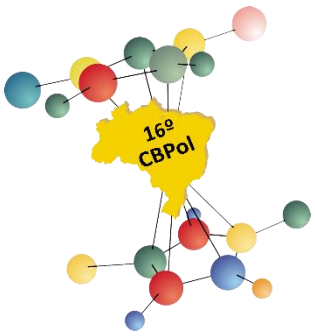

INFLUENCE OF THE INCORPORATION OF STABILIZERS OR VIRGIN RESIN ON THE RECYCLED POLYPROPYLENE FROM COFFEE CAPSULES: THERMAL PROPERTIES

Renata dos Reis Klering[1] and Ruth M. C. Santana[2]
1, 2 – Department of Materials Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil sreis.renata@gmail.com

Abstract - The coffee capsule is a rigid multilayer package, with a PP matrix, which has an excellent barrier property. However, due to its complexity, a large part of the waste has been disposed of in landfills. The present work has the objective of evaluating thermal properties in a mixture of recycled material from coffee capsules, with virgin polypropylene, and the recycled material added with stabilizers. The samples were characterized using thermogravimetry (TGA), differential scanning calorimetry (DSC), and induced oxidation time (OIT) techniques. The results of the analyzes indicated that the additive recycled material presented better thermal stability compared to the mixture with virgin polypropylene.
Keywords: *coffee capsule, polypropylene, mechanical recycling, thermal properties.*

Introduction

It is possible that more than any other material, plastic is associated with the idea of modernity and technological advancement.[1] It is seen as a competitive support for sectors such as automotive, agribusiness, electronics, civil construction and food.[2] Producing these very useful and good quality materials is just as critical as worrying about their fate after use.[1] A product that very well exemplifies this technical and modern advance in the use of plastic today is coffee capsules. In Brazil, around 1070 thousand tons of coffee were consumed in 2017, where 0.9% represents the consumption of coffee capsules, which are approximately 10 tons. In addition, the survey predicts significant growth as consumers have been attracted by falling machine prices, single servings and coffee varieties.[3] Post-consumer coffee capsules are a resource of great added value, as they can be transformed into a new raw material, also called secondary raw material. Several studies suggest that one of the most environmentally correct ways to reuse plastics is mechanical recycling.[4] A fundamental aspect of this type of recycling is the final quality of the processed resin.[5] A "start-up" that has a partnership initiative with Nescafé Dolce Gusto, recycles capsules made of polypropylene to become new products, usually small objects such as supports for the coffee capsules themselves. They have a technology monopoly to recycle this type of waste in the country, but face difficulties in reverse logistics.[6]

Polypropylene is used in several applications, as it has versatile properties, low density and good processability. Furthermore, it is a material that enables several transformation processes, such as extrusion, blowing and injection, which can be combined with each other. However, due to the presence of tertiary carbon in the polymer chain, it is susceptible to oxidation.[7,8]

Since mechanical recycling is one of the ideal strategies for reusing this material, this work aims to evaluate thermal properties in a mixture of recycled material with virgin polypropylene and also recycled material added with stabilizers through thermogravimetry (TGA), differential calorimetry scan (DSC), and induced oxidation time (OIT).

Experimental

Materials

For the mixture, recycled polypropylene (PPr) from the coffee capsules of the Nestlé Dolce Gusto coffee maker, collected from consumers of this type of packaging, was used; and Braskem's H606 virgin polypropylene (PPv) grade, which according to the catalog has characteristics similar to grades used in coffee capsules. The primary (AO1) and secondary (AO2) and photostabilizer (Anti-UV) were incorporated into the recycled PP. The compositions, in percentage by mass, of the evaluated samples are specified in Table 1.

Table 1- Composition of evaluated samples

Sample	PP Capsules (wt %)	PPv (wt %)	AO1 (%)	AO2(%)	Anti-UV (%)
PPr	100	-	-	-	-
PPr/PPv	50	50	-	-	-
PPv	-	100	-	-	-
PPr-a	100	-	0,5	0,8	1

Processing

The coffee capsules were ground in a knife grinder. And all samples were mixed and homogenized in a HAAKE Rheomix OS Polylab type mixer, at a temperature of 165°C, 100 rpm for 10 minutes, as shown in Figure 1.

Figure 1 – Whole coffee capsule, ground and after mixing in HAAKE.

Description

The thermal characterization of the samples was performed using the techniques of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and induced oxidation time (OIT). For the analyzes related to the variation of mass as a function of temperature, a TGA equipment [Q50, TA Instruments] programmed in the temperature range from 25 to 1000 °C with a heating rate of 20 °C/min, under N2 atmosphere, was used. as set forth in ASTM E-1131.[9] To obtain the melting temperatures and crystallization enthalpies of the samples, DSC equipment [Q20, TA Instruments] programmed in the temperature range from 25 to 200 °C with a heating / cooling ramp of 10 °C / min, under atmosphere was used of N2, according to ASTM D-3418 standard.[10] For the OIT analysis, the atmosphere of N2 was exchanged for flow of O2 in an isotherm of 200 °C.

Results and Discussion

Figure 2 shows the differential scanning calorimetry (DSC) thermal curves of the PPv, PPr, PPr-a, and PPr/PPv samples (50/50) where it is possible to verify the presence of two endothermic events in

the samples with PPr, corresponding to the melting of PP close to 160oC (most intense peak) and the second much smaller peak between 182 to 184oC corresponding to EVOH. The virgin PP sample presented only one higher peak (164°C) compared to the other two samples. The PPr/PPv mixture sample (50/50) had a melting temperature close to PPv of 163°C. Thus, we can see that, in relation to the melting temperature, the additive recycled sample does not present a significant difference in relation to the pure recycled sample. [10]

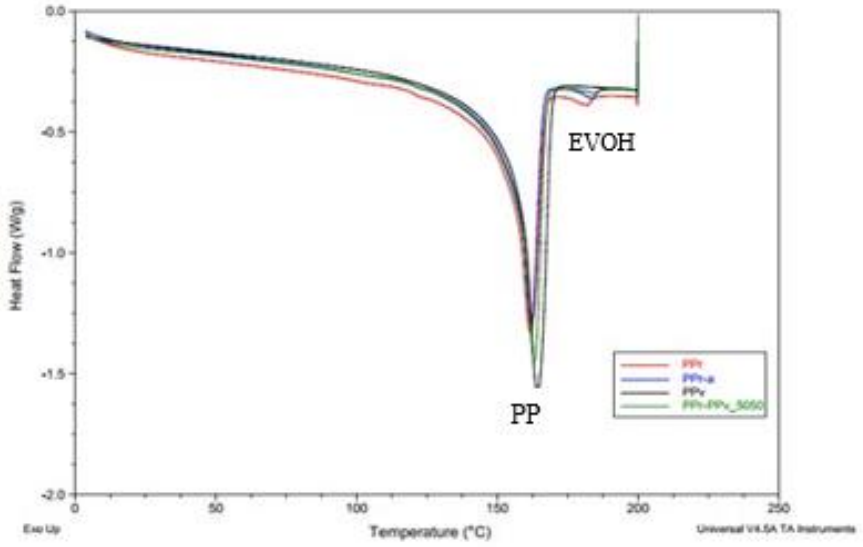

Figure 2 – Curvas térmicas de DSC das amostras PPv, PPr, PPR-a, e PPr/PPv.

Table 2 shows the data referring to the differential scanning calorimetry (DSC) test: melting temperatures (Tf), enthalpies (ΔH f) of melting and degree of crystallinity (Xc), referring to polypropylene and to the EVOH corresponding to each of the samples. Regarding the degree of crystallinity corresponding to polypropylene, the samples showed lower values compared to PPv. For EVOH, the degree of crystallinity reduces in the PPr/PPv sample, as the EVOH comes only from samples that contain PPr, which in this case corresponds to 50% by mass in this sample.

Tabela 2: Resultados das análises de DSC do segundo aquecimento das amostras avaliadas

Sample	$T_{f\ PP}$ (ºC)	$\Delta H_{f\ PP}$ (J/g)	$T_{f\ EVOH}$ (ºC)	$\Delta H_{f\ EVOH}$ (J/g)	$Xc_{\ PP}$ (%)	$Xc_{\ EVOH}$ (%)	OIT (min)
PPv	164	93	-	-	56	-	1
PPr	161	77	182	1,18	47	1,5	0,5
PPr-a	161	71	184	1,28	43	1,6	>8,5
PPr/PPv	163	84	184	0,51	51	0,6	3,5

Valor de referência para Xc (%) utilizado para PP: 165 Jg^{-1} e para EVOH 81 Jg^{-1} [11]

In terms of oxidative stability, table 2 shows the oxidative induction time of the samples, where it can be seen that the PPr sample had the lowest OIT value, starting its oxidation before the PPv sample, indicating a lower stability in this aspect of evaluation , as expected for being recycled, the PPr/PPv mixture in the 50-50 mass ratio showed greater stability compared to the PPr and PPv sample, indicating that in terms of oxidative stability the mixture has a similar or better behavior than the virgin resin evaluated . In PPr-a, however, there was a notable improvement in stability in an oxidizing environment, as shown in figure 3, in which it did not present an exothermic event under the same analysis conditions when compared to other samples, indicating that the incorporation of stabilizing additives exceeded the stability of PPv and PPr/PPv mix [10]

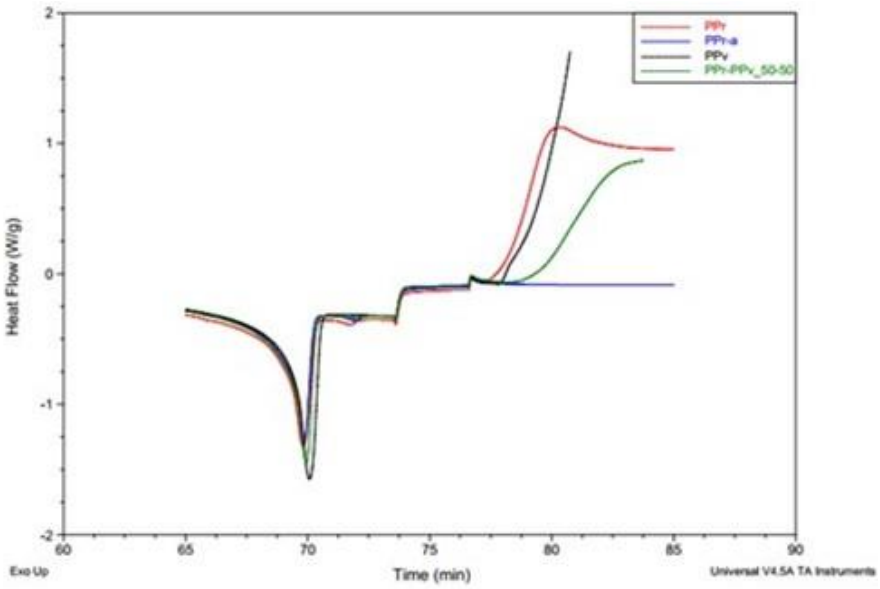

Figure 3 – Overlapping OIT curves for all samples.

Figure 4 shows the superposition of the thermogravimetric curves of the evaluated samples. The samples containing PPr showed two decomposition events, the first one with lower mass loss (5-10%), which may correspond to EVOH decomposition, and a second more intense event corresponding to PPr decomposition. The PPv sample presented only one decomposition event. The PPr/PPv (50/50) sample showed greater thermal stability than the other samples, followed by the PPr-a sample, as seen in the curve shift for higher temperatures.

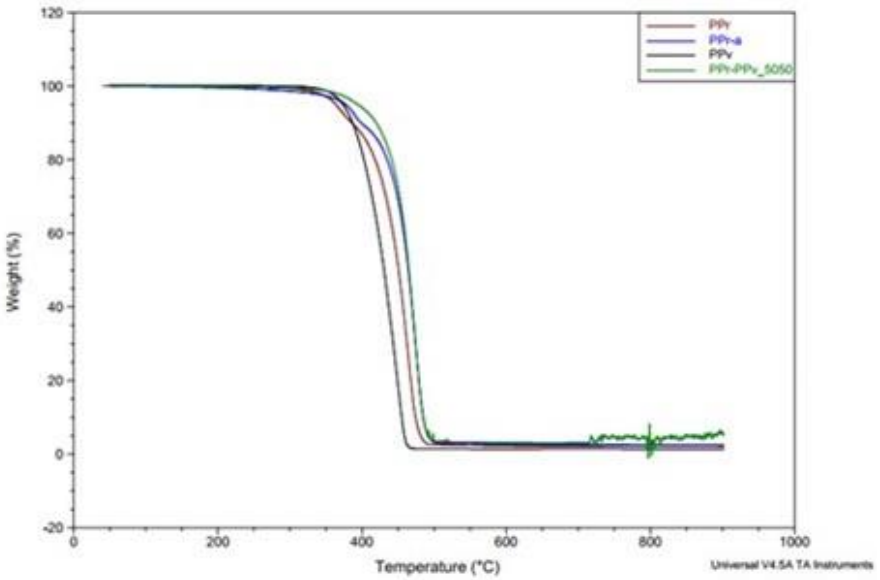

Figure 4 – Overlapping the TGA curves of all samples evaluated.

Table 3 shows the data referring to the thermogravimetry test (TGA), which demonstrate a comparison in relation to the thermal stability of the evaluated samples, the temperatures corresponding to the mass loss events, and the ash content, which are higher in the samples that it has PPr, which can be filler, pigment, or other impurities present. In 5%, the sample that showed greater thermal stability was PPr/PPv, followed by PPr-a, in 20% also presented greater thermal stability, consecutively, PPr/PPv and PPr-a samples. Regarding the maximum decomposition rate, the PPr-a

sample followed by the PPr/PPv sample were the ones with the highest peak temperature (Tp2) of the DTG. Regarding EVOH (Tp1), the maximum decomposition rate was also that of the PPr-a sample.

Table 3: TGA results of the evaluated samples

Sample	$T_{5\%}$ (ºC)	$T_{20\%}$ (ºC)	$\%m_1$	$\%m_2$	%cinzas	Tp_1 (ºC)	Tp_2 (ºC)
PPv	373,52	449,11	-	98,67	1,35	-	449,11
PPr	363,76	467,61	10,21	87,59	2,24	367,96	464,25
PPr-a	377,18	478,78	10,53	86,89	2,45	389,42	473,79
PPr/PPv	393,90	478,81	5,63	91,22	5,34	382,02	472,41

*****T5% and T 20% correspond to the temperature at the point where there was 5 and 20% of sample mass loss; %m1 and %m2 correspond respectively to the percentage of lost mass; Tp1 and Tp2 DTG peak temperatures;

Conclusions

The thermal scanning calorimetry (DSC) curves showed that there are no significant differences regarding the melting temperatures between the samples, but the degree of crystallinity was lower than virgin PP. It was possible to observe that the additive PPr sample presented the greatest stability in an oxidizing environment at high temperature among all. Regarding thermal stability, two samples stood out, PPr/PPv and PPr-a. Considering the results obtained, the additive sample had the best performance. The use of recycled polymer from coffee capsules, in relation to the evaluated properties, is possible.

Acknowledgements

We are grateful to Laboratory of Polymeric Materials (LAPOL) of the Federal University of Rio Grande do Sul, for all the support for the elaboration of this research.

References

1. ZANIN, Maria; MANCINI, Sandro Donnini. Resíduos plásticos e reciclagem: aspectos gerais e tecnologia. SciELO-EdUFSCar, 2015. (ABIPLAST, 2018)
2. Euromonitor, 2017. Tendências do Mercado de Café, Associação Brasileira da Indústria de Café (ABIC).
3. DE OLIVEIRA, M. C. B. R., Gestão de Resíduos Plásticos Pós-Consumo:
4. Perspectivas para a Reciclagem no Brasil. Dissertação de M.Sc., UFRJ/COPPE, Rio de Janeiro, RJ, Brasil, 2012.
5. SERRANTI, S.; BONIFAZI, G. Techniques for separation of plastic wastes. [s.l.] Elsevier Ltd, 2019.
6. FOLHA UOL. Folha de São Paulo: Seminários folha, 2017. Start-up recicla resíduos indesejados, das cápsulas de café às fraldas. Disponível em:< https://www1.folha.uol.com.br/seminariosfolha/2017/10/1924747-start-up-recicla-residuos-indesejados-das-capsulas-de-cafe-as-fraldas.shtml > Acesso em: junho de 2020.
7. LIBERMAN, Susana et al. Poly (propylene) Heterophasic Copolymers: Molecular Structure Analysis through Fractionation Techniques. Macromolecular Symposia, [s.l.], v. 330, n. 1, p.30-41, ago. 2013.
8. CORRÊA, A. X. Avaliação da influência da degradação com peróxidos nas propriedades de polipropileno randômico com eteno ou buteno. Universidade Federal do Rio Grande do Sul. Porto Alegre, p. 89. 2007.
9. ASTM E1131-20, Standard Test Method for Compositional Analysis by Thermogravimetry, ASTM International, West Conshohocken, PA, 2020.
10. DE PAOLI, M-A. Degradação e Estabilização de Polímeros. 2ª edição. Editado por João Carlos de Andrade, 2008.
11. MARK, James E. Polymer Data Handbook: Oxford University Press. 2 ed.1999.