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Rheological, Mechanical and Morphological Characterization of Monopolymer Blends Made by Virgin and Photo-Oxidized Polypropylene

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Abstract: In this work, monopolymer blends of virgin polypropylene and photo-oxidized polypropylene were prepare and characterized. The polypropylene samples were subjected to accelerated ageing to simulate the effects of outdoor exposure of polypropylene. After exposure, samples were pelletized and mixed with the same virgin polymer. The rheological, mechanical and morphological characterization was conducted on both the polymers and the blends. Both viscosity and mechanical properties decrease with increases in the content of recycled, photo-oxidized components and of the level of degradation of this component. In addition, the experimental data were compared with a model that takes into account both the effect of the change of the molecular weight and of the presence of oxygenated groups.

Keywords: monopolymer blend; polypropylene; additive model; accelerated weathering

1. Introduction

Blending of virgin and reprocessed or post-consumer polymers is a very popular method to reuse a polymer component coming from post-consumer items. Usually, this operation is conducted by blending only limited amounts of post-consumer polymer in order to avoid a drastic decrease of the processability and of the mechanical properties. These blends are, then, made by blending virgin polymer with the same post-consumer recycled polymer–monopolymer blends, and the fraction of the post-consumer polymer can be, in turn, made of several fractions of polymer recycled one or more times.

These monopolymer blends are made of the same polymer and, in general, present properties very similar to those of the virgin polymer when the reprocessed component comes from production waste. In this case, indeed, the properties of the reprocessed component are very similar to those of the virgin material as it has not undergone any severe degradation process, but only a decrease of the molecular weight due to the repetitive melt processing operations.

In our previous works, we have investigated the rheological and mechanical properties of monopolymer blends of high- and low-density polyethylene [1,2] as well as polypropylene [3,4], polyvinylchloride [5], polyethylenetherephthalate [6] and polyamide [7]. Similarly, other research groups have examined monopolymer blends of virgin and recycled acrylonitrile-butadiene-styrene (ABS) [8–11], high density polyethylene (HDPE) [12,13] and polyethylene terephthalate (PET) [14–16]. The different degradation processes occurring in the recycled polymer influence the properties of their blends and alter their compatibility to a certain extent. For example, the compatibility of blends may be affected by chemical groups (such as carbonyl groups) produced during thermo-oxidation. For this reason, the experimental results have shown that the rheological and mechanical properties of these blends can be lower than those expected on the basis of an additive law and are never easy to predict, in particular when the recycled components are severely degraded.

Recently [17], we used the typical industrial operation of blending virgin polymer with the same polymer reprocessed several times to compare an additive model to predict rheological and mechanical properties with experimental results. We concluded that the model was effective when applied to blends where the recycled component undergoes only a modification of the molecular structure.

In this study, monopolymer blends of virgin and photo-oxidized polypropylene were prepared and characterized. The accelerated weathering simulates the effect of the outdoor exposure of the polypropylene. Since photo-oxidation leads to the formation of oxygenated polar groups, [18,19] the two components will show some incompatibility between the apolar virgin PP and the recycled, polar PP. In this case, not only the molecular architecture is changed, but also the morphology of one component and of the blend. A model which takes into account both features is also proposed and compared with the experimental results.

2. Materials and Methods

2.1. Materials and Samples Preparation

The material used in this work was a polypropylene random copolymer sample, supplied by LyondellBasell (Houston, TX, USA) under the commercial name Hostalen PP H5416. Table 1 shows some relevant properties of polymer used.

Table 1. Relevant properties of the polymer investigated.

Polymer	Density, g/cm^3	MFI, g/10 min (2.16 kg at 230 $^\circ$C)	Melting Point, $^\circ$C
Hostalen PP H5416	0.897	0.3	139

Sheets of the samples were prepared by compression molding in a Carver (Carver, Wabash, IN, USA) laboratory hydraulic press at the temperature of 190 $^\circ$C under a mold pressure of 300 psi and for about 3 min.

The obtained specimens (thickness of about 300 um) were exposed to accelerated weathering in a QUV Chamber (Q-Labs Corp., Westlake, OH, USA) containing eight UVB-313 lamps for up to about 48 h at 70 $^\circ$C, according to the procedure described elsewhere [20].

After exposure, sheets were pelletized and blended with 70% virgin polymer by melt mixing in a Brabender mixer mod. PLE330 (Brabender, Duisburg, Germany) at 190 $^\circ$C and 60 rpm for 3 min, and then compression molded.

After each molding cycle, a number of specimens were sampled for testing and the remainder were again exposed to accelerated weathering, and then reprocessed. This procedure was repeated three times.

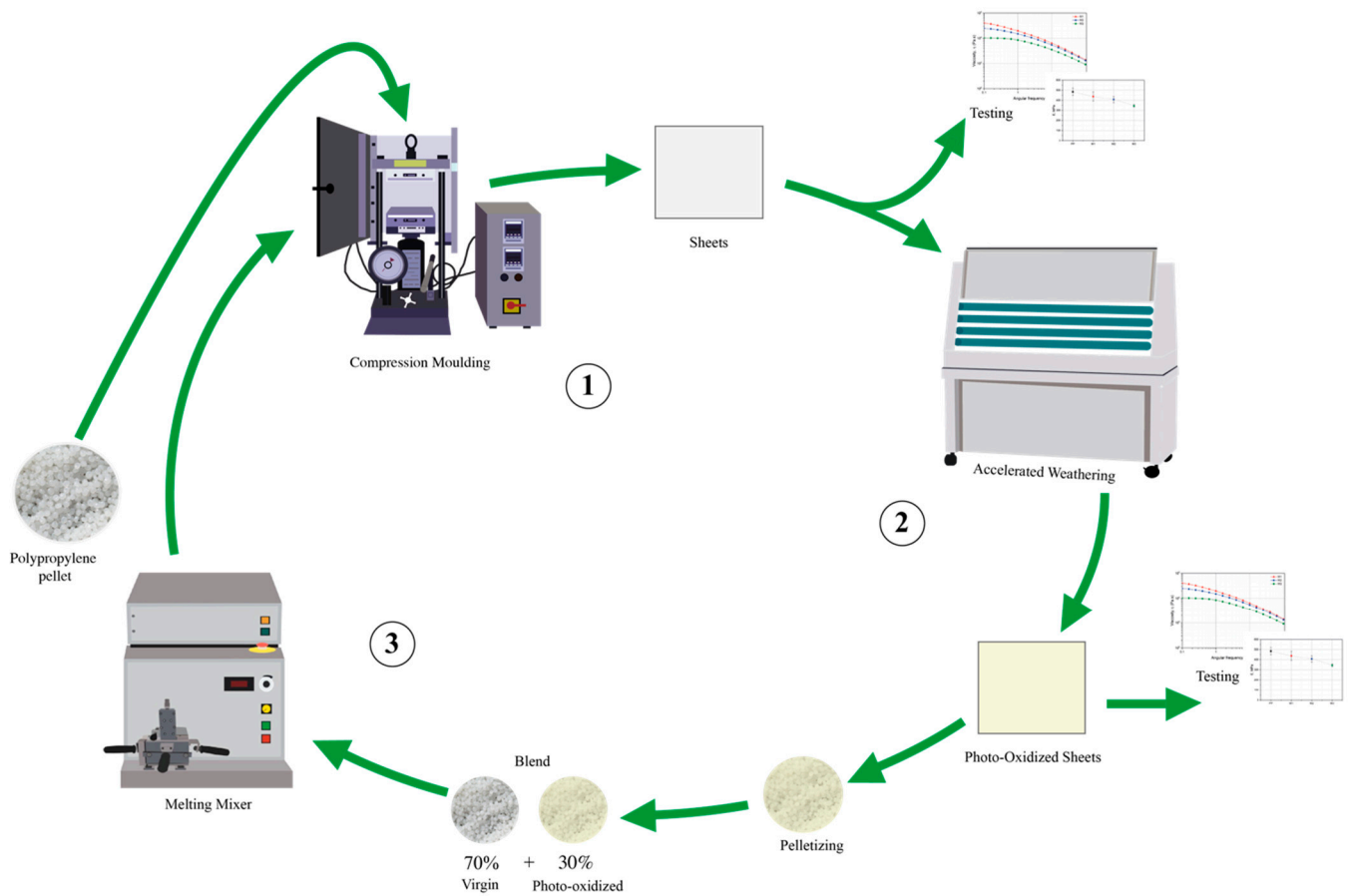Figure 1 depicts the process used in this work.

Figure 1. Scheme of procedure adopted in this work.

The composition of the samples coming from blending virgin and photo-oxidized polymer is:

$$M_1 = xPP + (1 - x)Ph_1 \tag{1}$$

$$M_2 = xPP + (1 - x)[xPh_1 + (1 - x)Ph_2] \tag{2}$$

and, then, in general for the sample containing the i-th reprocessed material:

$$M_i = xPP + (1 - x)[xPh_{i-2} + (1 - x)(xPh_{i-1} + (1 - x)Ph_i)] \tag{3}$$

where x is the weight fraction of the virgin polymer and Ph_i is the polymer photo-oxidized *i* times.

2.2. Characterization

The mechanical tests were carried out using in an Instron (Instron, High Wycombe, UK) universal testing machine (mod. 3365) according to ASTM D638.

Elastic modulus, E, tensile strength, TS, and elongation at break, EB, were measured and the data reported were determined as an average of seven samples. The elastic modulus was measured at deformation speed of 1 mm/m. When the deformation achieved 10% the cross-head speed was increased to 100 mm/m until final breaking.

The rheological behavior of samples was characterized using an ARES G2 (TA Instruments, New Castle, DE, USA), equipped with a 25 mm diameter parallel plate geometry and using a 1.5 mm gap. All measurements were set at 190 °C from 100 to 0.1 rad/s.

Fourier transform infrared spectroscopy (FT-IR) absorption spectra were recorded in the wavenumber range of 4000 to 400 cm^{-1} with 16 scans. Measurements were performed using a Perkin-Elmer FT-IR spectrometer (Perkin-Elmer, Norwalk, CT, USA) with

Spectrum software. Attenuated total reflectance (ATR) equipped with a single reflection diamond ATR crystal was used for all investigations. The area under the curves between 1800–1650 cm^{-1} and 3600–3300 cm^{-1} has been calculated in order to evaluate the formation of carbonyl and hydroxyl groups during photo-oxidation.

The DSC measurements were performed using a DSC-131 Setaram (Setaram, Austin, TX, USA) operating at a temperature range between +40 and +200 °C, with a heating rate of 5 °C/min. The nitrogen served as an inert atmosphere, and the average weight of the sample was 7 ± 2 mg.

The degree of crystallinity (X_C) was evaluated from the melting enthalpy results (ΔH_m) of each sample using the following Equation (4):

$$X_C, \% = \left(\frac{\Delta H_m}{\Delta H_{100}} \right) \times 100 \tag{4}$$

where ΔH_m is the enthalpy of fusion, ΔH_{100} is enthalpy of fusion for 100% crystalline polymer. For polypropylene, ΔH_{100} = 207 J/g.

3. Results and Discussion

3.1. Characterization of Photo-Oxidized PP

Table 2 reports the mechanical properties, elastic modulus, E, tensile strength, TS, and elongation at break, EB, of the virgin PP and of the photo-oxidized samples. In order to eliminate surface defects, the data in the following table were obtained when the samples were reprocessed [21].

Table 2. Mechanical properties of PP and of the photo-oxidative samples.

	E, MPa	TS, MPa	EB, %
PP	485 ± 25	30.2 ± 2.7	706 ± 30
Ph$_1$	522 ± 22	20.4 ± 1.6	568 ± 24
Ph$_2$	568 ± 18	13.7 ± 0.9	30 ± 2.8
Ph$_3$	641 ± 19	8.4 ± 1.1	5.7 ± 1.1

PP is the virgin sample and Ph$_1$, Ph$_2$ and Ph$_3$ are the photo-oxidized samples for 48, 96 and 144 h, respectively. The ultimate properties decrease dramatically with increasing photo-oxidation time, while the elastic modulus increases. In particular, after 144 h the PP becomes ductile. This increase of the elastic modulus has been already reported [2,7] and attributed to the increase of the crystallinity of the sample due to the cleavage of the macromolecules with consequent increase of the crystallization rate.

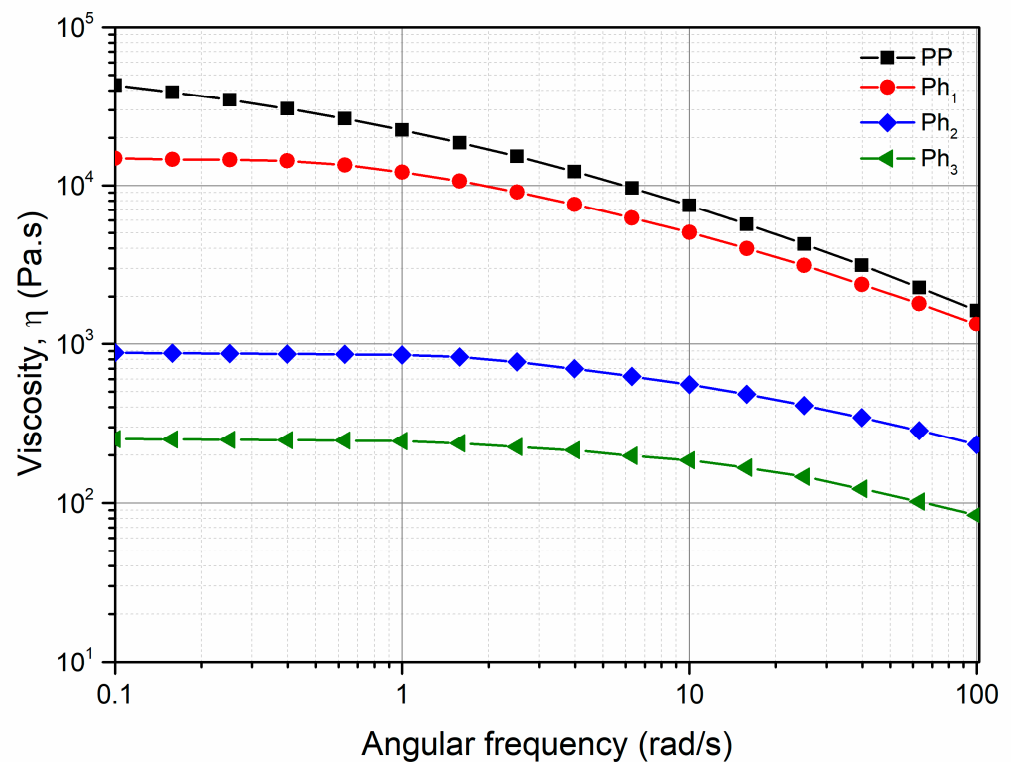Figure 2 reports the flow curves of the same samples.

Figure 2. Flow curves of the virgin PP and of the photo-oxidized samples.

Increasing the photo-oxidation time, the viscosity decreases, and the samples show a less pronounced non-Newtonian behavior. The decrease of the Newtonian viscosity is, in particular, very impressive as it is reduced by about two orders of magnitude.

The Newtonian viscosity is a strong function of the molecular weight (see Equation (5)) [17]:

$$\eta_0 = K\, Mw^{3.4} \tag{5}$$

and then, the molecular weight of the sample photo-oxidized can be calculated using Equation (6):

$$(\eta_0(Ph_i)/\eta_0\,(PP))^{1/3.4} = Mw(PP)/Mw(Ph_i) \tag{6}$$

Because the Newtonian viscosity value of PP is 43.177 Pa·s, Ph_1 is 14.860 Pa·s, Ph_2 is 878 Pa·s and Ph_3 252 Pa·s; this means that the decrease in molecular weight after photo-oxidation for Ph_1, Ph_2 and Ph_3 is about 27%, 68% and 78% of its initial value, respectively.

As reported before, the decrease of the molecular weight enhances the crystallization rate and the crystallinity degree. In Figure 3 the thermograms of the same samples are reported. The melting temperature decreases and a new peak appears for the photo-oxidized samples at 96 and 144 h.
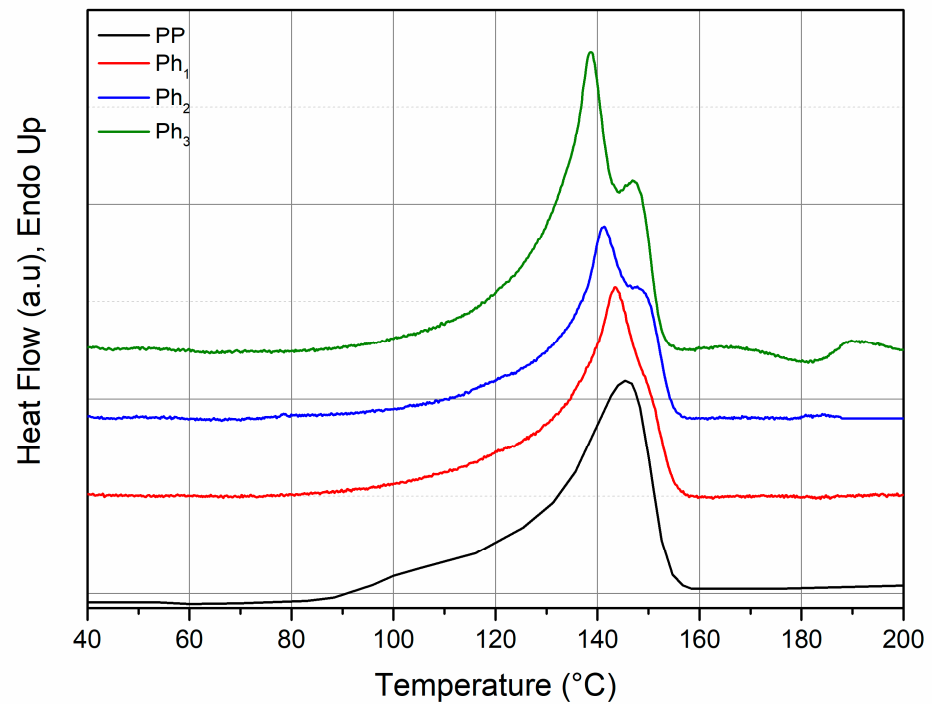
Figure 3. Thermograms of virgin PP and photo-oxidized samples.

In Table 3 the melting temperature, the melting enthalpy and the crystallinity degree of the virgin PP and photo-oxidized samples are reported.

Table 3. Melting temperature, melting enthalpy and crystallinity degree of the virgin PP and photo-oxidized samples.

	T_m, $^\circ$C	ΔH_m, J/g	X_c, %
PP	145.4	65.6 $\pm$ 1.8	31.7
Ph$_1$	143.4	68.3 $\pm$ 2.4	33.0
Ph$_2$	141.3	72.2 $\pm$ 2.6	34.8
Ph$_3$	138.6	85.1 $\pm$ 3.7	41.1

It is well evident that the crystallinity remarkably increases with the photo-oxidation time and then, with the level of degradation, confirming the interpretation given for the improvement of the elastic modulus with the photo-oxidation time.

The photo-oxidation breaks the macromolecular chains, but also induces the formation of oxygenated species in the apolar chains of the PP. In Figure 4 the ATR curves of the PP and of all the photo-oxidized samples are reported.
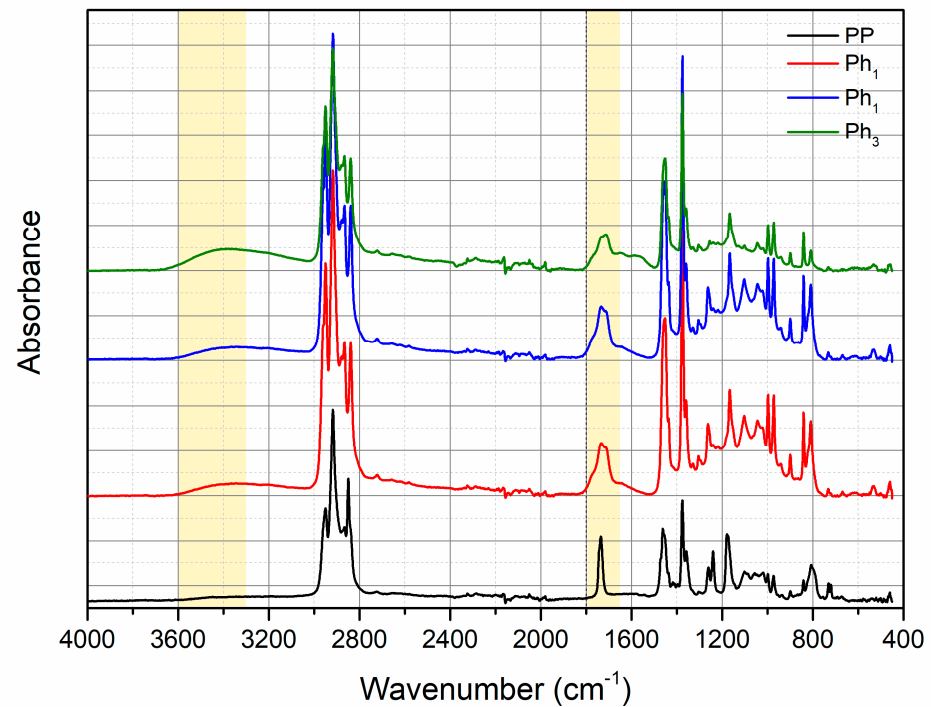
Figure 4. ATR curves of the virgin PP and of all the photo-oxidized samples.

It is well evident that the increase of the areas centered at about 1710 cm^{-1} and at about 3400 cm^{-1} represents the formation of carbonyl and hydroxyl groups. In Figure 5 the values of the dimensional areas under the carbonyl (1800–1650 cm^{-1}) and hydroxyl groups (3600–3300 cm^{-1}) are reported. The dimensionless values have been evaluated as the ratio between the area at a given time divided by that of the virgin sample.

Both values rise firstly in the first stage of photo-oxidation and then the increase becomes minor.

3.2. Characterization of the PP/Photo-Oxidized Blends

Figure 6 shows the flow curves of the three monopolymer blends. The viscosity decreases with increasing content of photo-oxidized polymer and, in particular, 30% of Ph$_1$ in M$_1$, 21% of Ph$_1$ and 9% of Ph$_2$ in M$_2$ and 21% of Ph$_1$, 6.3% of Ph$_2$ and 2.7% of Ph$_3$ in M$_3$. At the same time, the non-Newtonian behavior becomes less and less pronounced.
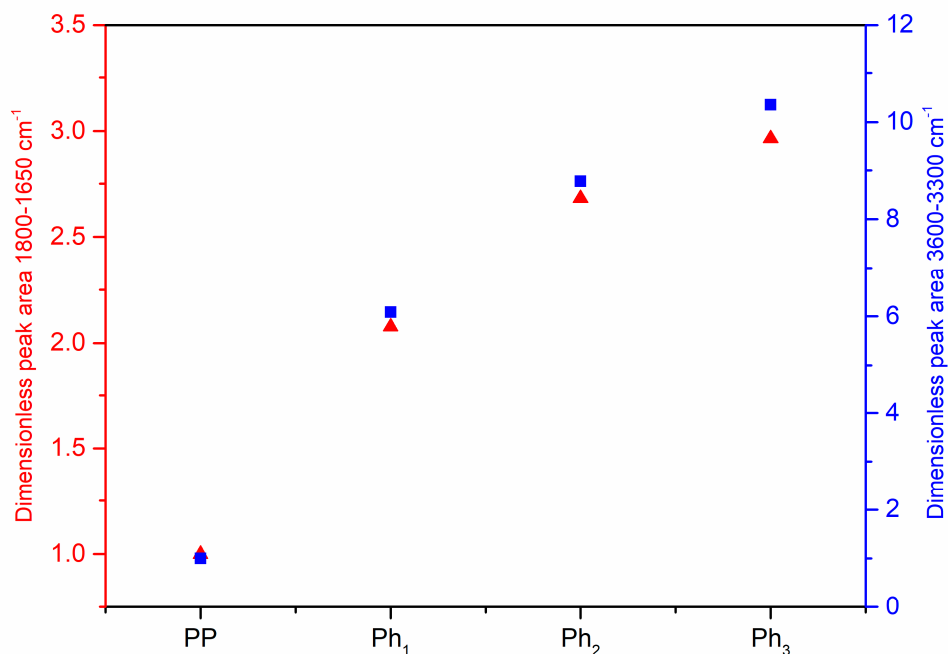
Figure 5. Dimensionless peak areas in the region 1800–1650 cm^{-1} and 3600–3300 cm^{-1}.
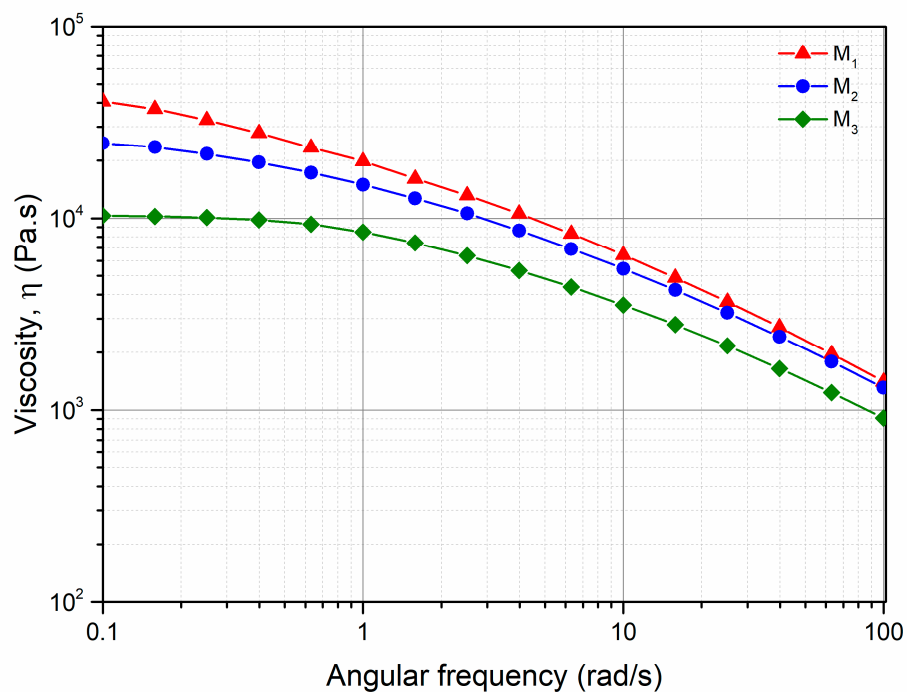

Figure 6. Flow curves of all the monopolymer blends.

The Newtonian viscosity of the three monopolymer blends is reported in Table 4. Of course, the Newtonian viscosity decreases with the increasing level of degradation of the photo-oxidized components.

Table 4. Newtonian viscosity values of the monopolymer blends.

	M_1	M_2	M_3
Newtonian Viscosity, η_0 (Pa·s)	40,570	24,651	10,329

The decrease of the viscosity is remarkable, as it is reduced by about four times; however, it is worth mentioning that the reduction of the viscosity of the photo-oxidized component is very large.

The values of the elastic modulus, tensile strength and elongation at break of all the monopolymer blends are reported in Figures 7–9. All these mechanical properties decrease with the increasing level of degradation of the three components.
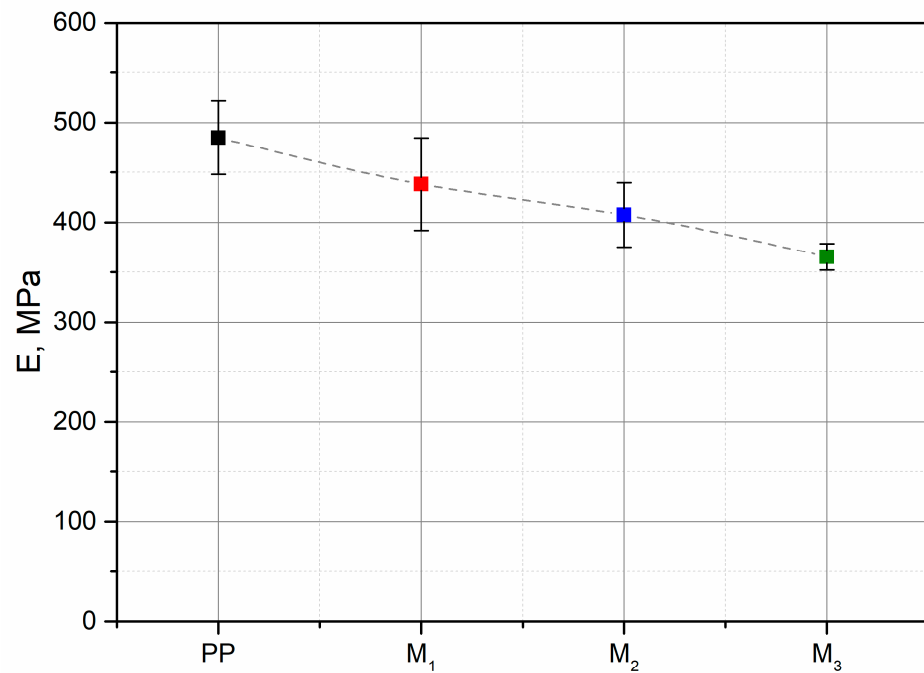

Figure 7. Elastic modulus (E) of the virgin PP sample and of all the monopolymer blends.
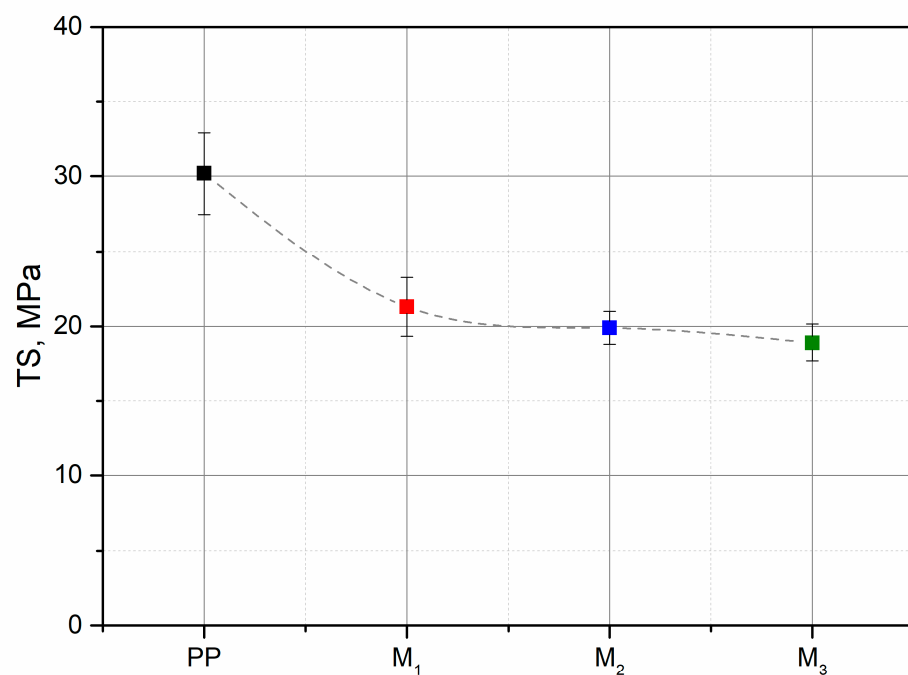

Figure 8. Tensile strength (TS) of the virgin PP sample and of all the monopolymer blends.
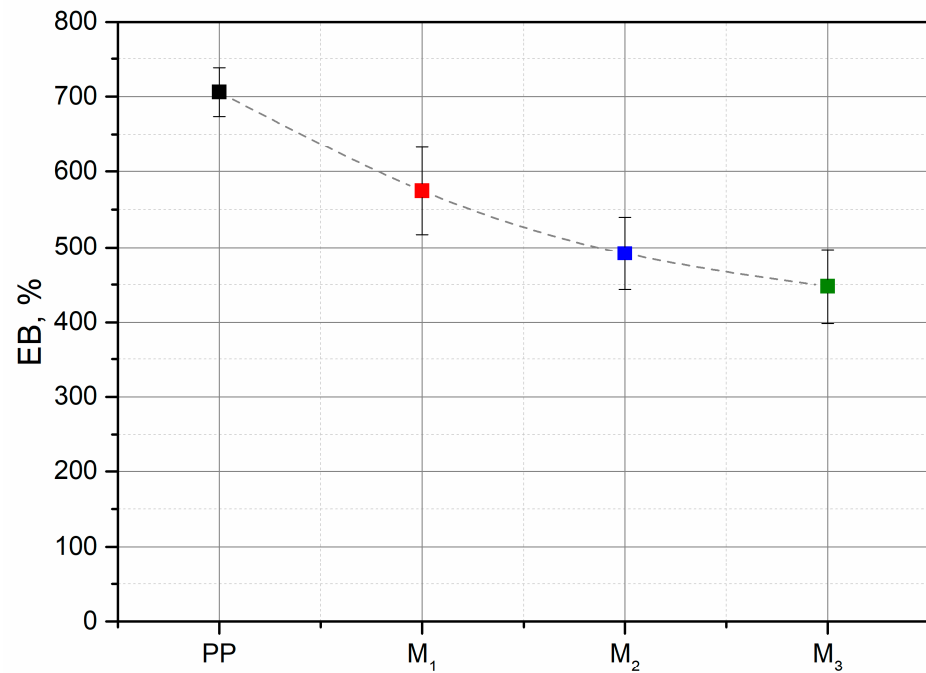
Figure 9. Elongation at break (EB) of the virgin PP sample and of all the monopolymer blends.

It is worth mentioning, however, that, while the results of the ultimate properties were expected, the decrease of the modulus is quite surprising considering that the crystallinity degree of the monopolymer blends is higher than that of the matrix (see Figure 10), due to the increase of the crystallinity degree of the photo-oxidized components.
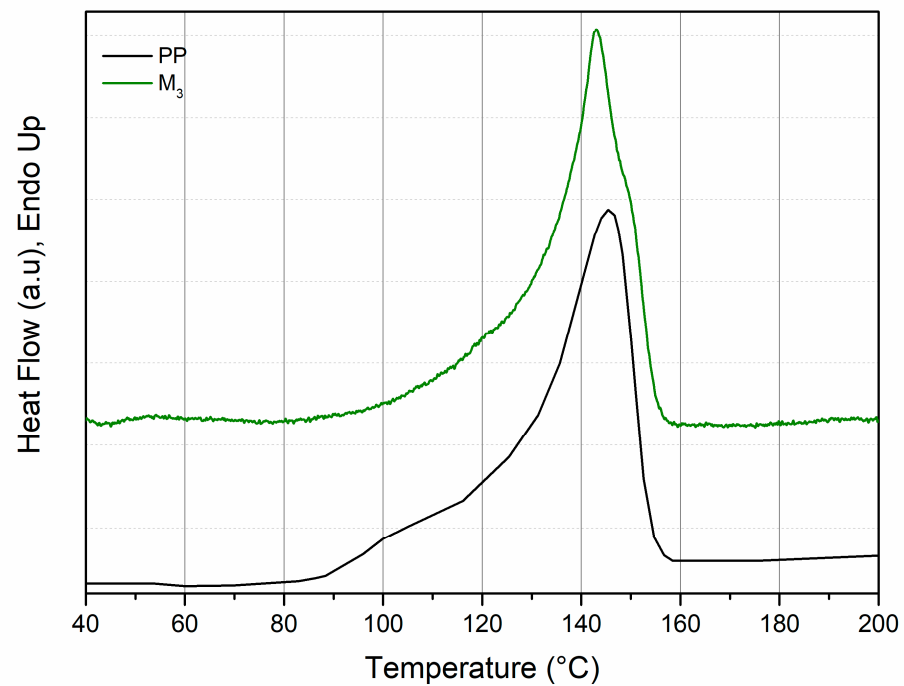

Figure 10. Thermograms of virgin PP and M_3 blend.

This behavior must be then attributed to some new morphological aspect arisen during the preparation of the blend.

3.3. Modeling

As reported above, the composition of the *i*-th sample coming from blending of virgin and photo-oxidized polymer is:

$$M_i = xPP + (1 - x)[xPh_{i-2} + (1 - x)(xPh_{i-1} + (1 - x)Ph_i)] \tag{7}$$

where x is the weight fraction of the virgin polymer and Ph_i is the weight fraction of the polymer photo-oxidized *i* times.

It has been already shown that if $P(M_i)$ is the value of the generic property of a mono-polymer blend having recycled fractions until the *i*-th photo-oxidized polymer, [17]:

$$P(M_i) = xP(PP) + (1 - x)[xP(Ph_{i-2}) + (1 - x)(xP(Ph_{i-1}) + (1 - x)P(Ph_i))] \tag{8}$$

where $P(PP)$ is the property of the virgin sample and $P(Ph_i)$ is the polymer photo-oxidized *i* times.

In the investigated case:

$$P(M_1) = 0.7\, P(PP) + 0.3\, P(Ph_1) \tag{9}$$

$$P(M_2) = 0.7\, P(PP) + 0.21\, P(Ph_1) + 0.09\, P(Ph_2) \tag{10}$$

$$P(M_3) = 0.7\, P(PP) + 0.21\, P(Ph_1) + 0.063\, P(Ph_2) + 0.027\, P(Ph_3) \tag{11}$$

The fitting is certainly not good (see Figures 11–13) and this is certainly due to the fact that the additive model takes into account only moderate change of the molecular weight that does not interfere with the chemical structure and with the morphology of the blends, because the two components are apolar and have the same morphology. On the contrary, the additive model does not take into account the incompatibility between the apolar virgin PP and the polar character of the protoxidized PP arisen because of the formation of oxygenated species and does not take into account that possible complex morphology can arise in these monopolymer blends [4].
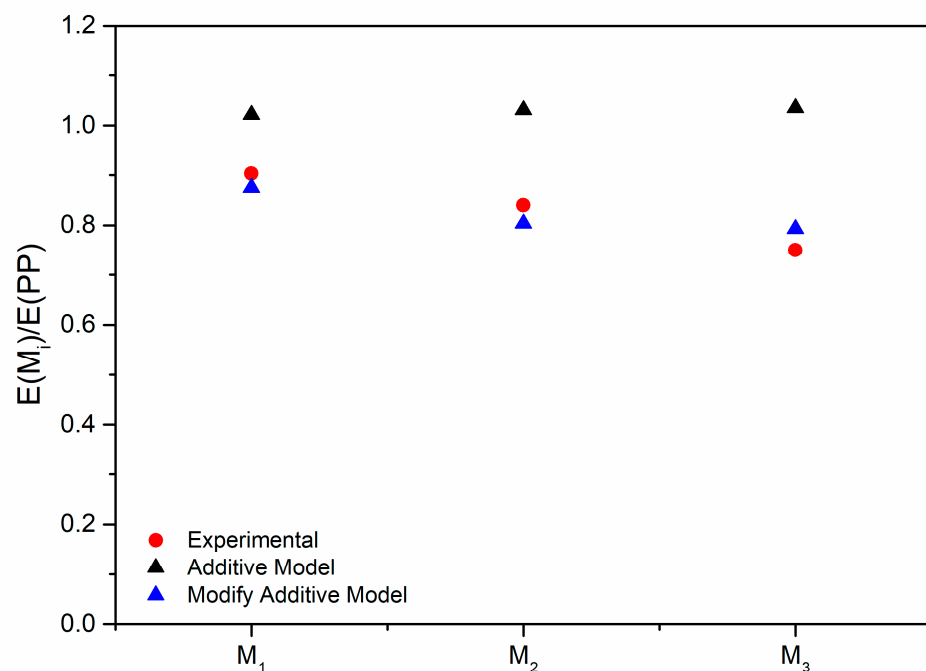

Figure 11. Experimental values of the elastic modulus of blends and theoretical values.
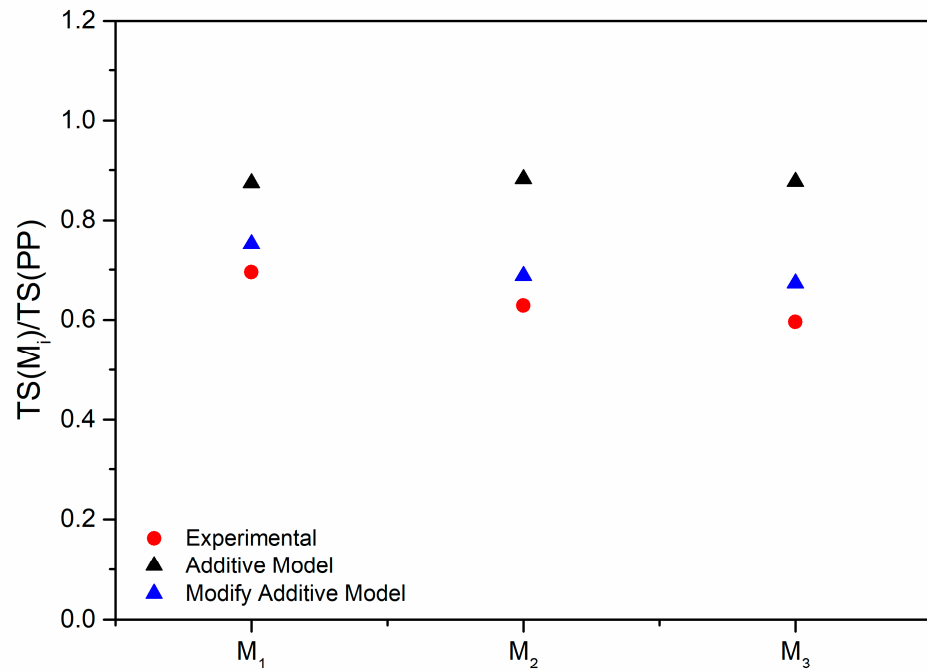
Figure 12. Experimental values of the tensile strength of blends and theoretical values.
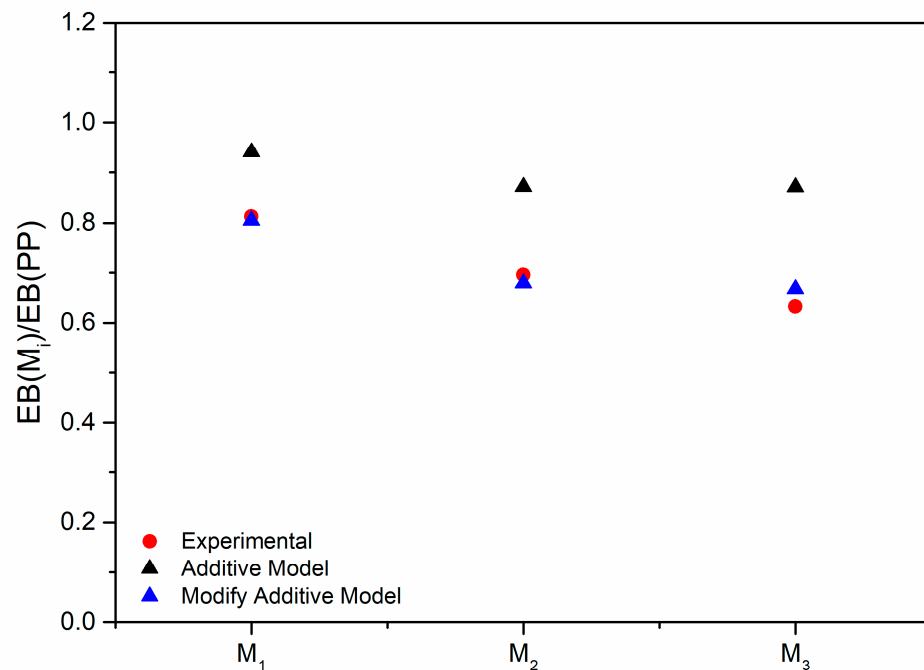

Figure 13. Experimental values of the elongation at break of blends and theoretical values.

The model reported above, then, considers only the effect of the change of the molecular weight on the properties of the monopolymer blends; in order to consider also the effect of the incompatibility and, in general, of the morphology due to the formation of oxygenated species in the photo-oxidized sample, we propose to add a second term depending on the amount of oxygenated species present in the recycled components. This parameter has been chosen because it is indubitably responsible for the incompatibility between the two PP phases. In particular:

$$P(M_1) = (0.7\,P(PP) + 0.3\,P(Ph_1)) \times \frac{k}{(0.7(CO+OH)_{PP} + 0.3(CO+OH)_{Ph_1})_{adim}} \tag{12}$$

$$P(M_2) = (0.7\,P(PP) + 0.21\,P(Ph_1) + 0.09\,P(Ph_2)) \times$$
$$\frac{k}{(0.7(CO+OH)_{PP} + 0.21(CO+OH)_{Ph_1} + 0.09(CO+OH)_{Ph_2})_{adim}} \tag{13}$$

$$P(M_3) = (0.7\,P(PP) + 0.21\,P(Ph_1) + 0.063\,P(Ph_2) + 0.027\,P(Ph_3)) \times$$
$$\frac{k}{(0.7(CO+OH)_{PP} + 0.21(CO+OH)_{Ph_1} + 0.063(CO+OH)_{Ph_2} + 0.027(CO+OH)_{Ph_3})_{adim}} \tag{14}$$

The first term is the same term of the additive model, while the second term depends on the number of total oxygenated groups (carbonyl and hydroxyl) formed during photo-oxidation. These last values are dimensionless by dividing the values at any photo-oxidation time by that of the virgin sample. The value of the constant k can be found by best fitting one of the properties of the blends.

In Figure 14 the theoretical curves of the dimensionless elongation at break and the dimensionless experimental values are reported. The three theoretical curves have been calculated, with three different values of the constant k calculated by best fitting with the curves of the elastic modulus, tensile strength and elongation at break.
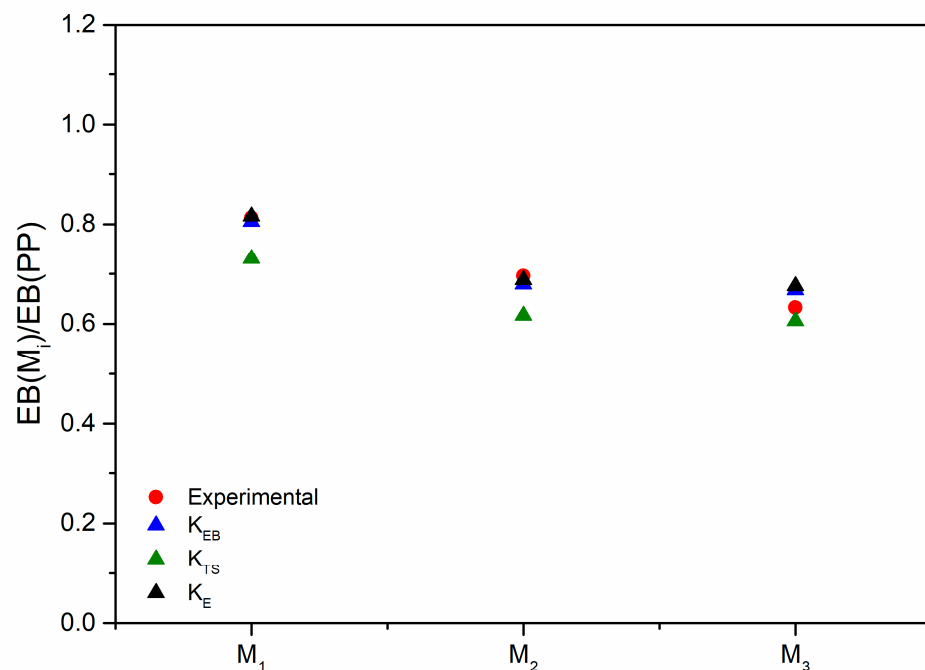

Figure 14. Values of the elongation at break and theoretical values from Equation (14) with the value of the constant found from the elastic modulus, tensile strength and elongation at break curves (Figures 11–13).

Of course, the three values of k are different (k_E is 1.651, k_{TS} is 1.481 and k_{EB} is 1.629) and this is well expected as the dependance of each mechanical property on the incompatibility and morphology is different. However, the differences are relatively low and we have used the value of 1.629, calculated from the elongation at break, in order to calculate the theoretical values for elastic modulus, tensile strength and elongation at break.

The values of the model are reported in Figures 11–13. The agreement is good because the model is able to fit correctly the shape of the curve and, with the value of the constant k known, the values of these three mechanical properties.

4. Conclusions

Monopolymer blends from virgin and recycled components are widely used in the plastic industry. If the recycled component has been subject to a severe degradation with formation of oxygenated groups, the blend becomes incompatible depending on the content and on the level of polar groups grown in the post-consumer component. For this reason, the content of recycled component is relatively low and it is not possible to predict the properties of these blends. In a previous paper [17], we have proposed a simple, additive model to predict rheological and mechanical properties of monopolymer blends where the recycled component was the waste of the processing, with a low level of degradation and without any presence of polar groups. In this work, we have characterized monopolymer blends where the recycled component was a post-consumer polymer severely degraded by photo-oxidation. For this sample the presence of polar, oxygenated groups depends on the time of exposure to UV radiation. The monopolymer blends were, then, composed of virgin, apolar PP and several post-consumer photo-oxidized polypropylene samples different in content and level of degradation.

The previous model was modified considering the presence of the polar groups and has been able to fit well elastic modulus, tensile strength and elongation at break of the blends.

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Conflicts of Interest: The authors declare no conflict of interest.

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