

## Biodegradability study of polypropylene fibers blended with disposable recycled poly(lactic acid) plastic flakes

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Received: 25.07.2018

Accepted/Published Online: 03.12.2018

Final Version: 03.04.2019

**Abstract:** Polymer blending as an efficient method for blending at least two polymers is usually used to create new materials with desirable physical properties. This article focuses on the biodegradability evaluation of polypropylene (PP) fibers modified with disposable recycled poly(lactic acid) (r-PLA) plastic flakes. Biodegradable modified PP fibers containing 30% r-PLA were prepared by melt spinning process and evaluated with different methods of biodegradation assays. The soil burial test method, CO<sub>2</sub> evolution analysis, weight loss, mechanical properties, and average molecular weight measurements and analysis of surface morphological changes were performed for biodegradability evaluation of the modified PP fibers. Surface morphology of the blend fibers illustrated that by increasing the soil burial period cracks were formed on the surfaces of fibers. While different testing methods showed different values for the biodegradation process, the results obtained from the CO<sub>2</sub> evolution analysis, weight loss, and variation of mechanical properties confirmed a good agreement between different degradation methods. After incubation in soil for a long period of time, the initial moduli and tenacity of the modified fibers decreased up to 72% and 53%, respectively. In addition, the average molecular weight measurement showed a 28% decrease in average molecular weight after 80 days of soil burial.

**Key words:** Polymer blend fiber, polypropylene, r-PLA, biodegradability, CO<sub>2</sub> evolution analysis, average molecular weight variation

### 1. Introduction

The use of biodegradable materials for making biodegradable blends has been under scrutiny since the late 1970s. For the first time in 1973, Griffin used starch powder to improve the biodegradability and biocompatibility of plastic packages.<sup>1</sup> The low cost and wide availability of starch, combined with its environmental benefits, enabled many producers to replace pure polyethylene (PE) with new blend materials. Starch-based blends do not have long durability because mold and mildew grow on the starch over time. High moisture absorption, moderately unpleasant smell, and poor strength in these materials have significantly reduced the interest in them.

Many studies have reported the production of nonbiodegradable-biodegradable polymer blends such as PE-poly butylene succinate,<sup>2,3</sup> PE-starch,<sup>1,4–5</sup> and PE-cellulose blends.<sup>6</sup> Several works have also been carried out to study the thermal, mechanical, and morphological properties of poly(lactic acid) (PLA)-polyolefin films or plastic blends.<sup>7–9</sup> Bijarimi et al. reported mechanical property enhancement of blends of PLA with polypropylene (PP) and liquid natural rubber as a compatibilizer agent.<sup>9</sup> Although many works have been done

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on blending of biodegradable polymers with nonbiodegradable ones, there is a lack of study on biodegradable fibers made of such polymer blends.

Melt recycling of PLA plastic wastes, which were employed to produce recycled PLA (r-PLA) fibers by melt spinning process, was studied in a previous work.<sup>10</sup> The results exhibited that PLA fibers with suitable properties could be obtained using r-PLA flakes of disposal packages by melt spinning process, and this recycled material was blended with other thermoplastic polymers for fiber production.

Modification of PP fibers by blending with r-PLA flakes in a melt spinning process has also been investigated.<sup>11</sup> In that work, biodegradability, mechanical properties, dyeability, washing, and light-fastness properties of the modified PP fibers were analyzed. The results obtained by the use of blending process showed an acceptable tenacity and initial modulus and a suitable biodegradability for the modified PP fibers.

The method used for measuring the biodegradability of modified PP/r-PLA fibers can be taken into account for direct measurement of biodegradable polymer groups. However, there is another approach for measuring the biodegradability of biodegradable polymers: indirect measurements like CO<sub>2</sub> production (ISO 14852 (1999), ISO 14855 (1999), ISO 14851 (1999), ISO 846 (1997)). Numerous standard methods describe biodegradation procedures.<sup>12</sup> Standards include indoor and outdoor procedures and many individual aspects for indicating the actual biodegradability of new polymeric materials. The biodegradability and rate of biodegradation can be completely determined with these standard methods, but they cannot clarify the advantages and disadvantages from the viewpoint of degradability compared to other biodegradable polymers.

This work reports the characterization of biodegradability properties of melt-spun PP/r-PLA blend fibers using direct and indirect methods. The main aim of this research work was to evaluate the biodegradation characteristics of the modified PP fibers by different direct and indirect methods and to reveal the relationships between the methods. Blend fibers with different blend ratios were characterized in our previous work<sup>11</sup> and then the ratio of 70/30 PP/r-PLA was selected and its biodegradable properties were deeply investigated by various measuring methods such as evolved CO<sub>2</sub>, weight loss, surface morphology (SEM micrographs), and average relative molecular weight.

This blend ratio was selected for the following reasons<sup>11</sup>:

- Acceptable mechanical properties: the spinnability and continuity of the blend fibers, as well as the PP and r-PLA pure fiber samples, were excellent and they had acceptable elongation at break and initial modulus in as-spun and drawn fibers of around 30%.
- Biodegradation evaluations: High decreasing ratio of mechanical properties.
- Thermal properties: Most uniform melting peak between poly-blend fiber structures.

## 2. Results and discussion

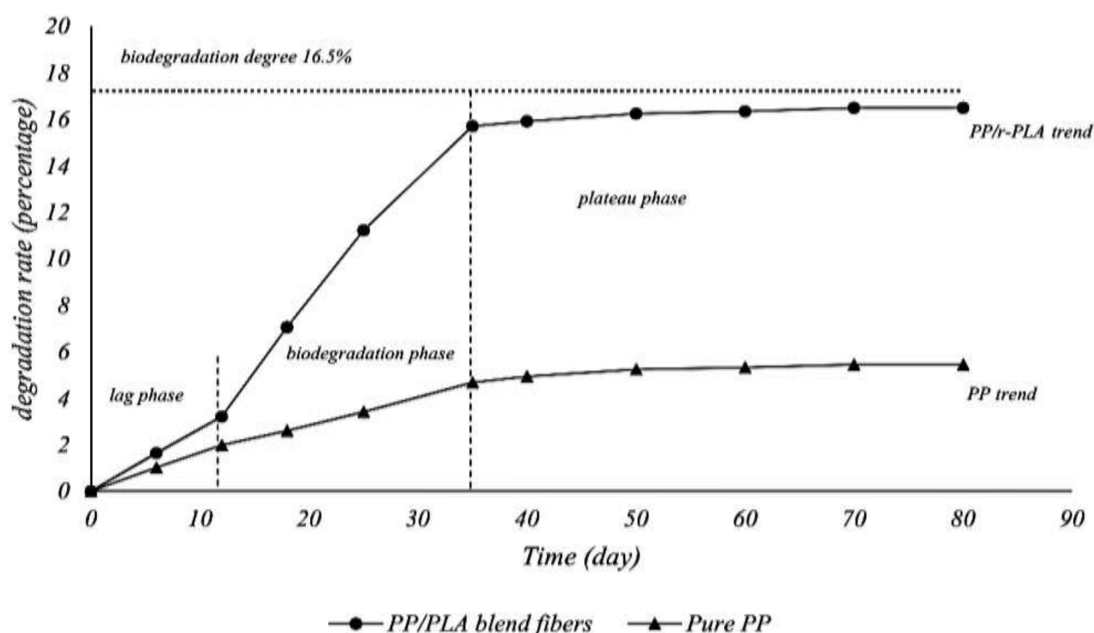
### 2.1. Biodegradability evaluation

#### 2.1.1. Evolved carbon dioxide analysis method

Biodegradation rate as evaluated by evolved carbon dioxide was found by Eq. (3) (see Section 3.3.2). Figure 1 shows the biodegradation rate of PP/r-PLA blend fibers in a controlled soil burial treatment at 58 °C. It was observed that the amount of CO<sub>2</sub> released by the PP fibers was equal to the amount of CO<sub>2</sub> released in the blank control bioreactor (only soil included), where the only carbon source was derived from the inoculation

soil. The pure PP fibers were not degraded significantly and were not affected by the evolved CO<sub>2</sub> amount during the experimental time period (80 days). The maximum degradation rate of the PP blend fibers was found to be 16% during 80 days. Degradation of the PP/r-PLA blend fibers started from about day 15 and reached its maximum at day 35.

The biodegradation trend of PP/r-PLA, as observed in Figure 1, is in good agreement with the trend of conventional biodegradable materials. First, a lag phase in Figure 1 occurs, during which the microbial population adapts to the available carbons of molecular chains of the PP/r-PLA fiber sample. The next phase is the biodegradation phase. In this period of the biodegradation process, microorganisms begin to consume carbon from the substrate and convert it into CO<sub>2</sub> in their metabolism. Finally, the biodegradation value reaches a plateau when the available carbon in the fiber sample is largely used.



Standard deviation of properties	Time	0	10	20	30	40	50	60	70	80
	PP/r-PLA		0.1105	0.1008	0.0984	0.0880	0.1210	0.0942	0.0966	0.1031
Pure PP		0.0775	0.0801	0.0915	0.0892	0.0900	0.0808	0.0943	0.0874	0.0945

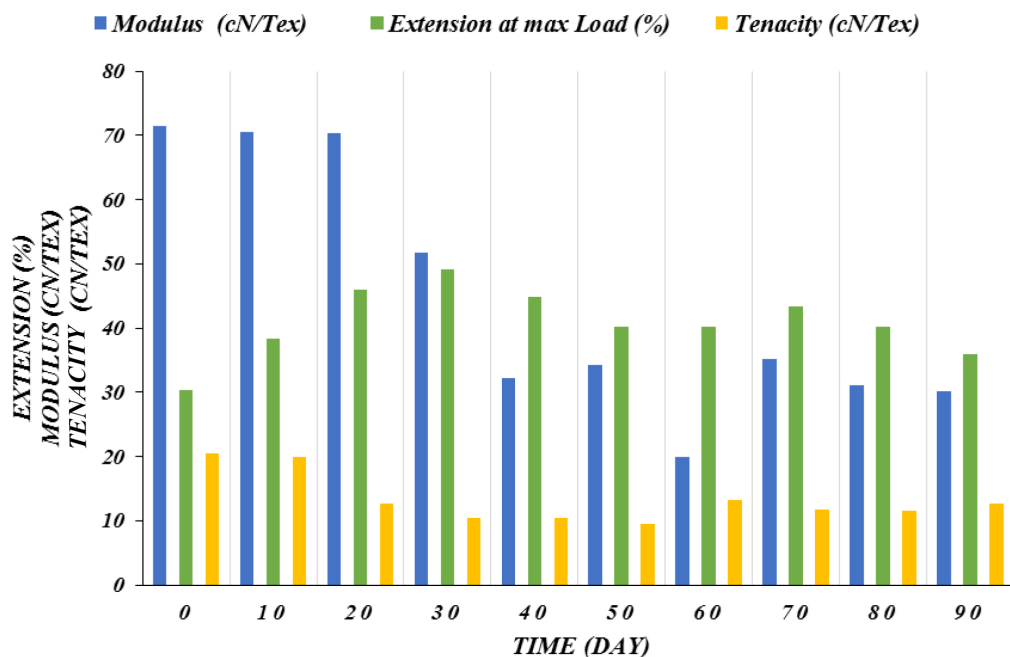
Figure 1. Biodegradation rate of pure PP and PP/r-PLA blend fibers detected by evolved carbon dioxide analysis.

## 2.2. Mechanical properties

A constant rate of elongation (CRE) tensile tester made by Iranian Elima Company was used for evaluation of the mechanical properties. The gauge distance and gauge speed were 5 cm and 50 cm/min, respectively. Fifteen tensile measurements were taken for each sample before and after the soil burial test. The average and percentage coefficients of variance (CV%) of the data were reported.

One of the most important parameters of the spinnability assessment of the fiber formation process is the evaluation of the mechanical properties of fibers, which were studied in our previous work.<sup>11</sup> The PP/r-PLA blend fibers with different blend ratios were successfully melt-spun along with a good continuity in spinning.

The mechanical properties of the as-spun and cold-drawn PP/r-PLA fibers were suitable and satisfactory for up to 40% r-PLA dispersed phase. Therefore, the mechanical properties of the blend fibers, before and after the soil burial test, are shown in Figure 2 and discussed here.



Standard deviation of properties	Time	0	10	20	30	40	50	60	70	80	90
	modulus (cN/TEX) S.D.		2.12	4.45	8.89	6.13	5.36	4.21	9.5	24.36	1.07
extension (%) S.D.		5.92	7.36	21.2	12.84	16.32	19.1	47.34	12.68	6.12	13.27
tenacity (cN/tex) S.D.		1	2.84	1.22	2.55	0.961	1.49	1.09	2.09	12.1	2.67

Figure 2. Mechanical properties variation in soil during the biodegradation.

Table. The mechanical properties of the PP/r-PLA fiber samples.

Time (day)	Elongation at break (%)		Tenacity (cN/tex)		Initial modulus (cN/tex)	
	Before	After	Before	After	Before	After
0	30.39	-	19.5	-	71.4	-
10	32.1	38.3	18.4	17.9	68.5	70.6
30	31.2	49.2	19.0	10.4	70.5	51.7
60	30.1	40.2	18.8	13.2	72.2	20.0
80	30.4	35.9	19.2	12.6	69.3	30.1

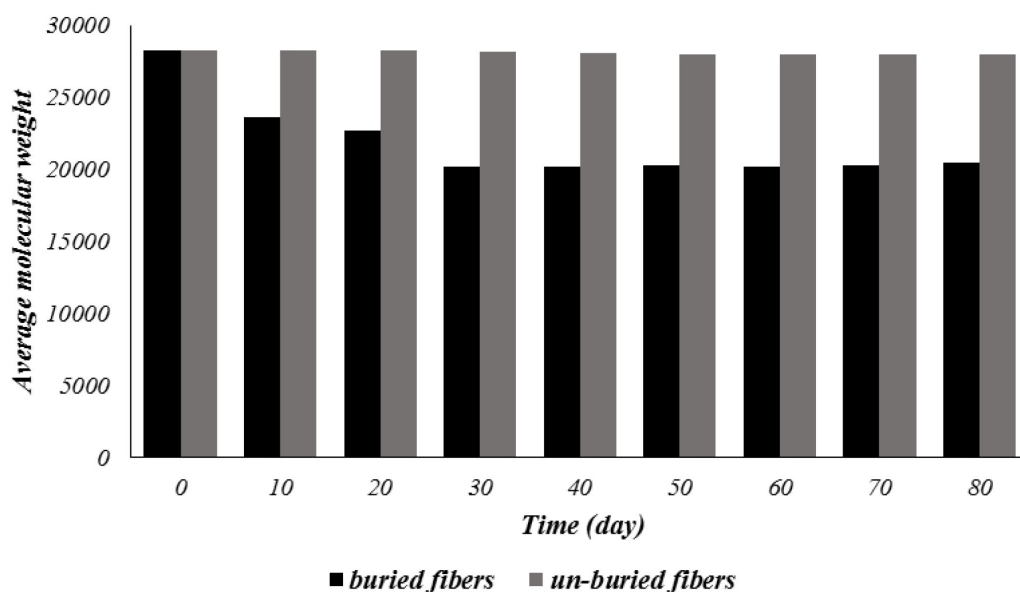
The Table shows the data on mechanical properties before and after the soil burial test. The initial moduli and tenacity decreased after incubation in soil at the beginning. The elongation-at-break of the samples increased until 30 days of incubation. Later it decreased until the last day of incubation. The main reason is decreasing of the chain lengths, which resulted from the biodegradation. Figure 3 shows the variation in the molecular weights of the samples during incubation.

The variation in these properties of the samples is presented in Figure 2. Reduction in the mechanical

properties of the PP/r-PLA blend fiber sample continued until the end of the biodegradation period (80 days). This result emphasizes that the carbon dioxide evolution analysis method is not a comprehensive method for determining the biodegradation value. Typically, the final product in the biodegradation process of biomaterials is CO<sub>2</sub>; however, the molecular chain breaking that causes a decrease of mechanical properties does not always lead to more CO<sub>2</sub>. Consequently, the biodegradation of the PP/r-PLA fiber sample continued with biodegradation of the fiber sample after 35 days of soil burial test. Very low variation of  $M_v$  before and after 30 days of biodegradation process confirms the disagreement between the mechanical properties and CO<sub>2</sub> evolution results.

### 2.3. Molecular weight

The value and variation of the viscosity-average molecular weight for the degraded fibers are shown in Figure 3. According to Figure 3, the  $M_v$  of the PP/r-PLA blend fiber is decreased with increasing degradation time. The decrease in the  $M_v$  values of r-PLA content of the modified PP fibers after soil burial test up to 30 days is in good agreement with the biodegradation results evaluated by the CO<sub>2</sub> evolution. Decreasing of the  $M_v$  of the r-PLA content means that the r-PLA molecular chain breaks and chain length shortens in the polymeric structure of the fibers. Consequently, the mechanical properties of the fiber samples decreased during the soil burial testing time. However, after 30 days of soil burial testing the PP modified fiber sample did not show significant changes in the  $M_v$  of r-PLA.



Standard Deviation of properties	Time	0	10	20	30	40	50	60	70	80
	Unburied fibers		0.01169	0.014142	0.022804	0.013038	0.008367	0.005477	0.006325	0.005477
Unried fibers		0.0085	0.0108	0.0091	0.0089	0.0120	0.0094	0.0094	0.0100	0.0091

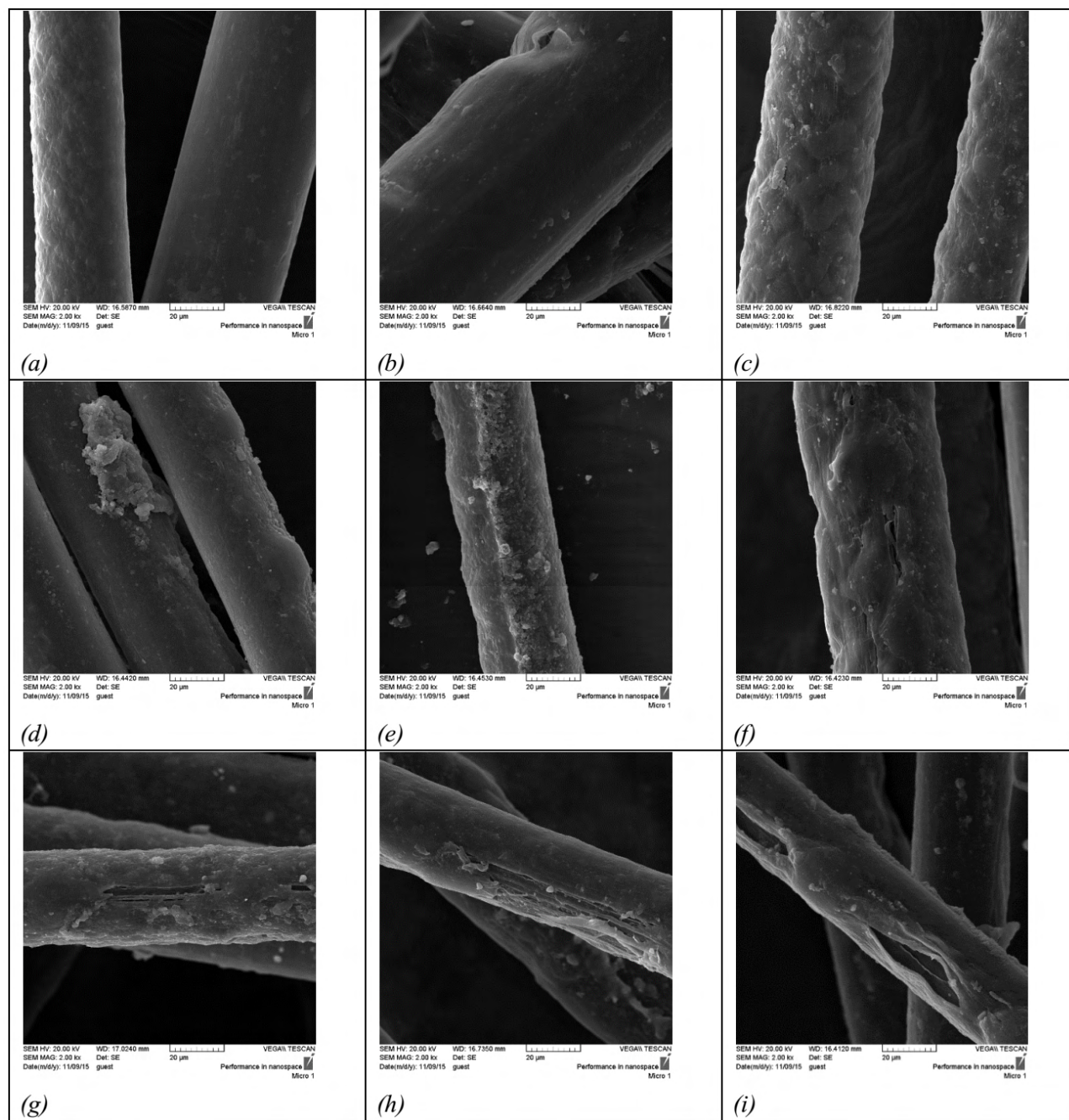
**Figure 3.** Variation of average viscosity molecular weight with burial time for buried and unburied fiber samples.

As observed in the evolved CO<sub>2</sub> test results, the biodegradation process was completely stopped and other parameters such as structural parameters affected the decrease of mechanical properties continuously.

Accordingly, some of these structural parameters are crystallinity, crystal size, and orientation of molecular chains in the amorphous regions.

## 2.4. Surface morphology

The micrographs of surfaces of the r-PLA/PP blend fibers are illustrated in Figure 4a. Figures 4b–4i display the morphological changes on the fiber surfaces during the soil biodegradation process.



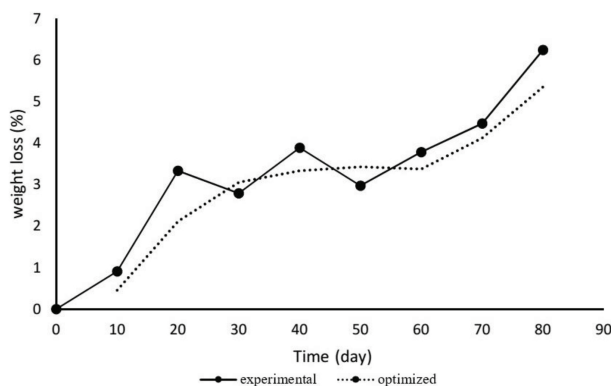
**Figure 4.** PP/r-PLA fiber surface morphologies: a) unburied and buried after b) 10, c) 20, d) 30, e) 40, f) 50, g) 60, h) 70, and i) 80 days.



The micrographs reveal that the degradation and microorganism amounts increased with time (cracks and biomass on the fibers). The heterogeneous holes visible on the micrographs clearly indicate the degradation of fibers with time because of the microorganisms' activity.<sup>13</sup>

## 2.5. Weight loss

Figure 5 shows the weight loss of PP modified fiber samples during the soil burial test period.



**Figure 5.** Estimation of biodegradability using weight loss as a function of soil burial time.

The amorphous regions in the internal structure of fibers are the first target for soil microorganisms; the microorganisms' activity removes the amorphous region and increases the crystallinity.<sup>14</sup> This may cause a decrease in weight loss rate as illustrated in Figure 5 (days 20 to 50). The change in weight of the samples (losing or gaining) is a competitive process in biodegradation. It is a competition mechanism between microorganisms growing and available carbon consumption process by microorganisms in fiber samples. The results obtained from this work show that the carbon consumption is dominant in the soil burial test (for 90 days). Accordingly, it can be said that the PP/r-PLA blend fiber sample has high biodegradation potential.

Generally, the experimental biodegradation results obtained from the weight loss evaluation procedure are smaller than those obtained from the mechanical properties variation and evolved CO<sub>2</sub> methods. When biodegradation occurs in an amorphous region, CO<sub>2</sub> evolution takes place and the breaking stress decreases. The CO<sub>2</sub> evolution depends on the carbon consumption but the weight loss and decreased breaking stress occur with defragmentation of fibers. This is why the CO<sub>2</sub> evolution stopped at day 30 but the weight loss and decrease in breaking stress continued.

The weight loss variation was in good agreement with the biodegradation behavior obtained from the CO<sub>2</sub> evolution method. However, when the graph obtained from the CO<sub>2</sub> evolution test reached the plateau phase, the weight loss in the fiber samples was still increasing. It could be described by the fragmentation process that occurred in the fiber sample. The SEM micrographs in Figure 4 verify these results.

In addition, a 6% weight loss over 80 days for the fiber sample confirmed the results obtained from the variation of mechanical properties.

The fiber biodegradation measured by the CO<sub>2</sub> evolution analysis showed 16% degradation at the end of the incubation period. The measurement of average molecular weight of the r-PLA chains also showed a 28% decrease in average molecular weight after 80 days of soil burial. The SEM micrographs similarly indicated that degradation occurred in the structure of fibers due to microorganisms. The heterogeneous holes visible

in the micrographs clearly indicated degradation of fibers during the burial process that resulted from the microorganisms' activity.

### 3. Experimental

This investigation was carried out on PP/r-PLA fibers prepared using isotactic PP (iPP), as a matrix, supplied by Sabic Co. (Saudi Arabia), and biodegradable PLA food packages, as the dispersed phase, which were purchased from Cuptainers Co. (USA). The melt flow rates of the dried (in a hot air oven at 82 °C for 14 h) r-PLA flakes and iPP were 6.5 and 25 g/10 min, respectively (carried out in a previous work).<sup>10</sup>

#### 3.1. Blend preparation

Physical mixing was used to prepare the blend samples of the PP granules and r-PLA flakes. Then true blending was carried out during the melt spinning process. Before melt spinning, the PLA flakes were dried in a hot air oven at 82 °C for 14 h. In this method, the water concentration after drying was expected to be 100 ppm. The blending ratio of PP/r-PLA was 70/30 by weight percent.

#### 3.2. Fiber production processes

Fibers were extruded from a laboratory mixing extruder made by Dynisco Co. (USA). The extruder was set with a standard orifice header having one orifice with diameter of 1 mm. The temperatures of the barrel and die zones were adjusted to 190 °C and the extruder screw rotation was adjusted to 12 rpm. The filaments were produced with a speed of about 70 m/min to form bundle samples of the as-spun filament yarns wound on a cardboard frame. The as-spun fibers were cold-drawn using a tensile tester made by Iranian Elima Company at a constant elongation speed of 50 cm/min at room temperature. The draw ratios were adjusted to obtain a final elongation-at-break of  $30 \pm 5\%$ .

#### 3.3. Biodegradability evaluation

##### 3.3.1. Soil burial method

AATCC soil burial method 30-1993, with natural soil, was used to fill a box to a depth of 11 cm. The fiber samples were buried in the soil at a depth of 3 cm and allowed to degrade for 80 days. During the degradation period, water was supplied at regular intervals. After degradation, the samples were rinsed with distilled water and conditioned at 23 °C and relative humidity of 65% for 48 h. Biodegradability was evaluated from the decreasing rate of breaking stress and weight loss values. The weight loss ratio was calculated from the weight of the specimen before and after biodegradation.

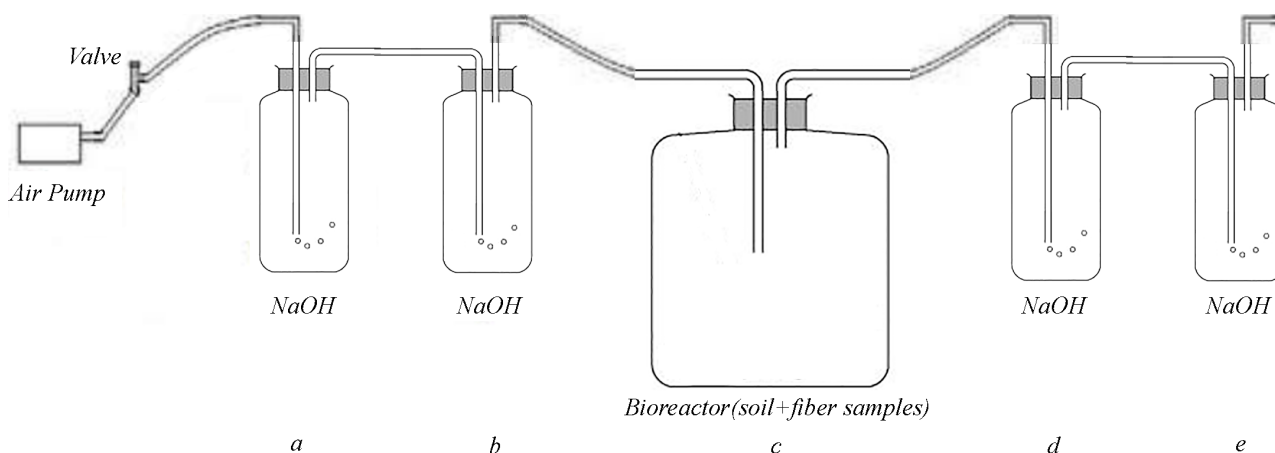
##### 3.3.2. Evolved carbon dioxide analysis method

Degradability of the fibers was determined by the ISO 14855-2 standard method. According to this standard, total organic carbon content (TOC) of the blend fiber was determined from Eq. (1):

$$TOC (\%) = \frac{\text{Organic Carbon (g)}}{W (g)} \times 100 \quad (1)$$

Here, Organic Carbon is the amount of carbon in the chemical formula of the material and W is the total molecular weight of the chemical formula. The degradation of samples was tested in the setup shown in Figure 6.





**Figure 6.** Bioreactor for detection of the CO<sub>2</sub> released by degradation.

Normal air (78% N<sub>2</sub>, 21% O<sub>2</sub>, and 0.03% CO<sub>2</sub>) was injected into flasks with an air pump at low constant pressure as illustrated in Figure 6.

Bottles (a) and (b) were filled with NaOH (300 mL of 2 M solution) for filtering pumped air and producing CO<sub>2</sub>-free air. Another bottle (c) was a bioreactor, filled with a combination of soil and fibers. Bottles (d) and (e) were filled with NaOH (300 mL of 0.5 M solution) to absorb CO<sub>2</sub> released from the bioreactor during biodegradation. A bottle (f) was filled with NaOH solution (300 mL of 0.5 M) as well, as an insurance of complete absorption of released CO<sub>2</sub>. The fiber sample was incubated for 80 days at 30 ± 5 °C. A blank control and a standard (pure PP) reactor with the same conditions and setup were also prepared. To determine the amount of CO<sub>2</sub> released by degradation the consumption of NaOH was determined by titration. All titrations were repeated three times; bottles (d) and (e) were mixed and 10 mL of the reacted NaOH sample was titrated using HCl (0.5 M). The titration indicator was phenolphthalein in all experiments.

In order to calculate amount of released CO<sub>2</sub>, Eq. (2) was used:

$$\sum (CO_2) = \frac{\Delta V}{10} \times K \quad (2)$$

Here,  $\sum (CO_2)$ ,  $\Delta V$ , and 10 are the amount of CO<sub>2</sub> released by the material, the volume of reacted NaOH solution (mL), and the NaOH volume (mL), respectively; K is the constant parameter of the amount of NaOH in bottles (d) and (e) (300 mL in this work) (total volume of absorption solution); the CO<sub>2</sub> absorber solution concentration is 0.5 M NaOH; and the molecular weight of CO<sub>2</sub> is 44 g/mol. The efficiency of the PP/r-PLA fiber degradation in soil was measured with Eq. (3) by calculating the ratio of released CO<sub>2</sub> against the maximum theoretical amount of CO<sub>2</sub> that could be released:

$$Bio_{material} = \frac{EvCO_2}{ThCO_2} = \frac{\sum (CO_2)_{Material} - \sum (CO_2)_{Blank}}{T} \times hCO_2_{Material} \times 100 \quad (3)$$

In this equation,  $Bio_{material}$  is the biodegradation efficiency,  $\sum (CO_2)_{Material}$  is the amount of CO<sub>2</sub> released from the bioreactor,  $\sum (CO_2)_{Blank}$  is the CO<sub>2</sub> from the blank test setup (only soil included), and  $ThCO_2$  is the maximum amount of CO<sub>2</sub> that could be released (theoretically), which can be obtained from Eq. (4):

$$ThCO_2 = m \times TOC (\%) \times C \quad (4)$$

Here,  $m$  and  $TOC$  (%) are the mass of the substrate (g) and the percentage of organic carbon content in the material, respectively. Constant parameter  $C$  is the ratio of molecular weight of  $CO_2$  to the atomic weight of carbon (44 g/mol and 12 g/mol).

### 3.4. Mechanical properties evaluation

A CRE tensile tester made by Iranian Elima Company was used for evaluation of the mechanical properties. The gauge distance and gauge speed were 5 cm and 50 cm/min, respectively. Fifteen tensile measurements were taken for each sample before and after the soil burial test. The average and CV% of the data were reported.

### 3.5. Molecular weight

Molecular weight of the samples was measured by the viscosity method in a diluted polymer/chloroform (PLA was dissolved and the PP portion was removed after 3 h) solution (0.5 g/dL) using an Ubbelohde viscometer (Type I) at 30 °C. The viscosity-average molecular weight ( $M_v$ ) was calculated for describing the molecular weight variations.  $M_v$  was calculated based on the Schindler and Harper method,<sup>15</sup> used by many authors.<sup>16,17</sup> Accordingly, the relative viscosity of each sample was measured using the standard dilution method (ASTM D 4603-03). Then intrinsic viscosity was calculated using the Solomon and Ciuta single-point method,<sup>18,19</sup> as in the following equation:

$$[\eta] = \frac{[2(\eta_r - 1 - \ln \eta_r)]^{1/2}}{c} \quad (5)$$

Here,  $\eta_r$  and  $c$  represent the relative viscosity and polymer/solvent concentration, respectively. Finally,  $M_v$  was calculated from  $[\eta]$  using the following equation:

$$[\eta] = 5.43 \times 10^{-4} M_v^{0.73} \quad (6)$$

The extent of decrease in  $M_v$  was obtained by the variation of the  $M_v$  of r-PLA before and after the soil burial test:

$$\Delta M_v = \frac{[M_{v1} - M_{v2}]}{M_{v1}} \times 100 \quad (7)$$

Here,  $M_{v1}$  and  $M_{v2}$  are the  $M_v$  values of r-PLA before and after melt spinning, respectively.

### 3.6. Surface morphology

A VEGA scanning electron microscope (TESCAN) was used to observe the surface morphology and longitudinal cross-section uniformity of the recycled PLA fiber samples at a magnification of 2000 × and acceleration voltage of 20 kV. The samples were coated with gold using a sputter-coater prior to observation by SEM.

### 3.7. Weight loss

Biodegradability was also evaluated by the decreasing rate of weight loss of the soil-buried tested samples. The weight loss ratio was calculated by the weight of the specimen before and after biodegradation.

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