation of agglomerates, responsible for material fragility.
An improvement in stress at break was, observed for treated composites compared to untreated composites.
Chemical changes in cellulose after irradiation are the consequence of unimolecular or bi-molecular radical reactions.

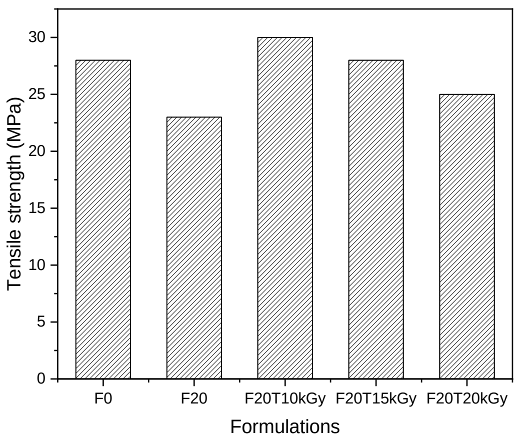

Figure 2. Tensile strength of PVC matrix and its composites reinforced with unirradiated and irradiated DSF at various doses of gamma radiation

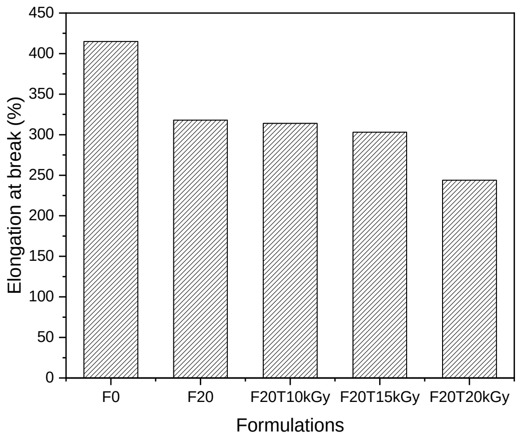

Figure 3. Elongation at break of PVC matrix and its composites reinforced with unirradiated and irradiated DSF at various doses of gamma radiation

Scission can lead to the opening of the anhydroglucose ring or the breaking of glucoside bonds. In both cases, carbonyl groups are, produced as a result, of chain scission into small fragments, there is, the possibility of conformational changes leading to increased intermolecular hydrogen bonding, leading to reinforcement of the three-dimensional structure. They found that at low doses of irradiation, dehydrogenation of cellulose by gamma radiation led to the formation of intermolecular bonds, resulting in increased tensile strength.

Takács E. et al. [15] found that intermolecular hydrogen bonds can replace intramolecular hydrogen bonds more and more as the irradiation dose increases. However, it is possible to produce cross-linking between neighboring chains by means of the radicals produced.

B. Measurement of water absorption rate

The evolution of the water absorption rate of PVC/DSF composites at different irradiation doses and as a function of immersion time is, illustrated in Figure 4.

Figure 4. The evolution of the water absorption rate of PVC/DSF composites at different irradiation doses, as a function of immersion time.

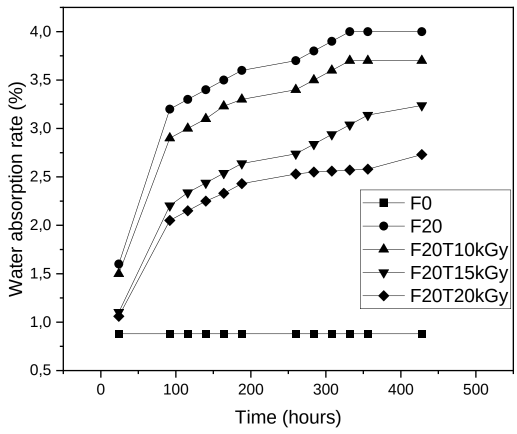

Figure 4. The evolution of the water absorption rate of PVC/DSF composites at different irradiation doses, as a function of immersion time.

The rate of water absorption increases with immersion time and after the addition of 20% DSF to the PVC matrix. This phenomenon is, attributed to the filler's high affinity with water. However, date stone flour is rich in hydroxyl groups, which form hydrogen bonds with water molecules.

Composites reinforced with irradiated filler absorbed less water than untreated composites. The lowest water absorption rates were, recorded by composites treated at 10 and 15 kGy.

The functional groups formed after irradiation react with the OH hydroxyl groups on the flour surface, preventing the cellulose flour from hydrogen bonding with water, thus reducing the amount of water absorbed.

For composites reinforced with the 10, 15 and 20kGy irradiated filler, maximum water absorption rates are, estimated at 3.5, 3.7 and 4% respectively. For virgin PVC, a very low water uptake of around 0.0414% was, recorded in 24 hours, and no more than 0.1904% in 30 days. This is due to the apolar nature of this polymer, which gives it a hydrophobic character, as confirmed by BELLILI et al [7].

C. Optical characterization

The dispersion of treated and untreated date stone flour in the PVC matrix was, verified by optical microscopy, and the micrographs obtained are, shown in Figure 5.

The micrograph of F0 shows a single phase, whereas that of the matrix reinforced with untreated filler shows the appearance of a phase corresponding to the filler, dispersed in another phase corresponding to the matrix. Date stone flour agglomeration was, observed in images of formulations containing untreated filler. This phenomenon was, explained by the poor dispersion of the hydrophilic filler in the hydrophobic matrix. Micrographs of composites reinforced with the irradiated filler showed fewer agglomerates, and the best dispersion was, observed for composites treated at 10 kGy. It can be, concluded that gamma irradiation treatment reduced the hydrophilic character of the filler, resulting in its good dispersion in the PVC matrix. This result confirms the results obtained by measuring the water absorption rate.

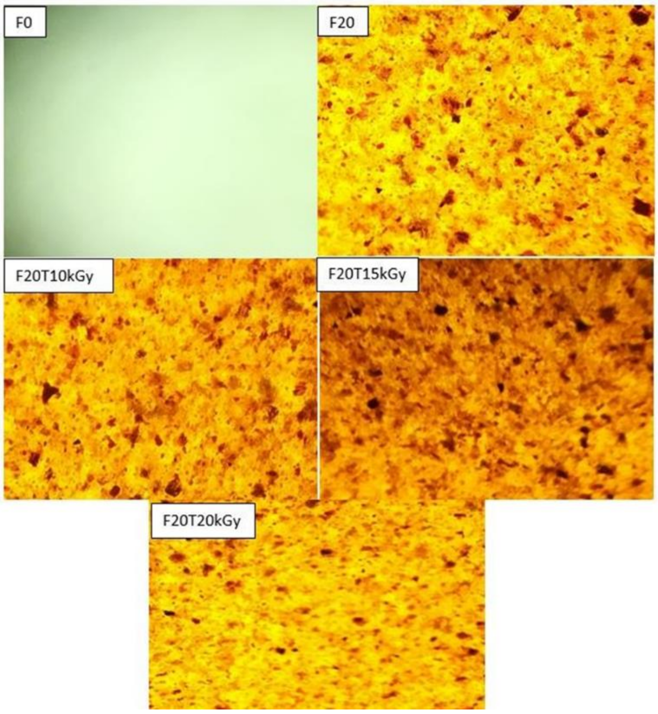

Figure 5. Micrographs of treated and untreated filler-reinforced composites obtained by optical microscopy

IV. Conclusions

In view of the results obtained, the following conclusions can be, drawn:

Mechanical characterization of the composites showed that:

- The behavior of the rigid phase of dispersed date stone flour gives high stiffness to the PVC matrix, leading to an increase in Young's modulus.
- A loss of stress and, strain is, observed due to poor interfacial adhesion between PVC and untreated date stone flour.
- Gamma irradiation-induced scission of chains into small fragments leads to the possibility of conformational changes, leading to an increase in intermolecular hydrogen bonding, which in turn increases tensile strength.

Physical characterization by measuring water absorption rates has enabled us to deduce that:

- The high affinity of the filler with water leads to an increase in the water absorption rate after the addition of 20% DSF to the PVC matrix. The interaction of the functional groups formed after irradiation with the OH hydroxyl groups on the flour surface decreased the amount of water absorbed.
- Micrographs obtained by optical microscopy showed that untreated date stone flour particles tended to aggregate and form agglomerates in the PVC matrix. In contrast, less agglomeration and better dispersion were, observed for composites reinforced with treated filler.

References

[1] M S-Shojai, G R-Bakhshandeh. Recycling of PVC wastes. Polymer Degradation and Stability, 96, 404 – 415, 2011.

[2] N. Yarahmadi, I. Jakubowicz, L. Martinsson. PVC floorings as post-consumer products for mechanical recycling and energy recovery. Polymer Degradation and Stability, 79, 439–448, 2003.

[3] H. Djidjelli, A. Boukerrou, A. Rabouhi, R. Founas, M. Kaci, O. Zefoun, N. Djillali, L. Belmouhoub. Effect of Olive Residue Benzylation on the Thermal and Mechanical Properties of Poly (vinyl chloride)/Olive Residue Composites. Journal of Applied Polymer Science.107, 1459–1465, 2008.

[4] M. N. Belgacem, M. Abdelmouleh, S. Boufi, A. P. Duarte, A. Ben Salah , A. Gandin. Modification of cellulosic fibers with functionalized silanes: Development of surface properties. International Journal of Adhesion and Adhesives, 24, 43–54, 2004.

[5] W. K. El-Zawawy, M. M. Ibrahim, A. Dufresne, A. F. Agblevor. Banana fibers and microfibrils as lignocellulosic reinforcements in polymer composites. Carbohydrate Polymers, 81, (4), 811-819, 2010.

[6] H. Ku, H. Wang, N. Pattarachaiyakoop, M.A. Trada. Review on the tensile properties of natural fiber reinforced polymer composites. Composites: Part B, 42, 856–873, 2011.

[7] N. Bellili, H. Djidjelli, A. Boukerrou, C. Barres, F. Fenouillot. Mechanical and Thermal Properties of Poly (Vinyl chloride) / Olive Residue Flour Blends Treated by Gamma Irradiation. Journal of Vinyl and Additive Technology. 22, (3), 273–278, 2016.

[8] B. Dairi, N. Bellili , N. Hamour, A. Boulassel, H. Djidjelli, A. Boukerrou , R. Bendib. Cork waste valorization as reinforcement in high-density polyethylene matrix. Materials Today: Proceedings, 53, 117–122, 2022.

[9] B. Dairi, H. Djidjelli, A. Boukerrou. Study and Characterization of Composites Materials Based on Poly (Vinyl Chloride) Loaded with Wood Flour. Journal of Materials Science and Engineering A, 3, (2), 110-116, 2013.

[10] H. Djidjelli, D. Benachour, A. Boukerrou, O. Zefouni, J. Martinez- Véga, J. Farenc, M. Kaci. Thermal, dielectric and mechanical study of poly (vinyl chloride)/olive pomace composites. Express Polymer Letters, 1, (12), 846–852, 2007.

[11] S.M. Sapuana, D. Bachtiar. Mechanical Properties of Sugar Palm Fiber Reinforced High Impact Polystyrene Composites. Procedia Chemistry, 4, 101 – 106, 2012.

[12] M. M. EL-Zayat, A. Abdel-Hakim, M. A. Mohamed. Effect of gamma radiation on the physic-o-mechanical properties of recycled HDPE/modified sugarcane

bagasse composite. Journal of Macromolecular Science Part A. Pure and Applied Chemistry, 56, 127–135, 2019.

[13] H. A. Raslan, E. S. Fathy, R. M. Mohamed. Effect of gamma irradiation and fiber surface treatment on the properties of bagasse fiber reinforced waste polypropylene composites. International Journal of Polymer Analysis and Characterization, 23,181–192, 2017.

[14] M. M. EL-Zayat, R. M. Mohamed, H. A. Raslan. Evaluation of surface treatment and gamma irradiation on the performance of palm fiber/natural rubber biocomposites. Journal of Macromolecular Science, Part A. Pure and Applied Chemistry, 57, 344–354, 2019.

[15] E. Takács, L. Wojnárovits, J. Borsa, Cs. Földváry, P. Hargittai, O. Zöld. Effect of γ-irradiation on cotton-cellulose. Radiation Physics and Chemistry, 55, 663–666, 1999.