XXI ENMC
ENCONTRO NACIONAL DE MODELAGEM COMPUTACIONAL
IX ECTM
ENCONTRO DE CIÊNCIA E TECNOLOGIA DE MATERIAIS

08 a 11 de Outubro de 2018
Instituto Federal Fluminense
Búzios - RJ

RHEOLOGICAL AND MECHANICAL PROPERTIES OF RECYCLED POLYPROPYLENE / VIRGIN POLYPROPYLENE BLENDS

Igor Toledo Pimentel [1] – igorpimentel@id.uff.br
Nancy Isabel Alvarez Acevedo[1] – nacevedo@iprj.uerj.br
Marisa Cristina Guimaraes Rocha[1] – mrocha@iprj.uerj.br

[1] Universidade do Estado do Rio de Janeiro, Instituto Politécnico – Nova Friburgo, RJ, Brazil

Abstract. *This paper analyzes the influence of the amount of recycled polypropylene added to virgin polypropylene on the mechanical and rheological properties of the resulting blends. The benefits of knowing these properties include the possibility of using recycled materials in applications which previously were not used because due to the need for superior mechanical properties that recycled material does not have and also to promote reuse of waste material. Results of MFI measurements indicated that increasing the amount of recycled PP in the blend improved the flow property. Results of rheometry tests showed that PPr does not produce a dramatic change in the behavior of PPr/PPv blends during the extrusion process. However, as the content of PP increased in the blend, the viscosity values decreased for a given shear rate. Also, when the temperature increased, a small reduction in viscosity values occurred. These results indicate that by increasing the amount of recycled material in the blend there is a tendency to increase the power index and decrease pseudoplasticity. By increasing the recycled PP content in the blend, i) the elastic modulus values no changed; and ii) yield strength decreased.*

Keywords: *Polypropylene. Blends. Recycling. Rheometry. Viscosity. Mechanical properties.*

1. INTRODUCTION

Polymers are present in virtually all aspects of our daily lives and demand for them continues to grow. Most of studies about developing and processing polymers are being performed considering environmental protection (US National Research Council, 1994). Thus, trends in polymeric materials science and technology involve the use of recycled and/or natural polymers, acting as fillers or reinforcement, for the development of new materials with improved properties, lower cost and better environmental sustainability (Martínez-Barrera et al., 2013).

Polypropylene (PP) is one of thermoplastic polymers with highest demand in the market, due to its attractive chemical, physical and mechanical properties and many applications (Iunolainen, 2017; Maddah, 2016). Consequently, PP also is one of principal producers of plastic wastes. The disposal of plastic articles such as polypropylene coffee cups is a growing social problem, due to the poor degradability and large volume occupied by these wastes in dumps and landfills. As observed by Horth and Halden (2013), this reduces land resources for other uses with higher social value. To tackle this and other problems generated by these huge volumes of post-consumer plastic wastes, recycling and blending for reuse are the most common strategies (Oliveira et al., 2016).

PP is a polymer that can be recycled. Recycled PP can be used pure or mixed with other recycled or virgin materials, whether from PP or other polymers, as shown by many studies reported in the literature (Oliveira et al., 2016; Gianelli, 2010; Nguyen-Tri et al., 2008; Fernandez & Dominguez, 2007). PP, whether virgin, recycled, neat or blended, before being transformed into the desired shapes, generally is submitted to melting processes. During these processes, the polymer fluid is exposed to complex stress and temperature fields, as well as abrupt variations in geometry. These factors affect the melt viscosity and consequently the processability of polymers (Ariff et al., 2012).

The melt processability of polymer materials is highly dependent on the rheological properties, so rheological measurements where the molten material is submitted to shear deformations are often used to characterize these materials (Vlachopoulos & Polychronopoulos, 2011). Rheological measurements can also be used as a quality control tool in polymer processing and to determine suitable processing conditions.

The melt flow index measurement is the most popular test used in the plastics industry to determine material viscosities. Raj et al. (2013) evaluated the mechanical properties of recycled PP blended with virgin PP and their correlation with the melt flow index. Blends containing 10% recycled PP presented the better response regarding tensile strength and impact strength. Gianelli (2010) used determination of the melt flow index to evaluate the homogenization grade of recycled PP/virgin PP blends during injection molding. Results of tests of Charpy impact strength, drop ball impact resistance and thermoxidative stability of the blends showed the viability of using recycled PP to manufacture wrap to wheel automotive industry.

However, to obtain more accurate and meaningful viscosity data, capillary rheometry is a often used. Iunolainen (2017) investigated the viability of manufacturing 3D printer filament from recycled PP based in the study the rheological and mechanical behavior of recycled PP processed by extrusion. Nguyen-Tri et al. (2008) studied the effect of recycling processes on the thermal, mechanical and rheological properties of PP and developed recycled polypropylene/modified clay nanocomposites with significantly improved mechanical properties.

Diverses studies prior to 2008 also showed it is possible to reuse PP without loss of performance of the final product, based on determination of the mechanical and thermal properties of virgin material when submitted to various reprocessing cycles (Costa et al., 2007; Rossini, 2005; Strapasson, 2004, Caraschi & Leão, 2002) .

The focus here is to comprehend the effect of insertion of recycled material obtained from disposable polypropylene cups on the rheological properties of blends with virgin PP. The evaluation was based on rheological properties of composites measured by using an extrusion plastometer and a capillary rheometer. The experiments were performed in the Polymer Technology Laboratory (TECPOL) at the Polytechnic Institute of Rio de Janeiro (IPRJ).

2. EXPERIMENTAL

The materials and methods used in this study are presented below.

2.1 Materials

The virgin polymer used in this study was polypropylene homopolymer PP H606 pellets (Braskem, Brazil), with a melt flow index (230°C/2.26 kg) of 2.0 g/10 min (ASTM D 1238). The recycled material used was obtained from disposable coffee cups made of PP collected at the Polytechnic Institute and other points in the city of Nova Friburgo. Irganox 1010 (CIBA Especialidades Químicas Ltda., Brazil) was used as antioxidant agent.

2.2 Methods

Process of recycling polypropylene from disposable cups . For this study, we collected 10 kilograms of disposable cups. The collected material was cleaned with pure water and immersed in a solution of water with common detergent for 24 hours in order to remove foreign materials contained on the surface. Next, the material was rinsed in pure water and dried in an oven (Marconi, MA035/1080/E) with forced air circulation at 50°C for 24 hours. Once clean and dried, the material was flaked using a cutting mill (Primotécnica LP1003). Finally, the flakes were sieved to remove powder which could cause problems during their processing to transform them into pellets of recycled PP (PPr) neat or blending with virgin PP.

Processing of materials by extrusion. Neat virgin PP (PPv), PPr and mixtures of PPv with different concentrations (20, 40, 60 or 80 wt%)/ of PPr were processed in a twin-screw extruder (Leistritz ZSE 18 MAXX) with length/diameter (L/D) ratio of 30, using a temperature profile, from feed to die, of 185/185/190/190/200/200/230/230/240/240°C at 100 rpm screw speed and 2.0 kg/h feed rate. First, PPv and PPr were dried for 12 hours at 50°C in the oven. Previous to extrusion, each formulation was supplemented with 0.5 wt% of the antioxidant Irganox 1010 and then pre-mixed by manual stirring during several minutes. Soon after to exiting of extruder, the extrudates were cooled in water at room temperature and immediately pelletized. Finally, the pellets were dried for 24 hours at 50°C.

Determination of melt flow rate of materials. The melt flow index (MFI) or melt flow rate (MFR) of materials was determined according to ASTM D 1238-13, using an extrusion plastometer (Instrons/Ceast 7021). The measurement was performed using three samples of each composition and seven measures for each sample. Experimental conditions were: temperature of 230°C, load of 2.16 kg, cutting range of 30 s and initial mass of 6 g.

Determination of rheological properties of material by capillary rheometry. The rheological behavior of blends was studied using a capillary rheometer (Goettfert, Reograph 25) with L/D = 30/2, and shear rate range of 10 s^{-1} to 10^3 s^{-1}, for temperatures of 180, 210 and 240°C. Viscosity and shear stress were obtained using Rabinovich correction with the WinRheo 2 software.

Determination of tensile properties of materials. The tensile properties of PPv, PPr and PPv/PPr blends were determined according to ASTM D 638, using V-type test specimens, seven for each composition. The test was carried out with a universal testing machine

(Shimadzu, AGX-Plus 100 kN), at a crosshead speed of 50 mm/min with load of 5 kN. The test specimens were obtained by machining with a milling machine (Roland, Desktop Engraver GX-350) from plates with dimensions of 109 mm x 107 mm x 4 mm; The plates were prepared by compression molding with a press (Carver, 3851-OC) at 210ºC with force of 10 tons, warm-up time of 5 min, residence time of 2 min, and cooling in ice water.

2.3 Results and discussion

Rheological properties of processed materials. Figure 1 illustrates the evolution of MFI values of neat PPv with the addition of PPr as filler. The nomenclature used in the identification of the blends indicates the corresponding recycled polypropylene content in wt%.

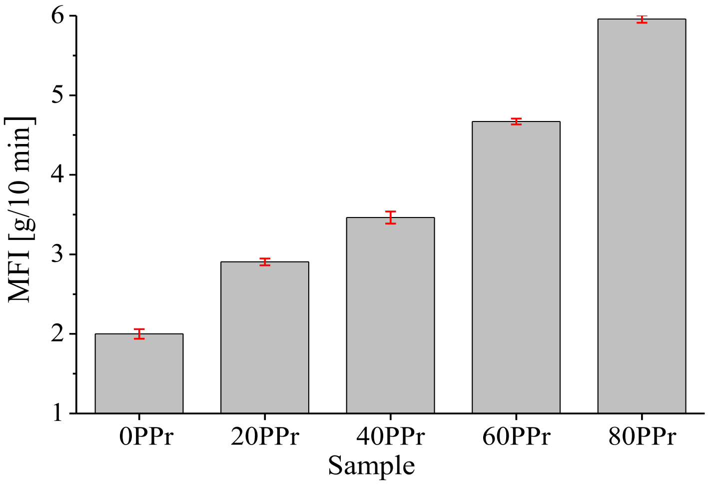

Figure 1- Variation of melt flow index of PPv and PPv/PPr blends.

Figure 1 shows the effect of PPr content on the processability of PPv. It is known that there is an inverse correlation between MFI and molecular mass of polymer and consequently with melt viscosity. A high MFI value indicates high flow and predominance of short chains, i.e., low viscosity and low molecular mass (Iunolaine, 2017; Ariff et al., 2012; Pesanha, 2009; Rocha et al., 1994). The increment of MFI values with increasing recycled PP content indicates that the recycled polypropylene has lower molecular mass than the virgin PP. Also, increasing the amount of recycled PP of the blend improved the flow property of the material.

MFI measurement is commonly used in the plastics industry to determine the flow properties of polymers, because it is inexpensive, fast and easy to perform. It should be noted that MFI only reflects the rheological properties of blends at low shear rate and for one temperature. The rheological behavior at high stress rate can be examined via capillary rheometer testing. Fig. 2 shows the flow curves for all samples at the temperatures used in this study.

PPv/PPr blends exhibited non-Newtonian pseudoplastic behavior (Fig. 2) in the shear rate range used. The shear rate range used in this study was that generally used in extrusion processing. The decrease of viscosity observed with increasing shear rate (shear thinning) is behavior typical of molten polymers according to their elastic nature and the effect of orientation of molecular chains along the flow as the shear rate increases (Aho, 2011). In our experiments, the PPr did not produce a dramatic change in the behavior of PPr/ PPv blends during the extrusion process. However, as the content of PP increased in the blend, the viscosity values decreased for a given shear rate.

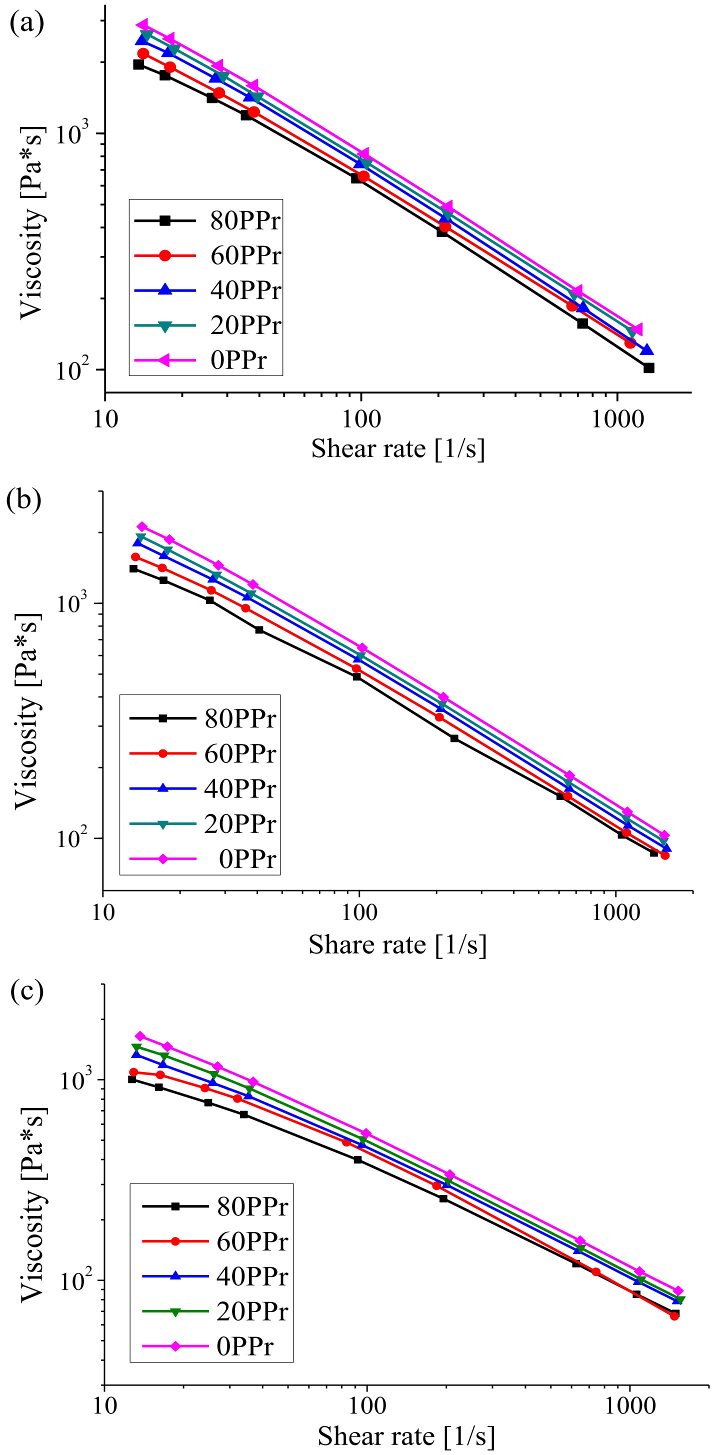

Figure 2- Viscosity of PPr/PPv blends with increasing shear rate at (a) 180°C, (b) 210°C and (c) 240°C.

Since the viscosity of a polymer is a direct function of its molecular mass, it is also possible to conclude that increasing the content of recycled material results in the reduction of the molecular mass of the blend. Reducing the viscosity of the blend with increasing content of recycled material can also be attributed to the likely smaller chain size of the recycled material due to the tendency of PP to degrade due to the tertiary carbon, leading to beta-cleavage.

It can also be noted that when the temperature increased, a small reduction in viscosity values occurred. This is because at high temperatures there is a reduction of intermolecular interaction due to the vibration of the polymer chains, increasing the free volume, thus reducing the friction between them and consequently the viscosity. These results indicate that by increasing the amount of recycled material in the blend, there is a tendency to increase the power index and decrease pseudoplasticity.

Results of tensile testing of processed materials: Table 1 presents the results obtained from tensile tests of samples of recycled polypropylene blended with virgin polypropylene. Figure 3 and 4 present the elastic modulus and yield strength, respectively, obtained for the materials.

Table 1 – Mean and standard deviation of elastic modulus and tensile strength for 0PPr, 20PPr, 40PPr, 60PPr and 80PPr samples

Sample (%PPr)	Elastic Modulus [MPa])	Yield Strength [MPa]
0PPr	1481.62 ± 40.65	37.34 ± 0.25
20PPr	1477.73 ± 106.22	36.87 ± 0.54
40PPr	1459.57 ± 28.81	36.46 ± 1.07
60PPr	1431.07 ± 75.08	36.05 ± 0.29
80PPr	1395.10 ± 75.50	35.86 ± 1.22

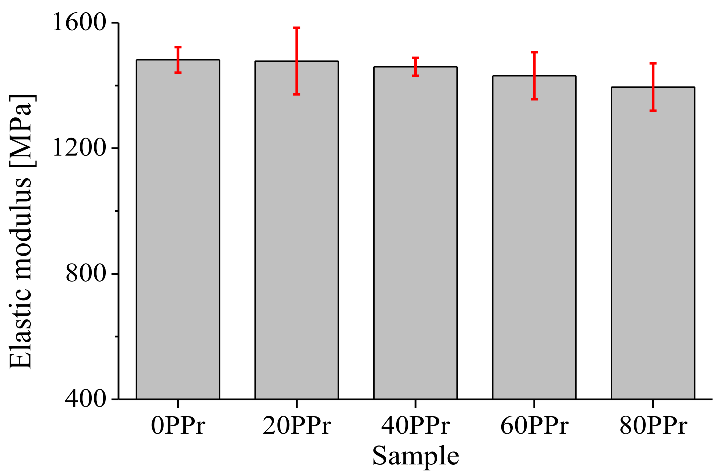

Figure 3- Elastic modulus of PPr/PPv blends.

The results in Fig. 3 show that the elastic modulus values of virgin and recycled PP blends were similar. However, there was a tendency for decreasing elastic modulus value with increasing recycled PP content in the blend. Virgin PP had the highest elastic modulus value, 1481.62 MPa. The decrease of the elastic modulus values of blends indicates there is a decrease in stiffness because the recycled PP has more short chains due to degradation during reprocessing.

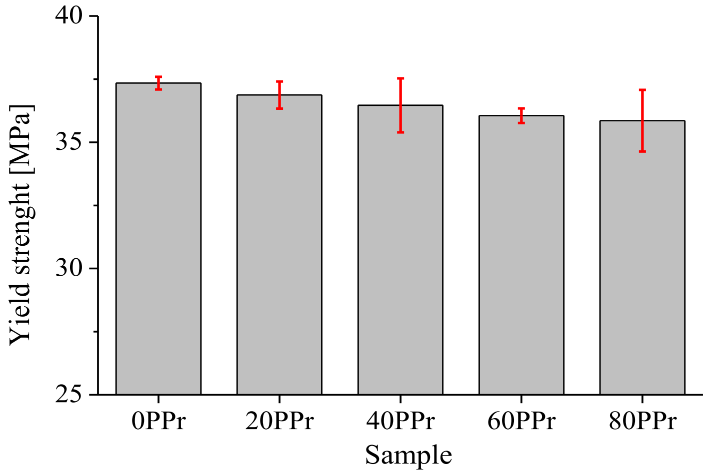

Figure 4- Yield strength of PPr/PPv blends.

Figure 4 shows decrease in the yield strength values with increase of the recycled PP content in the blend. This behavior was expected, since the recycled PP has lower molecular weight than the virgin PP due to the degradation during its reprocessing. Similar results for these properties were reported by Barbosa et al. (2017).

3. CONCLUSIONS

The results of the melt flow testing suggest that the viscosity of the blend decreases when recycled material is added. This is due to the lower molecular weight of the recycled material, so that by varying the ratio of virgin PP in the blend, the characteristics of the mixture become closer to the characteristics of the material with the highest content in the blend.

Analyzing the results of rheological properties indicate that adding recycled material to the virgin resin promotes a reduction in the molar mass of the mixtures and also an increase in the molar mass distribution. It also indicates that by increasing the amount of recycled material, the blend is more readily deformable. And finally, blends with recycled material are less pseudoplastic than the virgin resin.

REFERENCES

Aho, J. (2011), “Rheological characterization of polymer melts in shear and extension measurements reliability and data for paractical processing”. Doctoral Thesis, Tampere University of Technology, Tempere, Finlandia.

Ariff, Z.M., Ariffin, A., Jikan, S. S. and Rahim A.A. (2012), “Rheological Behaviour of Polypropylene Through Extrusion and Capillary Rheometry”. In: *Polypropylene*. Fatih Dogan (ed.), ISBN: 978-953-51-0636-4, In Tech, Croatia.

Barbosa, L.G., Piaia, M.P., Ceni, G. H. (2017), Analysys of Impact and Tensile properties of recycled polypropylene. International Journal of Materials Engineering, 7, 117 -120.

Carashi, J.C. and Leão, A.L. (2002), Avaliação das propriedades mecânicas dos plásticos reciclados provenientes de resíduos sólidos urbanos. Acta Scentiarum, 24, 1599-1602.

da Costa, D.A. , Oliveira, D.H., da Cunha, A.M., Leite, R.B., do Nacimento, J.E.L.M.F. and Araújo, E.M. (2007), “Estudo do reaproveitamento de polipropileno reciclado por medio da incorporação de resíduos de pneus e $CaCO_3$”. *IX Congresso Brasileiro de Polímeros*, Campina Grande.

Gianelli, E.G. (2010), "*Utilização de polipropileno reciclado na fabricação de envoltório de rodas para indústria automotiva*". Master Disssertation, Universidade de Taubaté, São Paulo.

Horth, E.J., Halden, R.U. (2013), Plastic and environmental health: The road ahead. Revista Environmental Health, 28, 1-8.

Iunolainen, E. (2017) "*Suitability of recycled PP for 3D printing filament*". Degree Thesis. Arcada University of Applied Sciences, Helsinsky, Finlandia.

Maddah, H.A. (2016), Polypropylene as a Promising Plastic: Review. American Journal of Polymer Science, 6, 1-11.

Martínez-Barrera, G., Gendel, O., Menchaca-Campos, C. and Vigueras-Santiago, E. (2013), Natural, synthetic, and recycled polymers in composite materials. International Journal of Polymer Science, 2013, Article ID 389162, 2 p.

U.S. National Research Council - Committee on Polymer Science and Engineering (1994) "*Polymer Science and Engineering: The Shifting Research Frontiers*". National Academy Press, Washington, D.C., USA.

Nguyen-Tri, P., Villoutreix, G., Bui, Ch. (2008), Recycling process of polypropylne and the mechanical properties of recycled polyproplene/organoclay nanocomposites. Jornal of Reinforced Plastics and Composites, 27, 1983-2000.

de Oliveira, R.R, de Oliveira, T.A., Barbosa, R., and Alves, T.S. (2016), "Avaliação de blendas recicladas de PP/PHB". *22º Congresso Brasileiro de Engenharia e Ciência dos Materiais*, Natal, 9780-9789.

Pesanha, A.B. (2009), "*Modificação do LLDPE através de silanos viabilizando a aplicação em camadas plásticas de linhas flexóveis*". Master´s Dissertation, UERJ, Rio de Janeiro.

Rocha, M.C.G. et al. (1994), Índice de Fluidez: Uma Variável de Controle de Processos de Degradação Controlada de Polipropileno por Extrusão Reativa. Polímeros, 4, 33-37.

Rossini, E.L. (2005),"*Obtenção de blenda polimérica PET/PP/PE/EVA a partir de "garrafas PETe estudo das modificações provocadas pela radiação ionizante*". Doctoral Thesis . Universidade de São Paulo, São Paulo.

Sadiku-Agboola, O., Rotimi Sadiku, E., Taoreed Adegbola, A. and Biotidara, O.F. (2011), Rheological Properties of Polymers: Structur and morphology of molten polimer blends. Materials Sciences and Applications, 2, 30-41.

Strapasson, R. (2004), "*Valorização do polipropileno através de sua mistura e reciclagem*"; Master Dissertation. Universidade Federal do Paraná, Curitiba.

Vlachopoulos, J. and Polychronopoulos, N. (2011), "Basic concepts in polymer melt rheology and their importance in processing". In: *Applied Polymer Rheology: Polymeric Fluid with industrial applications*. Kontopoulou, M. (ed.), John Wiley & Sons, New Jersey.