MONOFILAMENTS PRODUCED BY BLENDING VIRGIN WITH RECYCLED POLYPROPYLENE

HAM VE GERİ DÖNÜŞÜM POLİPROPİLEN POLİMERLERİİNİN KARIŞIMINDAN ELDE EDİLEN MONOFİLAMENTLER

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ABSTRACT

Our research addresses the use of 100% recycled polypropylene from separately collected packaging waste in Slovenia for the manufacture of monofilaments. The goal of this research was to optimise the melt spinning of monofilaments and to compare the properties of monofilaments obtained from the virgin polymer and from blends of virgin and recycled polymer. Monofilaments were spun from the pure virgin polymer, from a blend of 85% virgin and 15% recycled polymer, and from 50% virgin and 50% recycled polymer. It was established that the addition of the recycled polymer to the virgin polymer lowered the crystallinity and average molecular orientation of as-spun monofilaments, which influenced the tensile properties of the monofilaments. Because of the poor miscibility of the virgin with the recycled polypropylene, which also contained some fractions of polyethylene, the as-spun monofilaments were porous, brittle and rigid, and had a high tendency to break.

Key Words: Polypropylene, Recycled polymer, Melt spinning, Tensile properties, Monofilament.

ÖZET

Çalışmadada, Slovenya’da toplanan ambalaj teleflerinden elde edilen %100 geri dönüşüm polipropilen liflerinin kullanım ele alınmaktadır. Bu araştırmamızın amacı, eriyikten monofilament lif çekiminin optimizasyonu ve ham, geri dönüşüm polipropilen polimeri ve bunların karışılıklarından üretilen liflerin özelliklerinin karşılaştırılmasıdır. Monofilamentler; %100 ham polimer, %85 ham -%15 geri dönüşüm polimeri ve %50 ham -%50 geri dönüşüm polimerlerinden üretilmiştir. Ham polimer içerisinde geri kazan polimerin eklenmesinin kristaliteyi ve monofilamentlerin mukavemetlerini de etkileyen ortalamalı moleküler orantısını düşürdüğü bilinmektedir. Bir miktar pórolitên parçaları da içeren geri dönüşüm polimerinin, ham polimer ile karıştırlığının düşük olması sebebiyle karışım polimerinden elde edilen liflerin gözenekli, kolay kırtır ve sert olduğu, düşük kopma mukavemeti gösterdiği görülmektedir.

Anahtar Kelimeler: Polipropilen, Geri dönüşüm polimer, Eriyikten lif çekimi, Mukavemet özelliklerini, Monofilament.

1. INTRODUCTION

Reducing waste is an important issue for modern society. Each year, about 100 million tonnes of waste from households, commerce and industry are generated. Products, especially packaging, should be re-used or their materials recycled. The most represented polymers that are used in the manufacture of packaging and can be recycled are low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), poly(vinyl chloride) (PVC), poly(ethylene terephthalate) (PET) and polystyrene (PS) (1).

Post-consumer residuals are a mixture of different plastic resins generally contaminated with dirt or other residues, and recycling such residues is much more difficult than recycling pre-consumer plastic (2). Because the use of poly(vinyl chloride) for packaging is restricted and poly(ethylene terephthalate) bottles are separated from municipal plastic waste, the most important components of mixed post-consumer plastics designated for material recycling are various grades of polyethylene, isotactic polypropylene and styrenic plastics (3). However, the recycling of municipal plastic waste is often an arduous task due to the fact that this material is a mixture of several polymers, which makes processing more difficult and also limits the number of potential applications (4). Some studies have demonstrated that the recycling of post-consumer residuals in products of good quality is viable (5-8).

Our research studies the use of 100% recycled polypropylene from separately collected packaging waste in Slovenia for manufacturing monofilaments. The goal of our research was to optimise the melt spinning of monofilaments from recycled polypropylene polymer and to compare the properties of monofilaments obtained from virgin and recycled polymer. Some of the
results obtained for the as-spun and drawn monofilaments have already been presented (9). In this paper, some properties of as-spun monofilaments obtained from the virgin polypropylene and from the blend of virgin and recycled polypropylene are presented.

2. MATERIALS AND METHODS

Commercial Dow polypropylene chips (DOW H105), a plastic grade homopolymer, with MFR = 3.2 g/10 min, and recycled polypropylene, with MFR = 2.9 g/10 min, were used. The melt flow rate (MFR) was determined as the amount of polymer extruded at a temperature of 230°C with a forcing load of 2160 g in 10 min. By blending the virgin polymer with 50 and 15 percent of the recycled polymer by weight, two polymer blends were prepared. From the virgin polymer and polymer blends monofilaments were produced by melt spinning on an Extrusion Systems Ltd. laboratory spin-draw device. The monofilaments were extruded through a spinneret with a hole of a diameter 0.6 mm. The spinning temperature of 260°C and the mass outflow of 2.54 and 2.66 g/min were adjusted so that a continuous steady spinning could be carried out. The polymer jet was cooled in air as it emerged from the spinneret and was collected on a bobbin.

The tensile properties of the as-spun monofilaments were measured with an Instron 5567 tensile testing machine. During the sample stretching several load and elongation data per second were recorded until breakage of the sample occurred. The average molecular orientation and dynamic modulus were obtained by the sonic-velocity method. The velocity of sound waves in the monofilaments was measured on a Morgan’s Dynamic Modulus Tester PPM-5R. The melting behaviour of the samples was examined by visual sample inspection with the Mettler FP84HT Hot Stage thermal measuring cell and with a Perkin-Elmer DSC calorimeter in the temperature range from -10°C to 200°C at a constant heating rate of 10°C/min. The density of the drawn fibres was determined with the flotation method as described by Julfs, using a mixture of isopropanol alcohol and water. The morphological studies involved scanning electron microscopy of the monofilament surface and its cross-section. A JEOL SEM-6060LV electron microscope was used for morphological studies. The chemical composition of the monofilament surface was determined with the ATR-FTIR technique on a FTIR spectrometer PerkinElmer SpectrumGX.

3. RESULTS AND DISCUSSION

3.1 Spinnability and linear density of monofilaments

Polypropylene melts are highly viscous fluids. High molecular weight polymers, also called moulding grade polymers, have poor spinnability, and they are inconvenient for conventional melt spinning. For these polymers the spinning can be adjusted by raising the temperature of the melt. In our case, the temperature where the spinning of polymers could be performed was between 260°C and 290°C. The temperature of spinning was limited to the lower temperature range because of the brittle fracture of the extruded polymer jet and because of the polymer degradation and capillary break of the polymer jet in the higher temperature range. Because it is also convenient to keep the melt temperature as low as possible to avoid the thermal degradation of the polypropylene macromolecules and the drop of pressure, the temperature chosen for spinning was 260°C. Some spin-line instabilities were observed at this temperature, too, especially for the monofilament composed of 50% virgin and 50% recycled polymer. Instabilities resulted in the variation in thickness of the extruded jet and consequently in the unevenness of the linear density of monofilaments, as seen in figures 1a, 2a and 3a. The variation coefficient of the linear density was between 12 and 22 %, the higher being for monofilaments spun from blends (Table 1).

3.2 Surface properties of monofilaments

![Figure 1](image1.png)

Figure 1. SEM micrographs of monofilaments spun from 100% virgin polymer: (a.) 50x magnification, (b.) 400x magnification and (c.) 1500x magnification

![Figure 2](image2.png)

Figure 2. SEM micrographs of monofilaments spun from the 85% virgin/15% recycled polymer blend: (a.) 50x magnification, (b.) 400x magnification and (c.) 1500x magnification
Electron microscopy was used to examine in some detail the morphological structure of as-spun monofilaments. As seen from Figure 1, the surface of monofilament spun from 100% virgin polymer is uniform and even but not entirely smooth and at higher magnifications some surface features are seen (Figures 1b, 1c). Monofilaments spun from the blends have less uniform morphological structure. At the monofilament spun from the 85% virgin and 15% recycled polymer a longitudinally striation (in the direction of fibre axes) is seen (Figure 2a), and it seems that the monofilament is not completely circular in the cross-section. The most uneven surface, with many holes elongated in the direction of the fibre axis, is seen for the monofilament spun from 50% virgin and 50% recycled polymer (Figure 3a) and it looks as a coating layer on a fibre surface. At higher magnifications the surface of monofilaments spun from the blends is not as coarse as at monofilaments spun from the 100% virgin polymer. The surface features in the shape of rounded polygons are still seen, but as they are smaller and the grain boundaries between them are not so pronounced the surface is smoother (Figures 2b, 2c and 3b, 3c). Investigation of the surface by electron microscopy revealed the presence of spherulitic structure. The presence of spherulites was established with the polarisation microscopy examination as well. In Figure 4 the diameter of spherulites determined from SEM micrographs is shown. Spherulites formed are large and randomly distributed on the surface and have distinct boundaries. Much larger spherulites, with an average diameter of 24.7 μm, are present at the monofilament spun from the pure virgin polymer. The average diameter at monofilament spun from 85% virgin and 15% recycled polymer is 5.7 μm, and for the monofilament spun from 50% virgin and 50% recycled polymer, the average diameter is 5.25 μm. With the decrease in size of spherulites the coarseness of the filament surface has also decreased. According to Broda (10), the greatest spherulites are formed in gravity spun fibres, as the crystallisation proceeds at the lowest cooling rate and lowest orientation,
resulting in low nucleation density, and thus the spherulites have a great amount of space available to grow. Spherulites in monofilaments spun from the blend are much smaller. The smaller size of spherulites could be the consequence of impurities present in the recycled polymer. The impurities act as nucleating agents (a core) and increase the nucleation density, resulting in a higher number of spherulites formed and their smaller sizes.

It also seems that a skin/core structure is formed, with the recycled polymer mainly on the outside of the monofilament and the virgin polymer forming the core of the monofilament. The recycled polymer has dark grey colour, and the filament spun from the blend of 50% virgin and 50% recycled polymer has the same dark grey colour, whereas the monofilament spun from the blend of 85% virgin and 15% recycled polymer has light grey colour. On the other hand, the virgin polymer and the monofilament spun from the pure virgin polymer are white. By drawing the monofilaments spun from the blends, the skin stays unstretched, whereas the core is deformed (Figure 5). The deformation of the monofilament spun from the blend of 85% virgin and 15% recycled polymer is higher for monofilaments spun from the pure virgin polymer, whereas dynamic elastic modulus is determined as a ratio of the specific stress versus the strain, which is what is usually obtained. The elastic modulus is, beside the tensile strength, one of the most important properties of technical fibres. The static elastic modulus is determined as a product of the velocity of sound waves and the density of monofilaments. As-spun monofilaments have low values of moduli. The static elastic modulus is higher for monofilaments spun from the blends, whereas dynamic elastic modulus is higher for the monofilament spun from the virgin polypropylene.

### 3.3 Tensile properties of monofilaments

In Table 1 the linear density and tensile properties of monofilaments, spun from a virgin polypropylene and from blends of virgin and recycled polypropylene, are presented.

When blending virgin with recycled polypropylene, the lowering of force needed to break a sample was noted. Higher linear density and lower breaking load resulted in the lower tensile strength of monofilaments spun from the blends. With the addition of recycled polymer, the monofilaments became extremely brittle; then extension at break decreased from over 100% to less than 10% and the work of rupture from 8 J to 31 mJ and 7.5 mJ. Figure 6 clearly shows that monofilaments spun from the blends break at point, where for the monofilament spun from the pure virgin polymer not even a yield point is reached. The curves presented in Figure 6 are not smoothed. As the scattered of recorded data between single measurements is quite high, the variation coefficient being over 20%, the average curve constructed from twenty measured single curves deviates from a straight line, which is what is usually obtained. The elastic modulus is, beside the tensile strength, one of the most important properties of technical fibres. The static elastic modulus is determined as a product of the velocity of sound waves and the density of monofilaments. As-spun monofilaments have low values of moduli. The static elastic modulus is higher for monofilaments spun from the blends, whereas dynamic elastic modulus is higher for the monofilament spun from the virgin polypropylene.

### 3.4 Structural characteristics of monofilaments

In Table 2 some structural characteristics of monofilaments are presented. For all samples, a very low average molecular orientation was determined, the highest being for the monofilament spun from the pure virgin polymer, which decreased with the addition of recycled polymer to the blend (Table 2). The birefringence of monofilaments is also low, being higher for the monofilament spun from the pure virgin polymer and lower for the monofilaments spun from the blends. For the monofilament spun from the 50% virgin and 50% recycled polymer, the birefringence is very low, meaning that structure is mainly isotropic. Only a

<table>
<thead>
<tr>
<th>Linear density (tex)</th>
<th>100 v</th>
<th>85/15 v/r</th>
<th>50/50 v/r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific stress at break (cN/tex)</td>
<td>199.9</td>
<td>220.8</td>
<td>244.2</td>
</tr>
<tr>
<td>Breaking extension (%)</td>
<td>5.89</td>
<td>2.91</td>
<td>1.15</td>
</tr>
<tr>
<td>Work of rupture (J/g)</td>
<td>1189</td>
<td>6.46</td>
<td>3.67</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>8.0</td>
<td>0.031</td>
<td>0.007</td>
</tr>
<tr>
<td>Dynamic elastic modulus (GPa)</td>
<td>3.15</td>
<td>2.85</td>
<td>2.20</td>
</tr>
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| Degree of crystallinity (%) | 59.0 | 51.0 | 62.9 (53.4)* |

* crystallinity index determined after subtraction of lower peak

**Table 1.** Linear density and tensile properties of monofilaments spun from 100% virgin polymer (100 v), 85% virgin/15% recycled polymer blend (85/15 v/r) and 50% virgin/50% recycled polymer blend (50/50 v/r).

**Table 2.** Structural characteristics of monofilaments spun from 100% virgin polymer (100 v), 85% virgin/15% recycled polymer blend (85/15 v/r) and 50% virgin/50% recycled polymer blend (50/50 v/r).
small difference in melting temperature between the as-spun monofilaments was determined, highest for the monofilament spun from the pure virgin polypropylene, as seen in Table 2. The softening point and the temperature range where the melting of the crystalline structure occurs are also very similar for all three monofilaments, meaning that the crystalline structure must be very similar. By the DSC method the crystallinity index was derived as a ratio of the measured melt enthalpy (Table 2) to the melt enthalpy of the 100% crystalline polymer, with a value of 206 J/g. The crystallinity of the monofilament spun from the pure virgin polypropylene is higher than crystallinity of the monofilament spun from the blend composed of 85% virgin and 15% recycled polypropylene. Surprisingly, the crystallinity of the monofilament spun from the blend of 50% virgin and 50% recycled polypropylene is higher than crystallinity of the monofilament spun from the pure virgin polypropylene. As the melt enthalpy is mass based, the higher crystallinity is the consequence of the presence of the second peak, as seen from Figure 7c. With the subtraction of this second peak, the obtained crystallinity of polypropylene component is lower, similar to the crystallinity of the monofilament spun from the blend of 85% virgin and 15% recycled polypropylene.

The presence of the second component, polyethylene, in recycled polypropylene explains the lower spinnability of the recycled polymer, resulting in the poorer tensile properties of monofilaments spun from the blend containing recycled polymer. Because of the poor miscibility of virgin and recycled polypropylene, which contains fractions of polyethylene and other contaminants, holes several tens of microns in diameter are present in the as-spun monofilaments (Figure 8). Because of this structure, the density of monofilaments spun from the blend of 50% virgin and 50% recycled polypropylene is much lower. The crystallinity index calculated as a percentage based on measured densities using the following relation

\[ x_{\text{density}} = \frac{\rho - \rho_{am}}{\rho_{cryst} - \rho_{am}} \times 100 \ (\%) \]  

where \( \rho \) represents the density of sample, \( \rho_{cryst} \) the density of a perfect polymer crystal (0.938 g/cm\(^3\)) and \( \rho_{am} \) the density of an amorphous polymer (0.8545 g/cm\(^3\)), which does not give reliable results. The density of the monofilament spun from the blend of 50% virgin and 50% recycled polypropylene has the same value as the completely amorphous polymer. The reason for this is the presence of holes, which are not filled with the mixture of fluids during the measurement and influence the results.

Infrared spectroscopy provides the ability to study the interactions of the vibrational and rotational energies of atoms or groups of atoms within molecules. Thus, the spectrum can be used to identify the presence of a specific chemical compound or mixture of compounds. The infrared spectrum of polypropylene has a strong band near 2950 cm\(^{-1}\). The band vibration for the methyl group is a doublet at 1450 cm\(^{-1}\) and 1375 cm\(^{-1}\). Bands of medium intensity are observed near 1155 cm\(^{-1}\) and 970 cm\(^{-1}\) due to the CC stretching and CH\(_3\) rocking vibration and a number of sharp bands in the region 1250-835 cm\(^{-1}\). Figure 9 shows that the spectra of the monofilament spun from the pure virgin polymer is typical for polypropylene, whereas for monofilaments spun from the blends some peaks not typical for PP are also present. Peaks at 730 and 719 cm\(^{-1}\) in the spectrum of polypropylene mean that monofilaments produced with the
addition of recycled polypropylene contain a fraction of polyethylene as well.

It is well known that the crystallinity and orientation of macromolecules influence the mechanical properties of filaments. In Figure 10 it is clear that the specific stress of the monofilaments increases with the average molecular orientation and also with the crystallinity of the monofilaments. Similar results were obtained for the elastic modulus, where the dynamic modulus shows an increasing trend with the crystallinity (Figure 11) and average molecular orientation (Figure 12), whereas the static elastic modulus exhibits a decreasing trend. With the addition of recycled polymer to the virgin polymer, the crystallinity and average molecular orientation of the as-spun monofilaments decrease, which influences the tensile properties of monofilaments.

3.5 Environmental and economical aspect

One of the major challenges of our present society is the protection of the environment. Some of the important elements in this respect are the reduction of the consumption of energy and natural raw materials and consumption of waste materials. Waste minimization and end-of-life products recycling are getting considerable attention under sustainable development nowadays. Waste recycling is a measure of environmental preservation. It is very important to estimate whether the recycling process can reduce the environmental loading. Recycling of plastic is beneficial only where the post-shredding sorting and recycling process creates less environmental impacts than are created by making plastic using raw material (mining of crude oil, refining of oil and

![Figure 9. FTIR spectra of monofilaments spun from: (a.) 100% virgin polymer, (b.) 85% virgin/15% recycled polymer blend and (c.) 50% virgin/50% recycled polymer blend.](image)

![Figure 10. Specific stress of monofilaments versus average molecular orientation.](image)

\[ y = 0.7759e^{7.2805x} \]

\[ R^2 = 0.992 \]
decomposition into different substances, synthesis of resin). In the report on the production of carrier bags made from the recycled and virgin polyethylene was shown that use of recycled polymer resulted in reduction of energy consumption by two-thirds, production of only a third of SO$_2$ and reduction of CO$_2$ generation by 2.5-times (12). In another study (13) was shown that 86% of gross energy required to produce polypropylene resin represents energy of material resource, i.e. energy used to extract and process fuel and only 14% is used for transportation and process of resin production. In the same study is stated that at production of PP resin the greenhouse gas emission is 3-times higher at fuel related processes than at resin production. Noda et al. (14) evaluated the environmental loading with the amount of CO$_2$ emitted from the each process used at making polyethylene monofilaments from the pure virgin polymer and with the addition of recycled polymer. They also obtained much lower emission at regeneration of used plastic in comparison to production of virgin pellets. From these studies we can see that the production of polypropylene monofilaments from the blends of virgin and recycled polypropylene is environmentally and economically beneficial. As the price for the recycled polymer is approximately half the price for the virgin polymer, with replacing the virgin polymer with the recycled one the production costs are lowered and the manufacturing of monofilaments becomes more economical. In products, where lower tensile strength and lower extensibility is not so important, for example in fibre composites, the use of monofilaments spun from the blends is from the economical and environmental point of view more beneficial, as the energy consumption and greenhouse gas emission are lower.

4. CONCLUSION

Though higher molecular weight polypropylene is noted for its poor spinability, with adjustment of melt temperature and other spinning process variables, monofilaments, made from virgin polypropylene and from blends of virgin and recycled polypropylene, were obtained. As-spun monofilaments produced from the blends are much less extensible than monofilaments spun from the pure virgin polymer. The addition of recycled polypropylene resulted in the lower tenacity, much lower extension at break and work of rupture and higher static and lower dynamic elastic moduli of monofilaments. Because of the poor miscibility of recycled polypropylene, which contained some fractions of polyethylene, with virgin polypropylene, the as-spun monofilaments are porous, brittle and rigid and have a high tendency to break. By improving the miscibility of virgin and recycled polymers, better tensile properties of monofilaments can be obtained.

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REFERENCES / KAYNAKLAR


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