Article

An Additive Model to Predict the Rheological and Mechanical Properties of Polypropylene Blends Made by Virgin and Reprocessed Components

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Abstract: In this work, an additive model for the prediction of the rheological and mechanical properties of monopolymer blends made by virgin and reprocessed components is proposed. A polypropylene sample has been reprocessed more times in an extruder and monopolymer blends have been prepared by simulating an industrial process. The scraps are exposed to regrinding and are melt reprocessed before mixing with the virgin polymer. The reprocessed polymer is, then, subjected to some thermomechanical degradation. Rheological and mechanical experimental data have been compared with the theoretical predictions. The results obtained showed that the values of this simple additive model are a very good fit for the experimental values of both rheological and mechanical properties.

Keywords: monopolymer blends; additive model; polypropylene; reprocessing

1. Introduction

A very popular operation in the plastic industry is to mix virgin polymer with the same reprocessed polymer coming from their scraps. This is so-called primary recycling. The recycled polymer is, of course, not or slightly degraded and the properties of this monopolymer blend are certainly still good [1–15]. However, in general, low amounts of recycled polymer are usually mixed with the virgin polymer because, at least in some cases, increasing its content, the properties of the blend, and in particular the elongation at break, dramatically decay. As these blends are made of the same polymer, the two components are, of course, miscible if the thermomechanical degradation that occurs during the processing and the recycling operations does not significantly change the chemical nature of the recycled polymer, giving rise to the formation of oxygenated groups. In this case, the two components could become incompatible [7].

As said before, the recycled component is usually not degraded or slightly degraded after one recycling step, but, the recycled product of course contains fractions of polymers that were reprocessed more times. These fractions show more pronounced degradation and the final properties of the blend can strongly depend on the lower values of the properties of these fractions that were reprocessed more times.

In our other previous works, the properties of polyethylene [2,11], polypropylene [3,7], polyvinylchloride [5], polyethylenetherephthalate [6], and polyamide [9] monopolymer blends have been reported. In most cases, the rheological and mechanical properties of these blends are in between the properties of the two components when used alone. As said before, in the case of strongly degraded components, one sensible property like the elongation at break occurs with values that are below the values of the two components when each are utilized alone. This has been attributed to the strongly different molecular structure of the degraded component.

More recent studies [12–15] reported results on virgin-recycled ABS blends. Melt flow data indicated that all blends containing recycled material showed higher melt flow index values as compared to virgin polymer.

A study conducted by Bernardo et al. [4] proposed some theoretical models to predict the properties of monopolymer blends of virgin and reprocessed polymers. In this paper, the virgin polymer was mixed with the same polymer after regrinding the scraps of the same polymer following an injection molding operation.

In this work, a simple additive model to predict rheological and mechanical properties of these monopolymer blends is proposed. A polypropylene sample has been reprocessed more times in an extruder and mono-polymer blends have been prepared simulating an industrial process. Then, in contrast to previous works, in this case the scraps are not only reground and blended with the virgin polymer, but are also melt reprocessed before being mixed with the virgin polymer. This means that the reprocessed polymer is subjected to a more severe thermomechanical degradation that can modify the molecular structure of the polymer.

2. Materials and Methods

2.1. Material and Reprocessing

In this work, a polypropylene random copolymer sample, supplied by LyondellBasell (Houston, TX, USA) under the commercial name Hostalen PP H5416, was reprocessed in a single screw extruder (Thermo Scientific HAAKE PolyLab QC, Karlsruhe, Germany) until five successive extrusion cycles were completed. If A is the virgin polymer, then A_1, A_2, and A_i are the polymer reprocessed 1, 2, and i times. In a second step, a fixed fraction of the recycled PP (Polypropylene), 30%, was blended with 70% virgin polymer. In both steps, the temperature profile was set to 180–210–240–270 °C, while the rotational speed of the screw was 60 rpm.

The composition of all the investigated samples, Ri, is reported in Table 1.

Table 1. Composition of the investigated blends.

Sample Code	A	A_1	R_1	R_2	R_3	R_4
R_1	70	30				
R_2	70		30			
R_3	70			30		
R_4	70				30	
R_5	70					30

Of course, after each recycling step, the composition of the blend changed. Indeed, for example, after the second extrusion, the sample R_2 contained a fraction of the polymer that was extruded one time, A_1, and a minor fraction, A_2, was extruded two times. The composition of all the above blends can be depicted as in Figure 1.
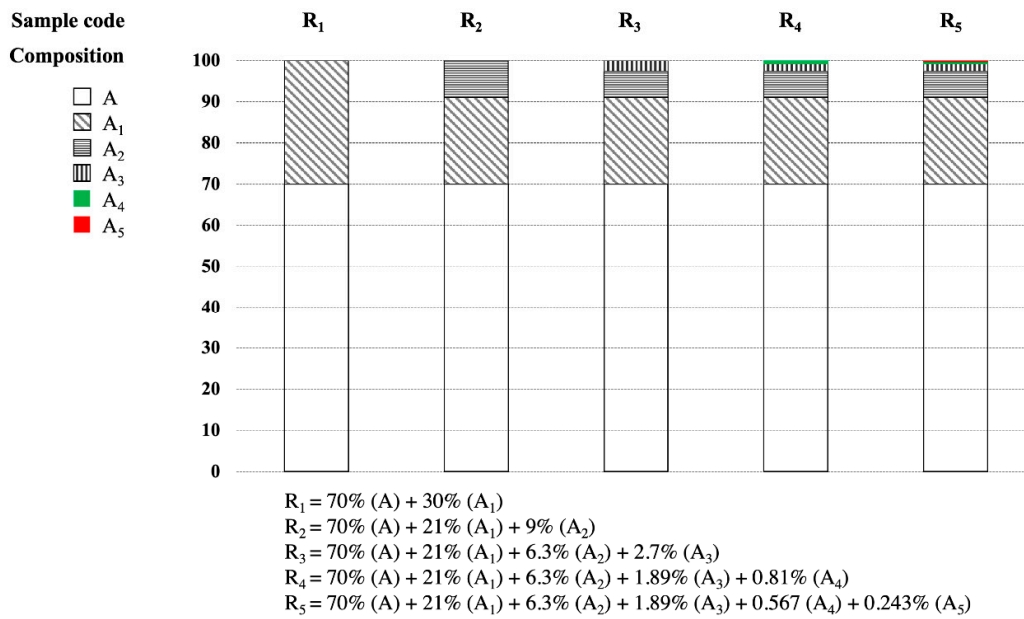
$R_1 = 70\% \ (A) + 30\% \ (A_1)$
$R_2 = 70\% \ (A) + 21\% \ (A_1) + 9\% \ (A_2)$
$R_3 = 70\% \ (A) + 21\% \ (A_1) + 6.3\% \ (A_2) + 2.7\% \ (A_3)$
$R_4 = 70\% \ (A) + 21\% \ (A_1) + 6.3\% \ (A_2) + 1.89\% \ (A_3) + 0.81\% \ (A_4)$
$R_5 = 70\% \ (A) + 21\% \ (A_1) + 6.3\% \ (A_2) + 1.89\% \ (A_3) + 0.567 \ (A_4) + 0.243\% \ (A_5)$

Figure 1. Composition of all the blends investigated.

2.2. Rheological, Mechanical and Structural Characterization

The rheological characterization was performed on disk-shaped samples, using an ARES G2 (TA Instruments, New Castle, DE, USA). The experiments were carried out in parallel plates with a gap of about 1.5 mm and a diameter of 25 mm. The shear viscosity values of the samples were measured at 210 °C from 100 to 0.1 rad/s.

Tensile properties tests were carried out using in an Instron (Instron, High Wycombe, UK) universal testing machine (mod. 3365) according to ASTM D638. The cross-head movement speed were of 1 mm/min up to 3 min; subsequently, the crosshead speed was increased to 100 mm/min until specimen failure occurred.

An 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.

Attenuated total reflection spectra were collected using a Perkin-Elmer FT-IR spectrometer (Perkin-Elmer, Norwalk, CT, USA) equipped with a single-reflection diamond ATR (Perkin-Elmer, Norwalk, CT, USA)

Spectra were collected in the range 4000–400 cm^{-1}, with an optical resolution of 4 cm^{-1}; the registered spectrum was the mean of 16 scans, and was executed in 3 min.

Thermal properties of the materials were evaluated by differential scanning calorimetry (DSC). DSC measurements were performed by a DSC-131 Setaram (Setaram, Hillsborough Township, NJ, USA), under a nitrogen gas atmosphere, using 10 ± 2 mg of sample and a 10 °C/min heating rate up to 210 °C/min.

2.3. The Additive Model

The composition of the sample coming from blending virgin and recycled polymer is:

$$R_1 = xA + (1 - x)A_1 \tag{1}$$

$$R_2 = xA + (1 - x)[xA_1 + (1 - x)A_2] \tag{2}$$

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

$$Ri = xA + (1 - x)[xAi{-}2 + (1 - x)(xAi{-}1 + (1 - x)Ai)] \tag{3}$$

where x is the weight fraction of the virgin polymer and A_i is the polymer extruded i times.

It was simply assumed that in this case where no dramatic change of the chemical nature and of the morphology occurred during reprocessing, all the properties of the recycled blends changed the same way for the composition considering that, due to having the same chemical nature, the two components were miscible and the additive rule could be applied to these samples. If $P(R_i)$ is the value of the generic property of a mono-polymer blend having recycled fractions until the i-th extruded polymer, then:

$$P(R_i) = xP(A) + (1 - x)[xP(A_{i-2})+(1 - x)(xP(A_{i-1}) + (1 - x)P(A_i))] \tag{4}$$

where $P(A)$ is the property of the virgin sample and $P(A_i)$ is the polymer extruded i times.

3. Results and Discussion

3.1. Characterization of the Recycled PP

The flow curves of some reprocessed samples are reported in Figure 2. For the sake of simplicity, only the flow curves of the virgin sample and of the samples reprocessed 1, 3, and 5 times are reported.
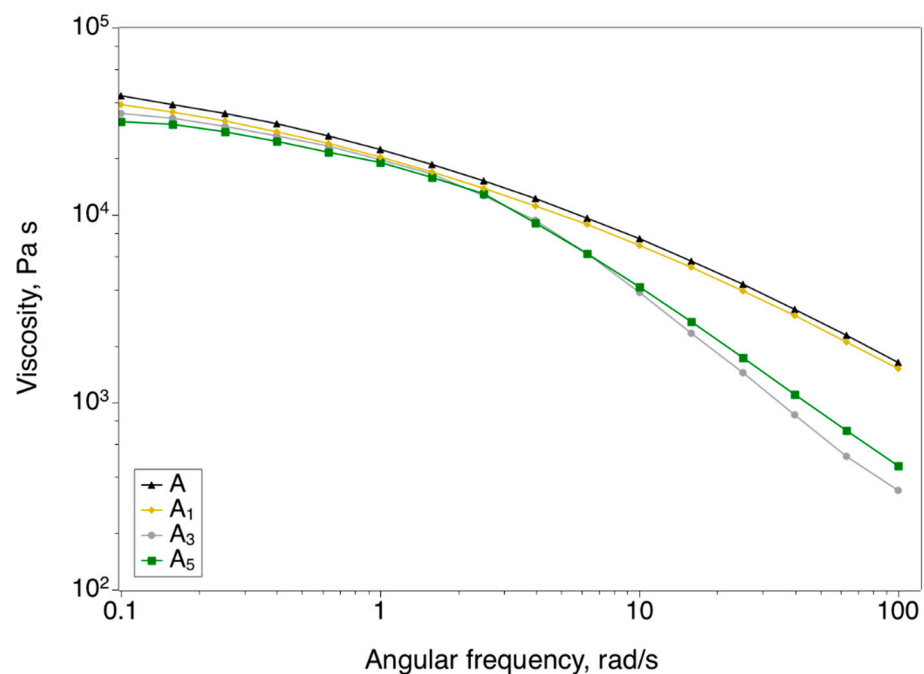

Figure 2. Flow curves of the virgin PP sample and of the samples reprocessed 3 and 5 times.

As expected, the Newtonian viscosity decreases upon increasing the reprocessing steps and the non-Newtonian behavior becomes less pronounced.

The Newtonian viscosity is a strong function of the molecular weight

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

and then, the molecular weight of the sample extruded i times can be calculated as:

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

Because the value of Newtonian Viscosity of A is 43,177 Pa·s and A_5 is 21,091 Pa·s, this means that the decrease of the molecular weight after 5 reprocessing steps is about 19%.

The less pronounced non-Newtonian behavior, which is highly evident from the lower slope of the flow curves observed upon increasing the reprocessing steps, is also a consequence of the reduction of the molecular weight.

Attenuated total reflection spectroscopy was used to identify possible functional groups formed during the processing steps because of the possible thermo-oxidative degradation. Figure 3 reports FTIR spectra of the virgin PP sample and of the sample reprocessed 5 times.
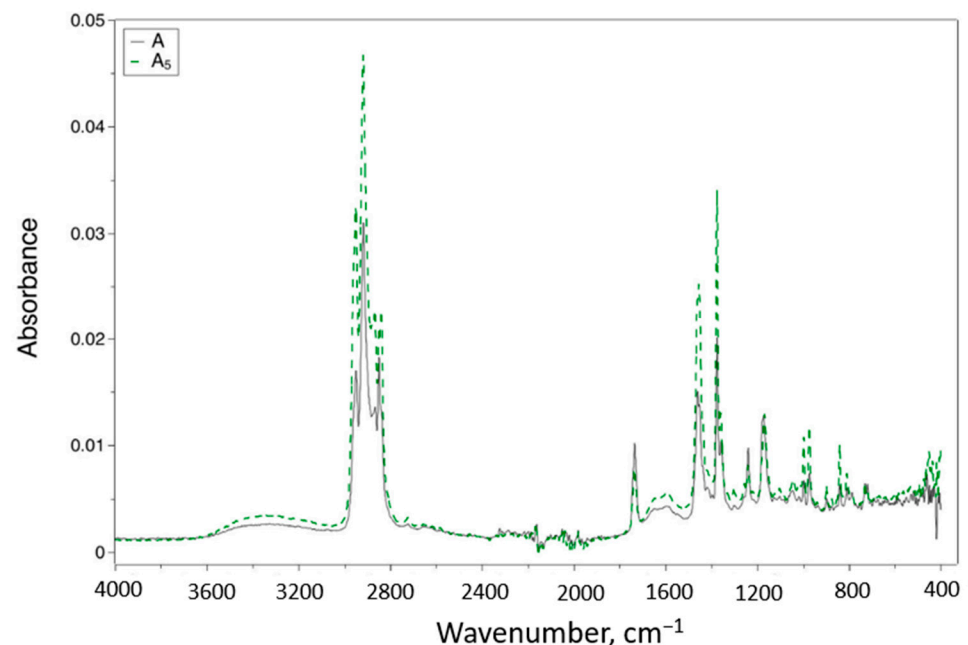

Figure 3. ATR spectra of the virgin PP sample and sample reprocessed 5 times.

As is seen from Figure 3, no significant change was observed in the two spectra in the carbonyl (1710–1780 cm^{-1}) and hydroxyl groups (around 3400 cm^{-1}) wavelength range. This means that the thermomechanical degradation at this stage does not produce any formation of oxygenated groups and the virgin and reprocessed PP have the same chemical nature. This result is important because the presence of oxygenated groups could yield two components that are incompatible with each other.

The effect of extrusion cycles and reprocessing on thermal properties of PP are shown in Figure 4.

For the samples, A and A_5, no significant variation in their thermal behavior was observed. The two samples show the same crystalline morphology and nearly the same value for melting temperatures. The crystallinity degree was slightly higher for the sample that was reprocessed 5 times (32.4% against 31.7%) and this was due to the decrease of the molecular weight. The same observations can be made for the recycled sample R_5. These results are important because the change of crystalline morphology has been considered to be responsible [7] for the strongly incompatible behavior shown by similar monopolymer blends where the recycled component was dramatically degraded.

Finally, Figure 5 reports the values of the elastic modulus (E), tensile strength (TS), and elongation at break (EB), for the reprocessed samples and for the virgin sample.

Tensile strength and elongation at break decrease upon increasing the number of reprocessing steps due to the decrease of the molecular weight. In contrast, the value of the elastic modulus was almost constant after a small initial decrease as a result of the reprocessing steps. This behavior and also an increase of the elastic modulus has already been observed for semicrystalline polymers and was attributed [7] to the effect of two different mechanisms. The elastic modulus decreases as a consequence of the reduction of the molecular weight but increases due to the slight rise of the crystallinity degree because of the decrease of the molecular weight.
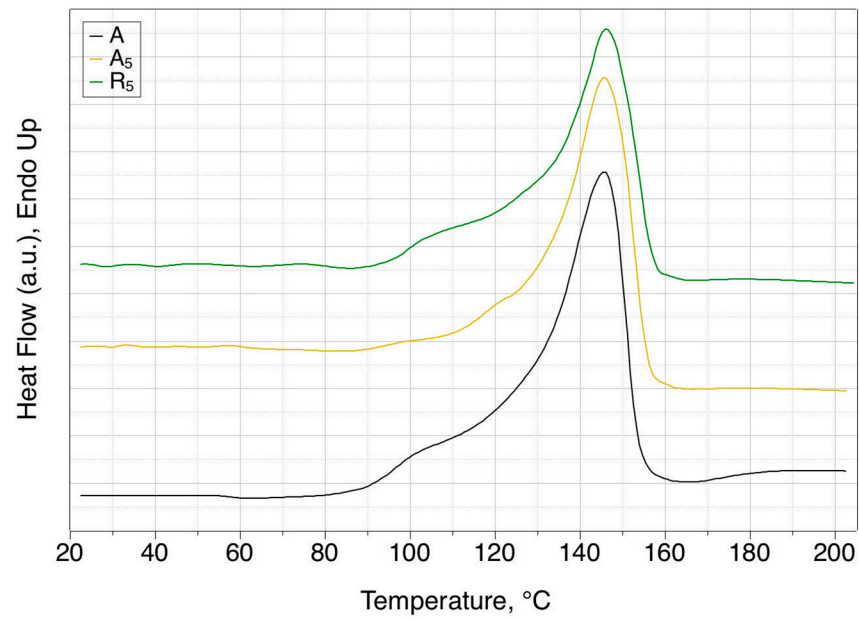
Figure 4. Thermograms of the virgin sample, retracted samples, and their blends.
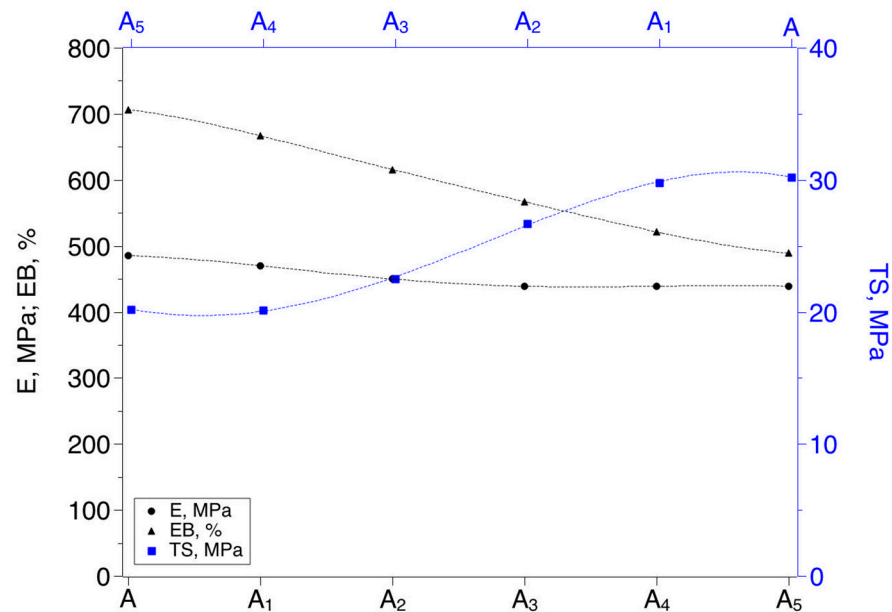

Figure 5. Elastic modulus (E), tensile strength (TS), and elongation at break (EB) of the virgin PP sample and of all the reprocessed samples.

3.2. Characterization or the Monopolymer Blends

In Figure 6 the flow curves of the samples R_1, R_3, and R_5 (see Table 1) are reported. The Newtonian viscosity and the non-Newtonian behavior are reduced upon increasing the amount of reprocessed material and upon increasing the number of reprocessing steps present in the monopolymer blend. This is, of course due to the reduced molecular weight and then due to the reduced viscosity of the reprocessed components present in the blend. Of course, the lower non-Newtonian behavior of the monopolymer blends with a higher content of polymer that was reprocessed more times gives rise to viscosities that become more different after increasing the shear rate.
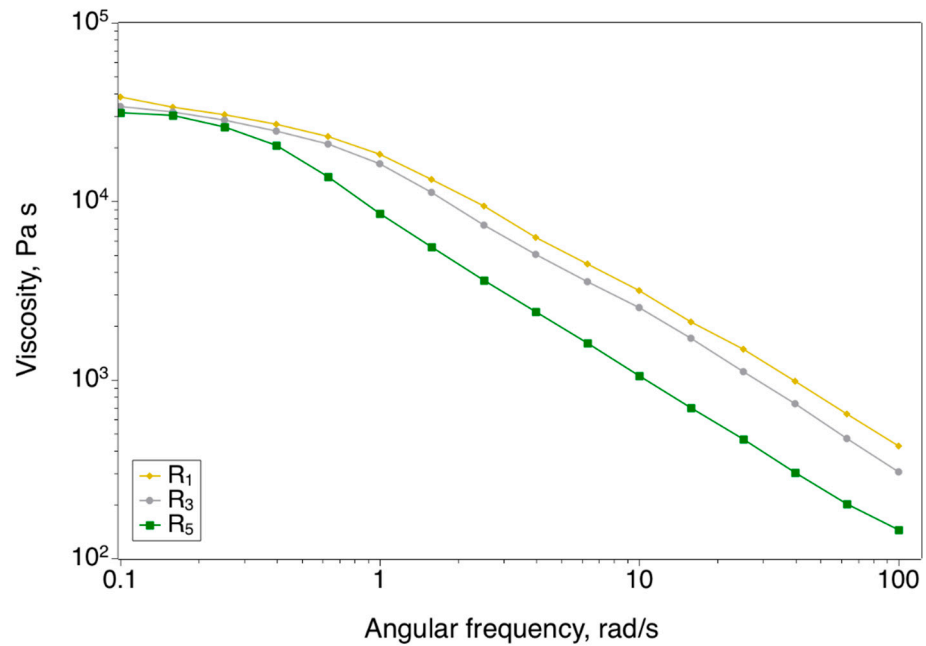
Figure 6. Flow curves of the blends reprocessed 1, 3, and 5 times.

In Figure 7, elastic modulus, tensile strength, and elongation at break of the same samples is reported. The modulus decreases slowly and then remains almost constant. More specifically, the overall reduction of the elastic modulus from the 1st to the 5th cycle was approximately 12%. This behavior of the monopolymer blends therefore reflects the behavior of the elastic modulus of the reprocessed polymer. The tensile strength decreases upon increasing the amount of reprocessed material and upon increasing the number of reprocessing steps present in the monopolymer blend. The decrease with respect to pure PP was about 4% during the first reprocessing, with an almost linear variation on the increasing content and reprocessing steps of the reprocessed component.
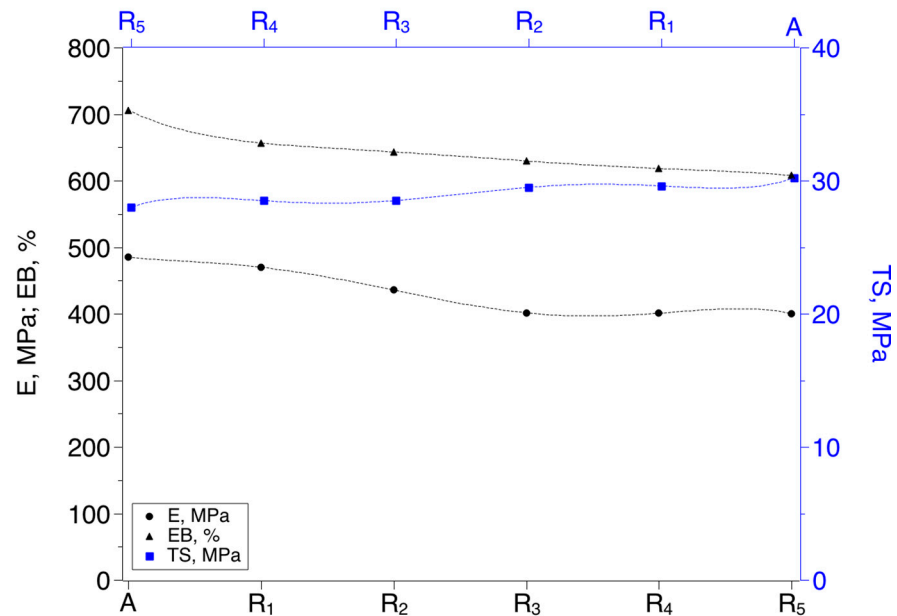

Figure 7. Elastic modulus (E), tensile strength (TS), and elongation at break (EB) of the blends that were reprocessed.

The elongation at break shows the same feature of the tensile strength. It decreases upon increasing the amount and the number of reprocessing steps of the reprocessed component in the monopolymer blend.

3.3. Comparison with the Additive Model

According to the above proposed model, if x = 30%, then the generic property of the blend can be calculated as:

$$P(R_1) = 0.7\,P(A) + 0.3\,P(A_1) \tag{7}$$

$$P(R_2) = 0.7\,P(A) + 0.21\,P(A_1) + 0.09\,P(A_2) \tag{8}$$

$$P(R_3) = 0.7\,P(A) + 0.21\,P(A_1) + 0.063\,P(A_2) + 0.027\,P(A_3) \tag{9}$$

$$P(R_4) = 0.7\,P(A) + 0.21\,P(A_1) + 0.063\,P(A_2) + 0.0189\,P(A_3) + 0.0081\,P(A_4) \tag{10}$$

$$P(R_5) = 0.7\,P(A) + 0.21\,P(A_1) + 0.063\,P(A_2) + 0.0189\,P(A_3) + 0.00567\,P(A_4) + 0.00243\,P(A_5). \tag{11}$$

However, as correctly observed by Bernardo et al. [4], certain properties can only be measured after completing the process used to produce test pieces. As a result, A cannot be determined a priori. For this reason, in this case, it was assumed that A coincides with A_1.

The evaluated Newtonian viscosity that formed the plateau region of the flow curves of Figure 5 is reported in Table 2.

Table 2. Newtonian viscosity values of the blends reprocessed 1, 3, and 5 times.

	R_1	R_3	R_5
Newtonian Viscosity, η_0 (Pa·s)	38,279	33,846	31,403

In Figure 8, the dimensionless values of the Newtonian viscosity of the monopolymer blends are reported together with the values calculated from the previous equations.
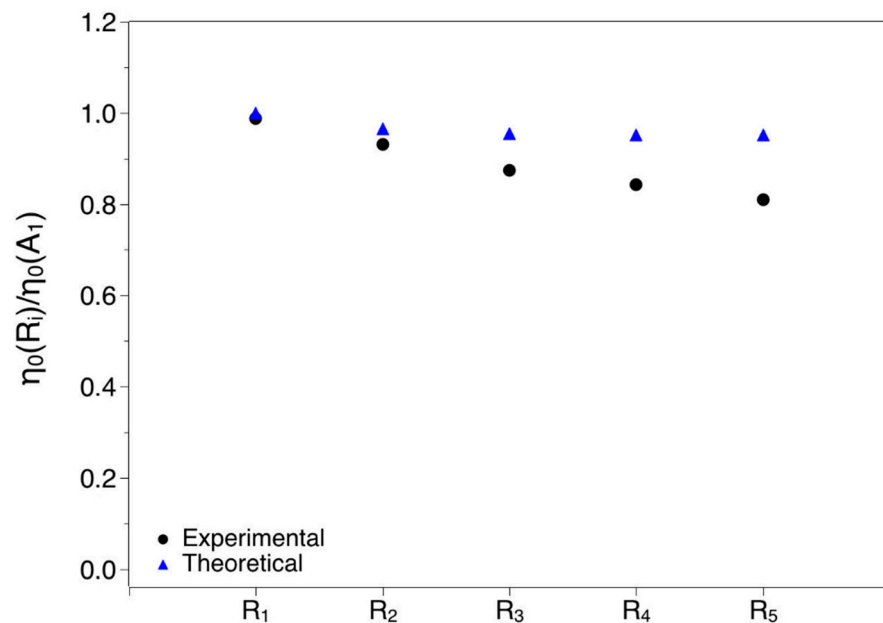

Figure 8. Experimental values of the Newtonian viscosity of the blends and values calculated from previous equations.

The dimensionless values have been calculated by dividing the values of the Newtonian viscosity of the monopolymer blends by the value of the Newtonian viscosity of

the PP sample extruded one time (A_1). It can be observed that the values of the theoretical result are close to the experimental values. The maximum difference is about 17% for the R_5 sample.

In the Figures 9–11, the values of the dimensionless values of the elastic modulus, of the tensile strength, and of the elongation at break of the monopolymer blends are reported together with the theoretical values calculated from the previous equations. Also, for the mechanical properties, the dimensionless values have been calculated by dividing the values of the mechanical property of the monopolymer blends by the value of the same property of the PP sample extruded one time (A_1).
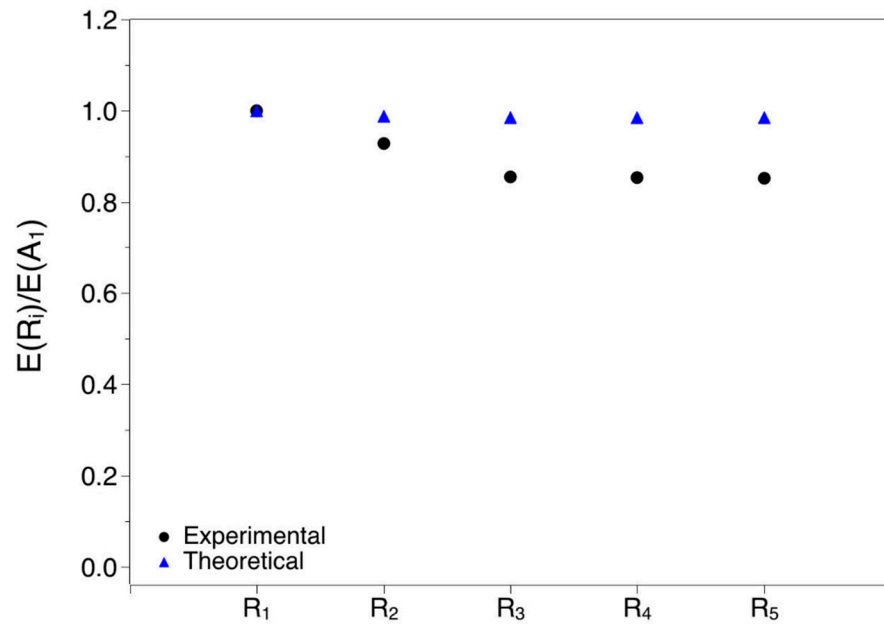

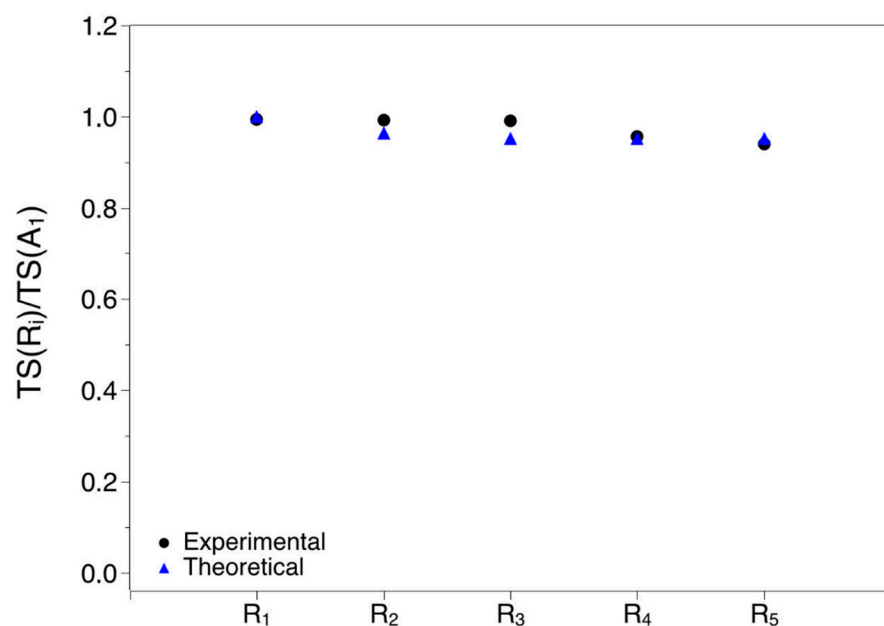**Figure 9.** Experimental values of the elastic modulus of the blends and values calculated from previous equations.

Figure 10. Experimental values of the tensile strength of the blends and values calculated from previous equations.
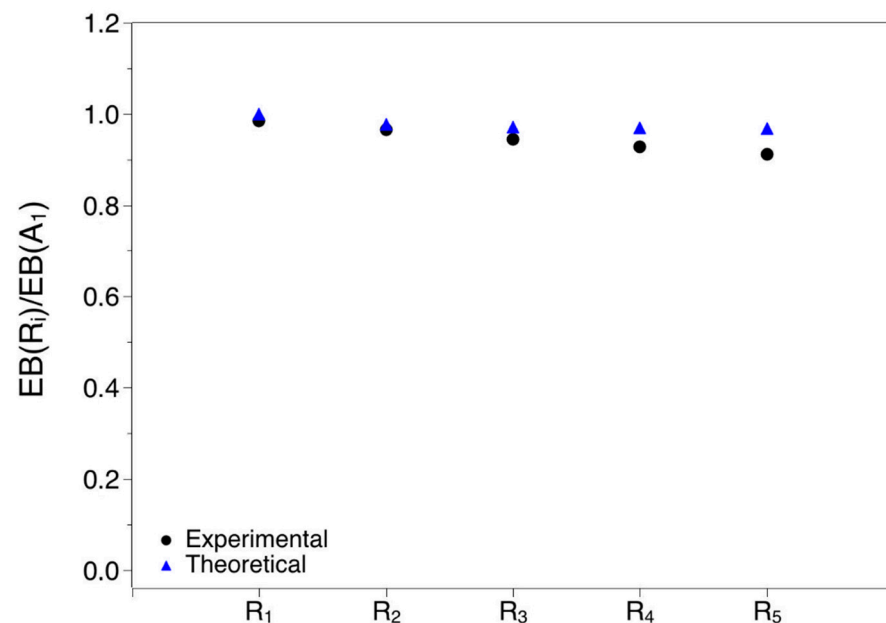
Figure 11. Experimental values of the elongation at break of the blends and values calculated from previous equations.

For the elastic modulus, as seen in Figure 9, the comparison with the experimental values is quite good, as the maximum discrepancy is about 15%. Moreover, the shape of the theoretical curve is very similar to that of the experimental curve, as the initial decrease is followed by a sort of plateau.

As for the tensile strength, as seen in Figure 10, it can be observed that the values of the theoretical result are very similar to the experimental values. The maximum difference is only about 1.5% for the R_5 sample.

Finally, as for the elongation at break, as seen in Figure 11, the values of the theoretical results are again very similar to the experimental values. The maximum difference is about 6% for the R_5 sample.

This simple additive mode, then, is able to quite effectively predict the values of the rheological and mechanical properties of these monopolymer blends, provided that the chemical nature and the morphology of the reprocessed components does not change significantly.

It is worth mentioning, however, that an additive model is, in general, based on the miscibility of the two components. For a polymers couple, this means that the virgin and the reprocessed materials should have the same chemical and molecular structure and then no severe degradation phenomena should have occurred. Indeed, a severe thermomechanical degradation could lead to the formation of polar oxygenated groups that yield two immiscible and incompatible components. Moreover, a strong decrease of the molecular weight could give rise to a different crystallization behavior and a consequent incompatibility in the solid state [7].

4. Conclusions

The typical industrial operation of mixing virgin polymer with the same polymer reprocessed more times implies that the final product is made from decreasing the amount of polymer which has been subjected to many reprocessing steps. This reprocessing which is carried out through a regrinding and an extrusion step can modify the molecular structure of the polymer because of the thermomechanical stress acting on the molten polymer. In order to evaluate the change of the rheological and mechanical properties with the amount and with the reprocessing steps of the recycled component, a simple additive rule is proposed. The values of Newtonian viscosity and tensile properties fit

the experimental values very well. However, this additive model can only be used if the compatibility between virgin and reprocessed material is preserved in order to avoid the risk that the presence of oxygenated groups or of groups of a different morphology give rise to an incompatible blend.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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