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Mechanical and Thermal Properties of PLA Films Irradiated by Ultra Violet Irradiation

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The degradation of polymers under ultraviolet (UV) irradiation has been a great concern for biomaterial and agricultural applications. The major objective of this study is to examine the effect of UV radiation on biodegradable polylactic acid (PLA), and to understand the mechanisms of degradation induced by radiation. The PLA studied in this work presented in the form of a film of two thicknesses, 100 and 200 μm. The samples are artificially aged under varying doses of irradiation. Study of virgin systems under deferent speeds by tensile drawing showed that Young modulus of the thick films is higher than that of thin films, the thick material loses its rigidity from speed 25 mm/min. Under UV irradiation, at ambient temperature and crosshead speed 12 mm/min, all samples show ductility at the neat state and become rigid for doses over 324 mJ/cm2. The Young modulus increases with the amount then goes down. This is due to the drop in molar mass, confirmed by GPC, induced by scission of macromolecular chains followed by an increase due to recombination of free radicals. The storage modulus and loss factor of PLA were also investigated by DMA, its value is changed for 1300 MPa to 1000 MPa then it increases to 3250 MPa. The information on the functions of the material before and after the irradiation, in particular the degradation and the crystallinity of the biomaterial in question. DSC allowed access to Tg as well as crystallinity before and after irradiation which are correlated with mechanical properties given by tensile test.
Keywords: Polylactic acid, degradation, UV irradiation, mechanical properties.

1. Introduction

In recent years, the interest in biodegradable polymers has increasingly grown all over the world. Biodegradable polymers are used in various applications such as agricultural mulch films, packaging films, containers for liquid foods etc. [1-2-3-4] In fact, thermal treatment, gamma, and Ultra-Violet (UV) irradiation, modify the physic-chemical properties of polymer materials [5-6]. Generally, this modification adversely affects the mechanical as well as the thermal properties. Chemical and irradiation treatments have been used to introduce crosslinking between macromolecular chains whereas the ionizing radiations are known to lead either to the structurization of polymers or to their degradation [7-8]. Photo-oxidation, one of the two major mechanisms involved in the photo-degradation of polymers, mainly involves the oxidation initiation by photolysis of hydroperoxides, propagation by chain reactions, and termination through bimolecular reactions of alkyl peroxy radicals [7-9].

However, almost commercial thermoplastic polymers are sensitive to photo-oxidation, eventually resulting in loss in their physical properties.[9] Because Polylactic acid (PLA) has recently gained much attention, more durable PLA is required especially with regard to thermal and light resistance. Ikada[10-12] suggested that the main chain scission of both PLA randomly occurred by UV irradiation not via Norrish Type I reaction but via Norrish Type II.

The aim of this work is to highlight the impact of UV irradiation on PLA mechanical and thermal properties. This study is relevant to PLA utilities in various fields such as: agriculture, industry and recycling with the vision of better improvement of PLA properties.

In this respect this work is divided into two sections. The first section deals with their radiation methods and analysis techniques carried out to define the mechanical properties of PLA samples with 100µm and 200µm thickness. In this regard the tensile test is carried out to show the impact of stretching speed on Young modulus (E), Yield stress (σ_y), stress at break (σ_r), strain at break (ε_r) and ductile-brittle transition. Moreover, Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC) techniques are carried out to define the thermal properties of PLA irradiated with UV. For these methods are meant to show the impact of UV irradiation doses on glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c), melting enthalpy (ΔH_m) and crystallinity degree(χ_c). However, the second section is devoted to discussing the obtained results throughout the different experiments to find out PLA mechanical and thermal behaviors and their relationship with chains scission and free radicals' recombination.

2. Experimental:

2.1. MATERIAL

The PLA used in this study is a poly (D, L-lactide) 4042D grade material purchased from Nature works (USA), it contains 4.3 mol % of D-isomer units. It is presented in the form of films which are prepared through an extrusion blowing process leading to two thicknesses 100 and 200µm.The number-average and weight-average molar masses are M_n=116 000g/mol and M_w=188 000g/mol, respectively, according to the supplier. Films are found to be perfectly amorphous and isotropic. The samples are kept in air without exposure to irradiation, in a low

humidity environment. They are sandwiched between two polyethylene sheets.

2.2. UV IRRADIATION OF PLA FILMS:

PLA samples are cut in rectangular form (120x190 mm^2). They are glued onto a plate and passed under UV radiation source of different doses in room temperature without moisture control. The UV radiation source is produced using an accelerated photo-aging apparatus (UV-Minicure©) equipped with two lamps emitting light in the wavelength range of 295–400nm.The irradiation dose for each pass under UV irradiation is on average equal to 57mJ/cm^2.

2.3. TENSILE TEST

UniversitéFerhat Abbas –Setif/ Algeria, 2016. PhD thesis.

PLA samples of rectangular shape were cut from 100µm and 200µm thick films and the effective sample dimensions are $24 \times 5 \times 0.1 mm^3$, these samples were tested in a tensile drawing machine Versa Test (MECMESIN), equipped with an Advanced Force Gauge (AFG) of 100N possessing are solution of 0.02N, using crosshead speeds of 12, 20, 25 and 50mm/min at room temperature (20°C). Eight independent measurements were carried out; before and after irradiation; the results presented in this report represent average values. Stress-strain curve until break of the sample gives different values corresponding to mechanical properties such as Young modulus, yield stress, stress and elongation at break.

2.4. DYNAMIC MECHANICAL ANALYSIS DMA

The storage modulus of non-irradiated and irradiated PLA films was measured as a function of temperature between 20°C and 160°C using a dynamic mechanical analyzer (DMA Q800, TA instrument) under tensile mode. The measurements were made at a frequency of 1Hz, and a heating rate of 3°C/min. The shape of PLA films is rectangular, with dimensions 10 x 6 x 0.1[mm^3].

2.5. GEL PERMEATION CHROMATOGRAPHY

The molecular weights of the PLA films before and after exposure to UV irradiation were determined by GPC. However, polymer properties are strongly dependent on chain length, and therefore for the purpose of our study monitoring molecular weight evolution is an appropriate probe of the effect of photo and ionizing degradation. The weight and number average molecular weights (M_w and M_n, respectively) as well as the molecular weight distribution (M_w/M_n) of the films (PLA-UV) were followed as a function of UV irradiation. Typically, a PLA film of 50mg was dissolved in 5ml of Tetrahydrofuran (THF). The solution was shaken for 2 days to get a homogeneous mixture and a complete dilution of the polymer. The nit was filtered through a THF resistant filter with a pore diameter of 0.45mm (hydrophobicpolytetrafluoroethylene, PTFE). After filtration, the solution was passed through the GPC system. These measurements were calibrated using narrow distributed polystyrene standards.

2.6. THERMAL ANALYSIS

DSC scans were recorded on a Differential scanning calorimeter Q2000 from TA Instrument in inert atmosphere (nitrogen), with a heating rate of 10°C/min. The samples (5 - 7mg) were

placed into alumina crucibles. After the first heating -72°C to 200°C, the samples were cooled to -72°C and subsequently heated again and thermograms for second heating were recorded. The melting temperature (T_m) is taken from the end of the melting peak, whereas the crystallization temperature (T_c) is considered as the minimum of the exothermic peak. The crystallinity degree χ_c induced by irradiation could be deduced from the heat flow signal obtained by DSC, using the following equation:

$$\chi_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \quad (1)$$

where ΔH_m stands for the enthalpy of fusion of the irradiated sample, ΔH_c is the enthalpy of crystallization, and ΔH_f^0 represents the corresponding value for a 100% crystalline PLA (ΔH_m^0= 93,1J/g, value taken from literature [13]).

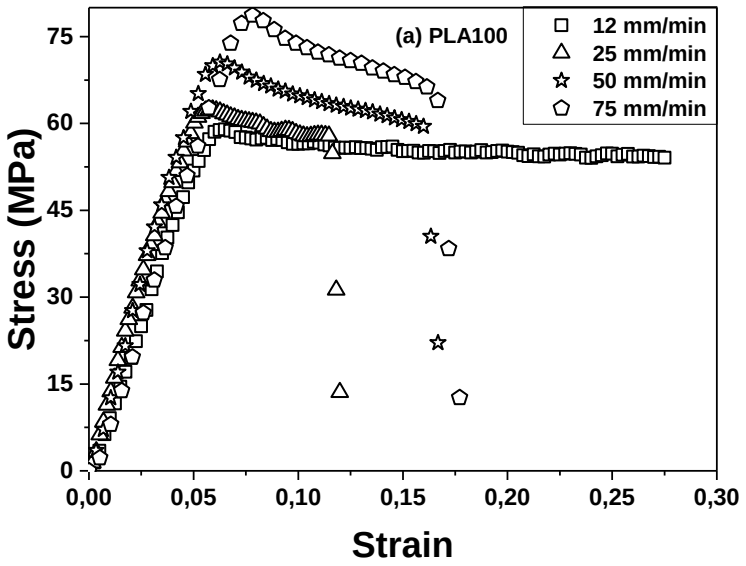
3. Results and Discussion

3.1. TENSILE TEST

The mechanical properties, which are of importance to this study, were evaluated via tensile testing and Dynamic Mechanical Analysis of neat PLA and irradiated samples.

3.1.1. NON-IRRADIATED PLA

First, non-irradiated PLA samples are studied to investigate mechanical properties. Figure1 (a) and (b) shows the stress-strain curves of the non-irradiated PLA thickness of 100µm (PLA100) and 200µm (PLA200) depending on the rate of stretching at temperature 20°C.



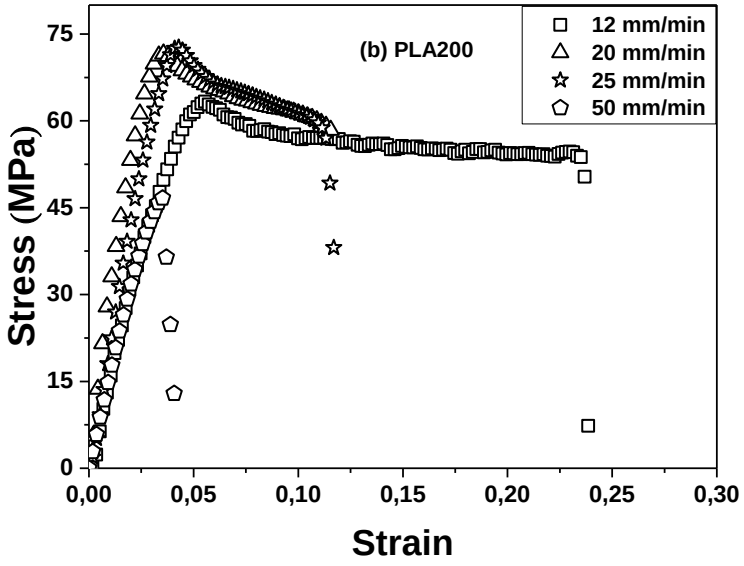


Fig.1.Stress-strain curves at different crosshead speed of (a) PLA100 and (b) PLA200.

The two PLA (PLA100 and PLA200) have a ductility for a crosshead speed of 12 mm/min with a similar stress at break (54 MPa) and a more pronounced deformation at break for the PLA100 (ε=0.27). With the increase of the stretching speed on the two PLA samples, the plastic plate decreases and the yield stress increases. The curves do not show hardening before rupture, characterizing high crystallinity induced by the deformation rate for both samples and for all speeds.

Depending on the stress conditions, the same material may behave either brittle or ductile. If break occurs at the elastic deformation regime, the behavior is brittle characterized by a stress called brittle strength σ_B. Ductile rupture, characterized by plastic flow σ_y (Yield stress), occurs after plastic deformation of the material. In case of PLA100 the behavior is ductile at the speed 12 mm/min and tends towards a semi-ductile behavior at the speed 75 mm/min, but over. For PLA200, the material is semi-ductile up to 25 mm/min and brittle at 50mm/min.

Young's modulus evolution as a function of the strain rate for PLA100 and PLA200 is illustrated in Figure 2. For all studied speeds, PLA200 moduli are higher than PLA100. For the speed 12 mm/min, the modulus is 1645 MPa for the PLA200 and 1027 MPa for the PLA100. The maximum values of Young modulus for both PLA100 and PLA200 at 25 mm/min speed are 1311 MPa and 2540 MPa respectively. PLA100 moves from ductile to semi-ductile behavior characterized by a decrease in Young modulus, whereas PLA200 loses its rigidity and breaks during traction tests at the speed 50 mm/min and above.

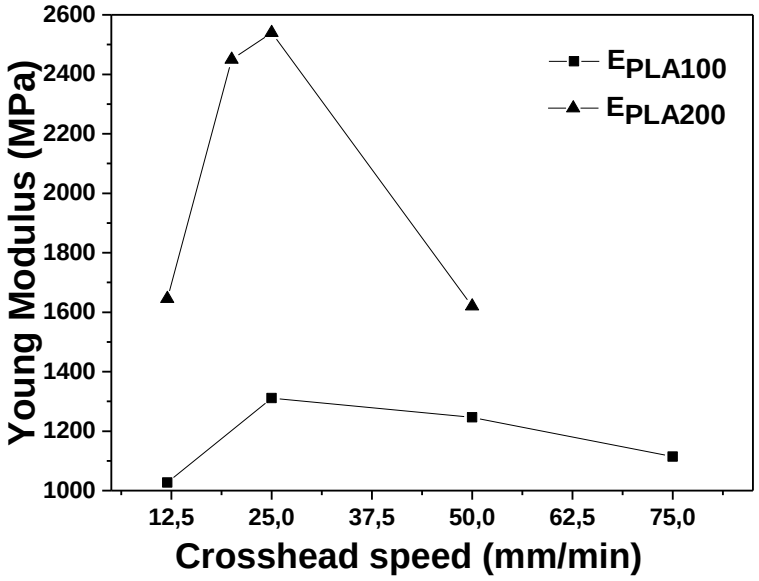


Fig.2. Young's modulus as a function of crosshead speed of PLA100 and PLA200.

The mechanical properties of both PLA such as yield stress σ_y, the stress at break σ_r and the strain at break ε_r, are shown in Table 1.

Table1. Mechanical properties of PLA100 and PLA200 at different crosshead speed: yield stress σ_y, stress at break σ_r and strain at break ε_r.

Crosshead speed	σ_y		σ_r		ε_r	
(mm/min)	PLA 100	PLA 200	PLA 100	PLA 200	PLA 100	PLA 200
12	61.74	63.5	57.29	52.6	0.27	0.15
20	/	74	/	61	/	0.07
25	64.89	66.3	57.24	55.16	0.11	0.07
50	67.86	/	57.85	46.64	0.15	0.03
75	74.1	/	64.67	/	0.16	/

For PLA100 yield stress (σ_y) increases with speed, from 61.74 MPa to 74.1 MPa, where the sample becomes semi-ductile. In the case of PLA200, σ_y reaches its maximum at the speed 20 mm/min, and suddenly falls down at the speed 50 mm/min where the sample becomes brittle. The deformation at break decreases gradually until the crosshead speed 25 mm/min, then it stabilizes around 15% for PLA100, whereas it stabilizes around 3% for PLA200. PLA100 shows ductility at crosshead speed 12 mm/min and becomes semi-ductile around 75 mm/min. PLA200, on the other hand, shows ductility at 12 mm/min, however it disappears at 50 mm/min.

Results reported in figure 2 and table 1 show that around the speed 25 mm/min properties of the material change independently of the thickness. Thus the modulus, which reflects the rigidity of the polymer, goes through a maximum in the case of the two PLAs with a high value in the case of the PLA200. For the other properties, the elastic plate having good ductility at 12 mm/min, observes a strong decrease around the speed of 25 mm/min with an increase in the elastic limit σ_y. These effects are the same as those observed during a classic ductile-rigid transition under temperature. The speed 25 mm/min can then be considered as a ductile-rigid transition speed.

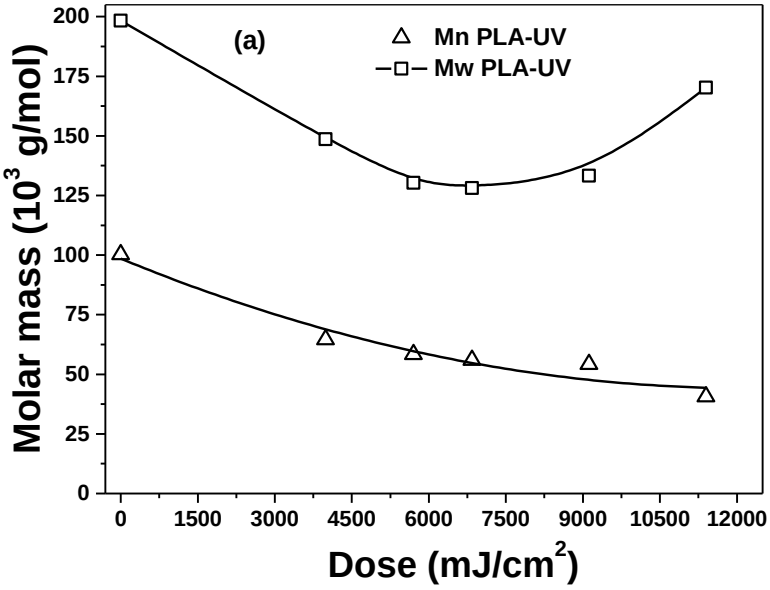
PLA100 and PLA200 films have ductility at low speed and above 25 mm/min, become semi-ductile and ductile-brittle, respectively. This change in behavior around 25 mm/min is explained by a ductile-brittle transition of the material [14].

3.1.2. IRRADIATED PLA

3.1.2.1 AVERAGE MOLAR MASSES

Figure 3a plots the number and weight average molecular weight (M_n and M_w; respectively) of the UV irradiated PLA-UV samples against radiation dose. The two molecular masses M_W and M_n fall until the amount 5700 MJ/cm^2 beyond which M_W increases over 9000 mJ/cm^2 while M_n remains at least constant with amount UV.

Increase of M_w in the case of UV is due to the selective nature of UV radiation, on the other hand and for other radiation which is random, produces much more free radicals. Consequently, the chains recombination is much more favorable where modulus stability is acquired.



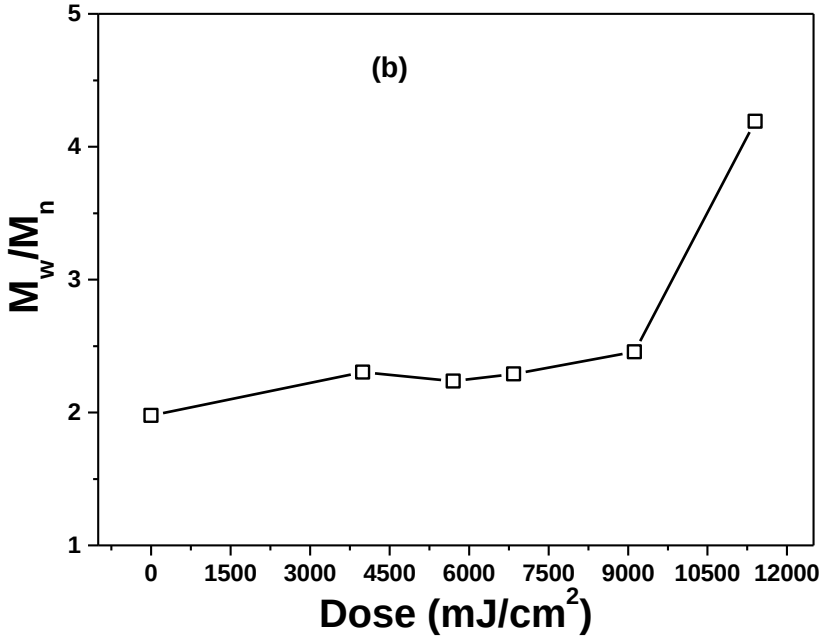


Fig.3. (a) Number and weight average molar masses M_n and M_w of PLA-UV samples irradiated under nitrogen atmosphere versus UV dose. (b) Evolution of the polydispersity index of PLA-UV vs. irradiation dose.

This type of irradiation cause a drop in mass possibly due to the scission and recombination of chains after the dose 5700 mJ/cm^2 . This result has been confirmed also in the works of Mansouri et .al [6]. Figure 3b shows a sharp increase of the polydispersity of PLA as function of radiation dose yielding values around 4.19 for PLA-UV from 9000mJ/cm^2, well above 2, which represents one more reason to confirm the occurrence of chain scission, in good agreement with the work of Charlesby [15].

The number of scissions, which indicates average number of dissociated bonds resulted from photo cleavage in the main chain scission, is simply expressed by the following equation [16] to estimate the scission rate S, given in mol/kg,

$$s(D) = \frac{1}{M_n(D)} - \frac{1}{M_n(0)} \qquad (2)$$

where $M_n(0)$ is the molar mass of the initial sample and $M_n(D)$ is the molar mass of the aged sample after an exposure to UV irradiation.

Figure 4 shows the increasing average number of scissions in PLA chain with irradiation dose. As is seen in this figure, the number of scissions increases approximately with irradiation dose. Accordingly, absorbed photon contributes to the main chain scission.

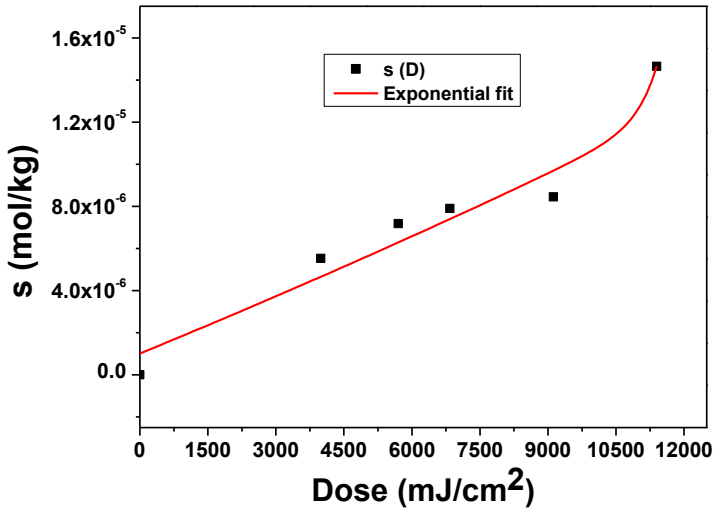
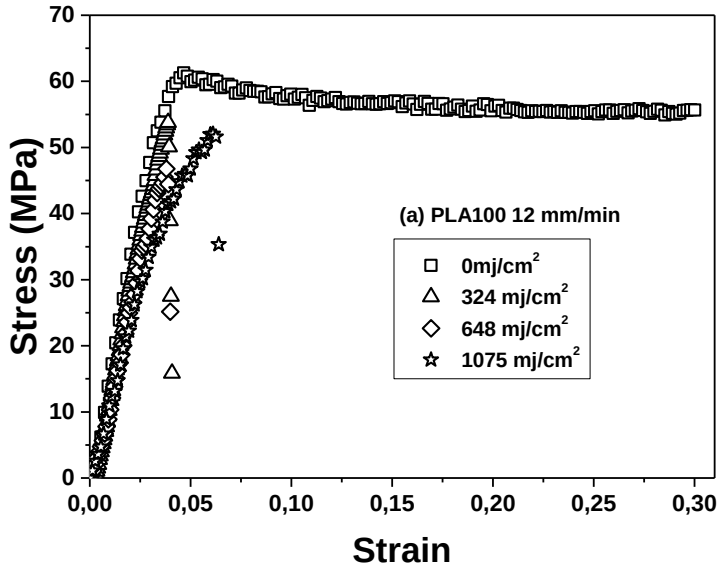


Fig. 4. Relationship between irradiation dose and the number of main chain scission of irradiated PLA.

3.1.2.2. STRESS STRAIN CURVES

PLA100 and PLA200 samples show strong ductility when stretched up with 12 mm/min speed that is the minimum speed of the machine. Therefore, we propose to study these samples applying different doses of irradiation.



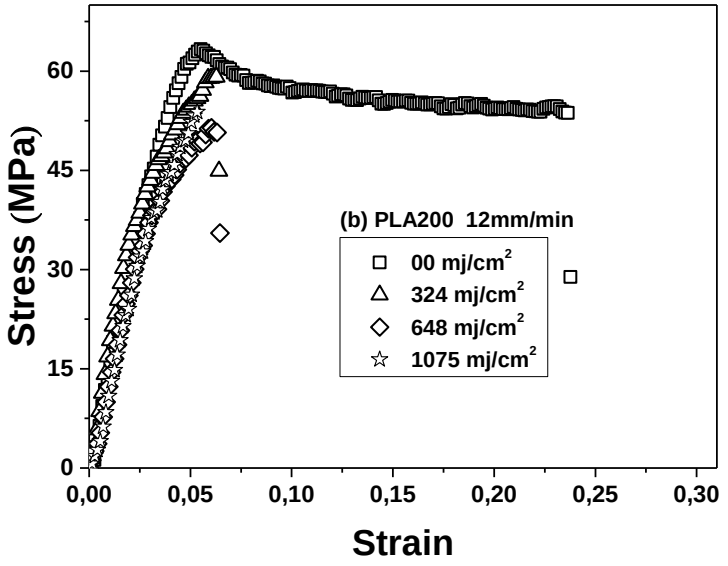


Fig. 5.Stress-strain curves of (a) PLA100 and (b) PLA200 stretched up at 12mm/min speed irradiated with different UV doses.

Figures 5(a) and (b) show the stress-strain curves of PLA100 and PLA200 stretched up at 12 mm/min speed irradiated with different UV doses

At 20°C and 12mm/min, PLA100 and PLA200 samples show ductility at the neat state and become rigid for doses over 324 mJ/cm^2. Table 2 summarizes the different mechanical properties of PLA100 and PLA200 under UV irradiation.

Table2 Mechanical properties of PLA100 and PLA200 under UV irradiation.

Dose (mJ/cm^2)	PLA100				PLA200			
	E	σ_y	σ_r	ε_r	E	σ_y	σ_r	ε_r
0	1027	70.1	63.4	0.11	1645	67	54.4	0.21
324	1460	/	53.4	0.038	1512	/	53.5	0.061
648	1340	/	47	0.038	1462	/	60	0.072
1075	1200	/	51	0.062	1187	/	53	0.053
2150	1330	/	27	0.021	/	/	/	/

Figure 6 illustrates the evolution of elasticity modulus of PLA100-UV samples irradiated with different UV doses [6]. This is due to the drop in molecular weight induced by the scission of the macromolecular chains followed by an increase explained by the recombination of free radicals. This result has been also highlighted in literature[6].

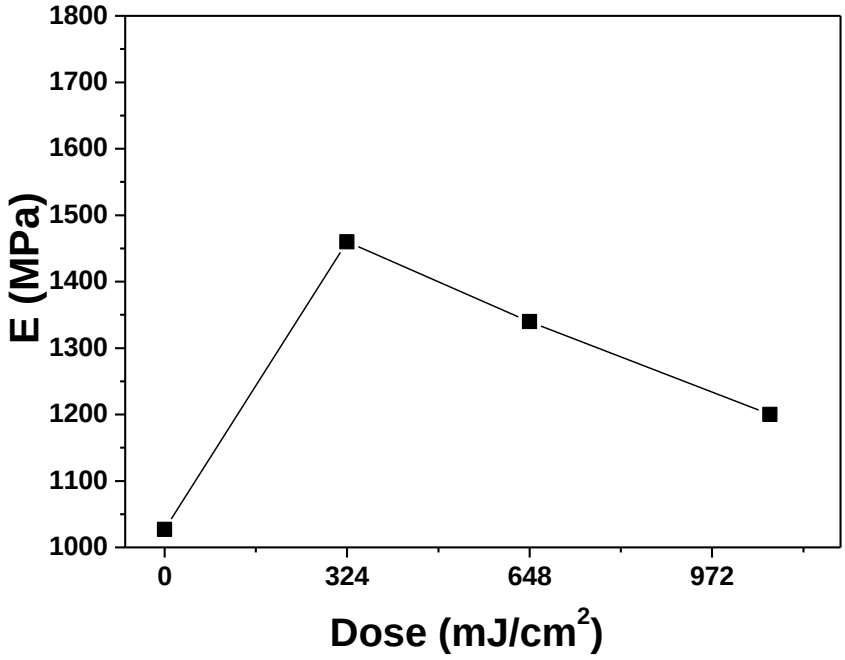


Fig. 6. Young's moduli of PLA100 under UV radiation.

The first rise is due to the very small crystallinity which plays the role of crosslinking points and which gives high rigidity to the material for the PLA-UV system.

Beyond 300 mJ/cm^2, the modulus drops by approximately 20% towards the dose 1200 mJ/cm^2, this is due to the drop in molecular mass given by Figure 3a, in this case, the drop in mass is dominant.

Above 1300 mJ/cm^2, the modulus stabilizes, due to the recombination of radicals.

Table3 sums up constraint values at the yield stress σ_y and break properties σ_r and ε_r. In the case of UV, deformation at break drops with the increase of the dose up to 648 mj/cm^2, due to the drop in molecular weight, followed by as light increase over this dose explained by the recombination of chains. This goes in parallel with works admitted by Mansouri et al. [6] for samples aged by EB radiation.

The yield stress decreases with the dose and the material passes directly from semi-ductile state to brittle state. The different properties are given in Table3.

Table 3 Mechanical properties of PLA100-UV at 12mm/min speed.

PLA-UV				
Dose (mJ/cm^2)	E	σ_y	σ_r	ε_r
0	1027	70.1	63.4	0.11

324	1460	/	53.4	0.038
648	1340	/	47	0.038
1075	1200	/	51	0.062
2150	1330	/	27	0.021

3.2. THERMAL ANALYSIS

DSC thermograms of PLA-UV samples are showed in Figure 7. The thermal characteristics; glass transition temperature (T_g), cold crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating cycle. The degree of crystallinity (χ_c) of thePLA samples was calculated using equation (1). In the case of UV, χ_c has a value below 2% indicating that the sample is perfectly amorphous up to the dose 648mJ/cm^2, beyond which it quickly rises to 7% for the dose 1075mJ/cm^2.

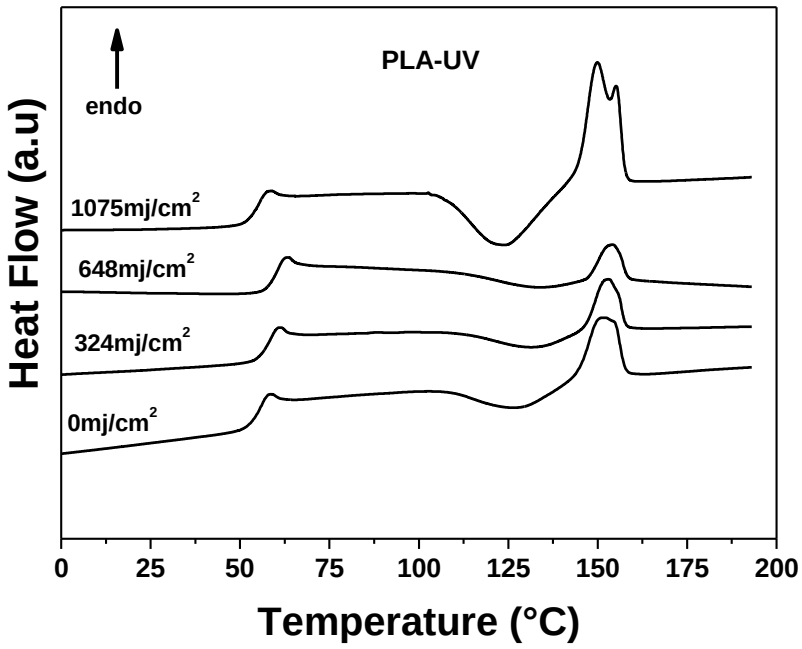


Fig. 7. DSC thermograms of PLA-UV irradiated at different UV doses, applying a heating rate of 10°C/min.

Table 5. Effect of UV irradiation on PLA thermal properties.

Doses (mJ/cm^2)	T_g(°C)	T_c(°C)	ΔH_c (J/g)	T_{m1}(°C)	T_{m2}(°C)	ΔH_m (J/g)	χ_c (%)
00	60.41	134.23	1.587	153.61	/	1.706	0.1
324	58.93	132.53	6.094	153.01	/	4.425	0.3
648	60.65	132.49	3.345	154.32	/	3.007	1.7

1075	55.38	124.49	18.86	149.90	155.06	12.19	7.1

According to Table 5 thermal properties of PLA-UV are summarized as follows; glass transition temperature T_g, as the dose increases, T_g decreases to stabilize around 55°C , this decrease is due to chains mobility, consequently PLA samples witness structural degradation. Crystallization temperature T_c, increases slightly then decreases due to chains recombination. For melting temperature T_m, it decreases which means that there is ductility in PLA, it should be noticed that for irradiated PLA, the lowest temperature endothermic peak was generally attributed to perfect crystal melting, associated with defective crystal transformation into more perfect crystals and the highest temperature endothermic peak corresponds to perfect crystal melting, associated to fusion-recrystallization or from defective crystal transformation [6, 17]. On the other hand; crystallization enthalpy ΔH_c, increases with the increasing radiation dose. This can be attributed probably to radiation induced degradation of PLA chains which could rearrange more easily. Melting enthalpy ΔH_m, increases slightly due to chains mobility indicating a slight crystallinity as well.

Figure 8 show degree of crystallinity χ_c calculated from equation (1) for the system. χ_c of PLA-UV samples, changes considerably according to UV irradiation doses. This change is due to the phenomenon of chain scission processes and recombination of free radicals occurring during irradiation. The rate of crystallinity increases slightly at the beginning up to 324mJ/cm^2, then it decreases at 648mJ/cm^2. It increases monotonously above this dose this is due to chains scission which increases their mobility, which favors the crystalline part, this has been confirmed by the increase in Young modulus E and storage modulus E' [18].

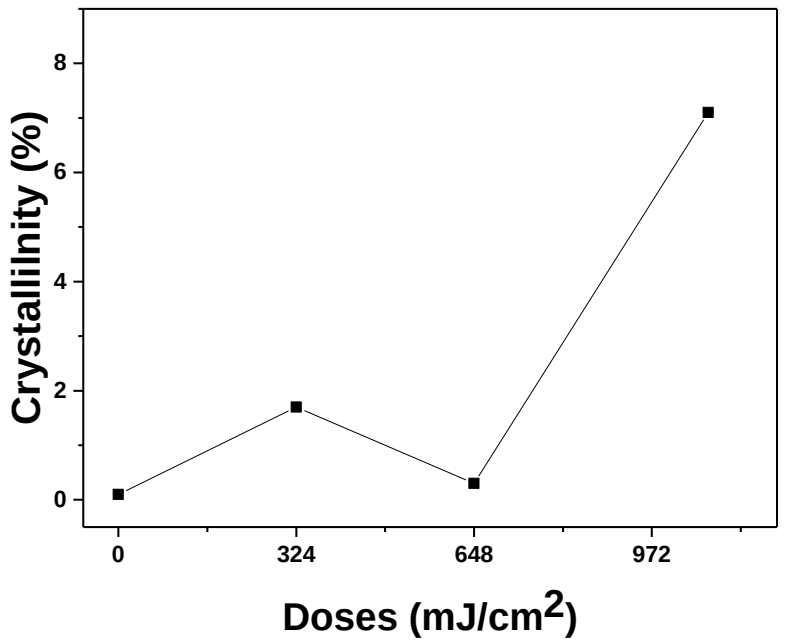


Fig. 8. Degree of crystallinity χ_c versus UV dose, using a heating rate of 10°C/min

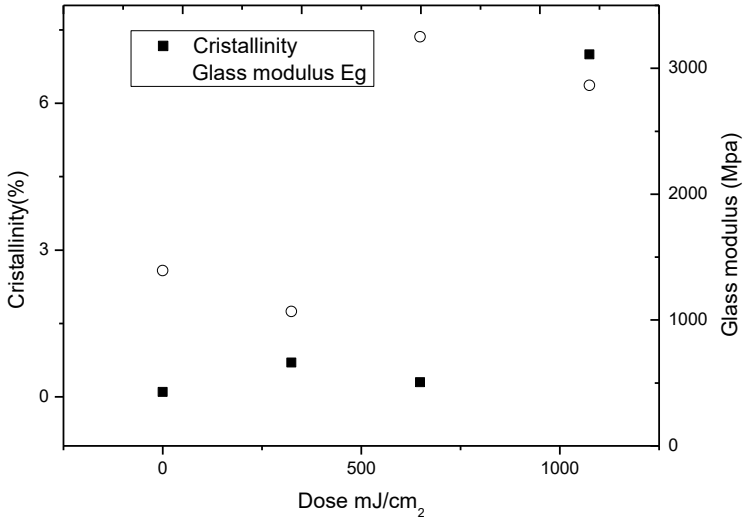


Fig. 9. Glass modulus Eg and degree of crystallinity χ_c versus UV dose.

Hence, neat PLA as well as PLA-UV share the similar thermal behavior under the same conditions. This behavior can be sum up as follows:

a) A decrease in T_g within the range of 3°C to 5°C.

b) A decrease in T_m within the range of 3°C to 4°C.

c) A decrease in T_c around 10°C for PLA-UV.

d) An increase in ΔH_c within the range of 10J/g to 12J/g.

ΔHm increases in PLA-UV, this fact is justified by the nature of the irradiation since UV irradiation is selective.

3.3. DYNAMIC MECHANICAL ANALYSIS (DMA)

in Dynamic analysis of samples is done order to evaluate the effects of UV irradiation doses on PLA properties. Figure 8 illustrates DMA curves of neat as well as irradiated PLA samples. Figures 8a illustrates the evolution of storage moduli versus temperature for PLA samples irradiated with different UV doses, called PLA-UV.

Table 4 summarizes the essential data of PLA-UV thermograms. Towards low temperatures, the glassy plate modulus E_g characterizing the rigidity of the material have very dispersed values in the case of UV irradiation, E_g decreases slightly from 1400 to 1050 MPa for the dose 324mJ/cm^2, due to the drop in mass and increases rapidly with the dose towards the value 3250 Mpa, and stabilizes around 2850 MPa towards the dose 1075 mJ/cm^2. The increase in E_g is certainly not due to crystallinity. On the other hand, this low crystallinity can produce an infinity of very small crystallites which can play the role of multitudes of crosslinking points, thus giving strong rigidity to the material.

Table 4. Mechanical properties of PLA100-UV at 12mm/min speed.

Parameters	UV (mJ/cm^2)			
	00	324	648	1075
Eg(MPa)	1393	1068	3250	2865
T_g (°C)	66.03	72.92	72.61	75.25
T_c (°C)	90	107	115	116

The main parameters of samples are given in Table 4. Storage Modulus E'of neat PLA100 is around 1393 MPa. In the case of PLA-UV, E' decreases until 1068 MPa, eventually due to the loss in weight, then it increases according with doses until 3250 MPa and decrease to 2865 MPa, due to increase of molar mass caused by recombination of free radicals.

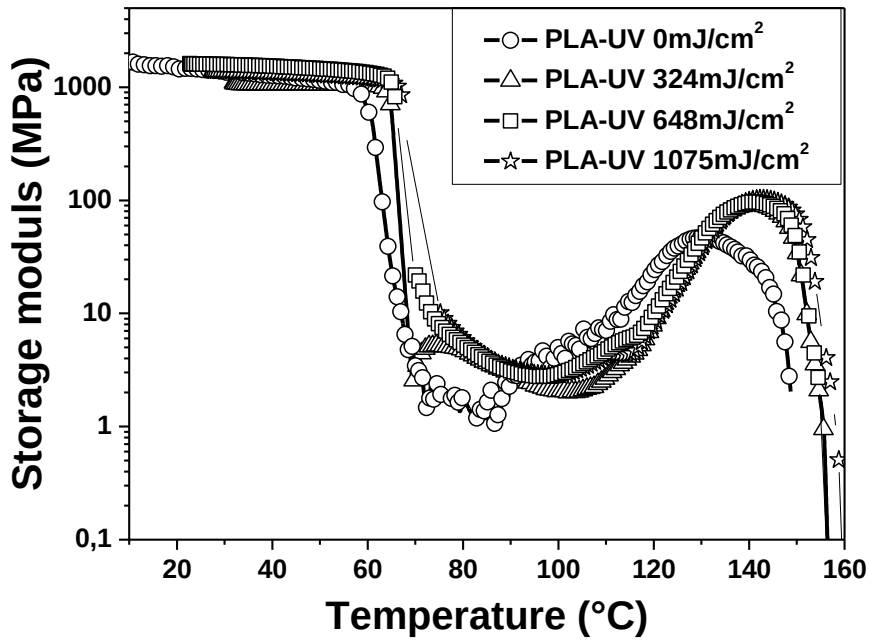


Fig. 8. Storage Moduli: PLA100-UV.

4. Conclusions

In regard to the major importance given to biodegradable polymers PLA in daily life notably for agricultural ends and 3D printing, the present study has dealt with the degradation of their mechanical and thermal properties. Throughout this work, different techniques of analysis such as: tensile test, dynamic mechanical analysis and differential scanning calorimetry were carried out to find common behavior between neat PLA as well as irradiated PLA with selective UV.

Tensile test was carried out using neat PLA samples of 100µm and 200µm thickness on one hand, and PLA 100µm thickness irradiated with UV different doses on the other hand. The obtained results show a decrease in Young Modulus E and a transition from ductile to brittle state. This shift in mechanical properties is due to chains scission and recombination of free radicals.

However, DMA and DSC techniques were carried out to define thermal behaviors common to PLA irradiated with UV in one hand and other at the other hand. Therefore, results have shown similar shift in thermal properties presented in a decrease in T_g, T_c and T_m according to UV doses justified by chains scission.

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