THERMOPHYSICAL AND MECHANICAL EVALUATION OF BLENDS BASED ON RECYCLED POLY(ETHYLENE TEREPHTHALATE) - PET AND POLY(HIGH DENSITY ETHYLENE) – PEAD

André Ricardo de Souza[1], Marco Elisio Marques[1], Kássio A. Lacerda[1*]
1 – Faculdade de Engenharia e Arquitetura, Universidade FUMEC, Belo Horizonte, MG.
kassio@fumec.br

Abstract: The roof is an important construction element for thermal control, inside buildings. The use of thermal insulation and use natural lighting promote reductions in energy consumption and are more environmental friendly approaches. In this work we sought to evaluate thermoacoustic roof tiles based on recycled PET, as an engineering solution. The work was splitted in two steps: 1 - to produce a PET blend with additions of 10% and 30% by mass of HDPE, in extrusion steps for mixing, followed by thermoforming by injection or hot pressing. 2 - the blends were characterized by FTIR spectroscopy, thermal analysis, SEM, as well as a mechanical and thermophysical evaluation. The thermophysical properties were evaluated by the thermal quadrupole method. The proposed material presents an engineering solution for lightweight roofing with environmental comfort, which meets the performance standard for residential buildings ABNT NBR 15.575-2013, thermal comfort aspect. The results showed a physical blend of low miscibility of HDPE in PET. However, the preliminary mechanical results showed gains compared to pure recycled PET. Thermophysical evaluation results met the values recommended for the reference materials indicated by ABNT NBR 15.575-2013. By this set of results, it was possible to conclude that the polymeric blends PET/HDPE, with 10% by mass, is a viable constructive solution for lightweight roofing of horizontal buildings.

Keywords: PET. PET/PEAD blends, Thermoacoustic roofing. Environmental Comfort. Thermal Comfort.

Introduction

From a functional point of view, the roof of a building can be made of any type of material, as long as it meets the basic requirements of watertightness and liquid flow over its surface. It is intended to protect the entire building against the weather conditions, such as rain, wind, insolation, snow, as well as dust particles and noise from outside. In horizontal buildings, besides their safety and protection functions, roofs should also fulfill thermal and acoustic performance requirements, because in this typology the roof is the most building susceptible part to sound absorption and most exposed to solar radiation, absorbing most of the thermal energy, transferring it to the inside of the rooms, raising their internal temperature [1]. Thus, it is paramount to consider the thermal comfort of users in roofing selection. In this context, thermal comfort as defined in ISO 7730:2005, is a: "...condition of mind that expresses satisfaction with the thermal environment" [2].

The demands for buildings to use more efficient building materials, processes, methods, and techniques have been the focal point in the areas of civil construction, and they are supported by technical standards that assess quality and performance. Thus, to conduct a thermal performance, according to Brazilian standards it is necessary to apply the framework of Brazilian standards: ABNT NBR 15220-2:2005 [3] and ABNT NBR 15575-5:2005 [4]. These standards present the criteria for the evaluation of the thermal performance through the simplified method and establish the maximum admissible values for the thermal transmittance (U) of roofs, considering a descending thermal flow, in function of the bioclimatic zones, and present the performance level (minimum - M, intermediate - I and superior - S).

The potential of using pure polymers and/or blends can be fully explored when the possibility of their use as parts, with structural or compositional functions, is envisioned [5]. In this context, the proposition of a blend of PET-R with HDPE, can present advantages in several aspects such as reproducibility in industrialized processes, as well as, reduction of emissions with disposal of PET-based polymers in the environment. HDPE can modify the properties of PET, as it has high impact strength and good resistance to chemical solvents. On the other hand, PET can improve the thermal properties of HDPE [6]. However, according to Marconcini and Filho [7], blends of PET with polyolefins (HDPE, LDPE, PP, EVA, PB, and GDP) can provide an attractive balance of mechanical properties, barrier properties, and processability, but with low miscibility between the phases involved. However, it is possible to improve the miscibility of PET/HDPE blends by using compatibilizers [8].

Experiment

A productive arrangement was carried out, guided by polymer processing and blends with recycled PET from soft drink bottles, adding 10% and 30% by mass of HDP. In this process, the PET-R was thermally treated in a Solotest oven, model 150L, under a thermal regime of 135 ºC, for 3 hours. After pre-drying, the material was homogenized in a ball mill for 10 min and submitted to injection, which proved to be efficient in the production of specimens for mechanical tests according to ASTM D638 [9]. The injection stage used a Jetmaster injection molding machine model JN35-E (35 t). The injection operation was conducted with a pressure of 350 bar, with screw rotation of 50 rpm, with heating distributed in 4 zones starting at 190ºC until the final zone with 270ºC. A Sagec press of 15 t was used for the thermophysical tests, thermoforming was conducted with a pressure of 18.5 MPa and processing temperature of 190ºC
After production, samples were characterized by: FTIR spectroscopy, thermal analysis, mechanical and thermophysical evaluations, as well as the analysis of fractures in electron microscopy. For the determination of thermal diffusivity, the thermal quadrupole method developed by Degiovanni [10] was used. This method is an analytical tool for mathematical modeling of the one-dimensional heat transfer of a flat, homogeneous wall. The samples were heated by a light beam that falls on one of its faces and, through the method of least squares, the theoretical curve is obtained for comparison with the experimental curve.
For the diffusivity experiment, it was used a diffusivimeter Protolab, Quadruflash 1200, which consists of a xenon lamp (1200 J), responsible for the energy pulse, three special class K-type thermocouples, an InSb infrared detector, a resistive oven for heating the samples and the signal processing unit. All samples were coated with a layer of graphite-based paint to improve the absorption of the energy emitted by the xenon lamp. Finally, a simplified evaluation of the thermal performance of a hypothetical cover was performed. The values of thermal transmittance of the samples, obtained wit Eq. 1, were compared with the theoretical reference value presented in ABNT NBR 15220-2:2005, example C.6 [3]. This choice was made because this simulates the summer condition, the predominant condition in Brazil, following the reference typology (see Table 1) of ABNT NBR 15220-2:2005 [3]

$$U = \frac{1}{R_T} \quad (1).$$

Table 1 - Reference roof typology data and reference thermophysical properties

Item	Value	Measurement type	Value	Unit
Roof length	7,00 m	Fiber-cement roof tile thermal conductivity	0,65	$W \cdot m^{-1} \cdot K^{-1}$
Height of the ventilation opening (at each eave)	0,05 m	Thermal conductivity of pine lining	0,15	$W \cdot m^{-1} \cdot K^{-1}$
		Thermal resistance of the air chamber	0,61	$m2 \cdot K \cdot W^{-1}$
Vent length (at each eave)	7,00 m	Internal surface thermal resistance (Rsi)	0,17	$m2 \cdot K \cdot W^{-1}$
		External surface thermal resistance (Rse)	0,04	$m2 \cdot K \cdot W^{-1}$

Source: ABNT NBR 15220-2:2005 [3].

Results and Discussion

Samples of pure PET-R and blends of PET-R/PEAD at 10% and 30% m/m, experienced blending steps by single-screw extrusion, followed by injection operations or thermoforming into specimens suitable for mechanical and thermophysical characterizations were produced.

The two-step polymer processing, extrusion and injection, produced degradation of the blend under analysis. During the processing to produce a PET-R/PEAD blend, gas release along with the extruded product and an intermittent output of the final product were observed, despite the continuous feeding of the blend into the extruder. This gas release can be attributed to a polymer degradation process, both thermal and oxidative, generating mass loss with consequent gas formation and release. The intermittent product output is possibly due to gas formation inside the extruder [11]. Pietrasanta [12] pointed out that compatibility of PET blends with HDPE can be achieved in single-step processing. The mechanical properties of blends prepared by injection molding show better than those of blends prepared by extrusion followed by injection molding. The shear rate in the injection molding process was sufficient to ensure a dispersion of the dispersed phase and a reduction in interfacial tension.

For all samples analyzed by FTIR in the region of 4000 to 650 cm^{-1}, the spectral signatures of ester groups recurrent in PET were evidenced [13], as well as the absorptions of aliphatic groups recurrent in HDPE in the PET-R/HDPE blends. Also, it was noticed the absorption bands at 1780-1650 cm^{-1} and 920-820 cm^{-1}, as well as, the peak at 1235 cm^{-1}, that are characteristic of the carbonyl group (-CO-). The absorptions indicated at 2924 and 2852 cm^{-1}, are due to symmetric and asymmetric stretching of the C-H bonds of aliphatic and aromatic groups present in the molecule of the blends. Confirmations of the absorptions of aliphatic groups are indicated by the wave numbers of the said absorptions are 1090 - 1016 and 725 cm^{-1} [13].

The physical-chemical analyses (TG/DTG-DSC), revealed the composition of the recycled starting materials indicating mainly that the materials worked were polyethylene terephthalate - PET, with no mixtures of other polymers, additives or contaminants. Regarding the thermal stability of the materials, the samples responded according to their inherent properties, presenting thermal degradation of 80% to 95% in the temperature range between 430°C and 440°C. The blends showed semi-crystalline structure, with predominance of a crystalline arrangement, with Tg at 75°C.

A pre-assessment of the mechanical properties (Table 2) was conducted, following the procedures of ASTM D638-2014 [9]. The addition of 10% by mass of HDPE in the PET-R blends produced an increase in the average of the Modulus of Elasticity, Tensile and the Breaking strength compared to PET. The addition of 30% by mass of HDPE in the PET-R blends produced increased average Tensile Strength limit compared to PET. It was also noticed that elongation to failure was decreased when we compare the pure PET, as reference, with the blends tested. In fact, the addition of 30% HDPE to PET-R showed to be exessive, saturating the mixture and harming the modulus of elasticity - weakening the material and not adding considerable performance in other mechanical properties. Anova was performed for each mechanical characteristic, the p values were calculated and are also showed in Table 2. Although the values are high to have a clear conclusion is worth point out the small number of samples tested.

Table 2 - Results of the mechanical tests of PET-R/PEAD blends.

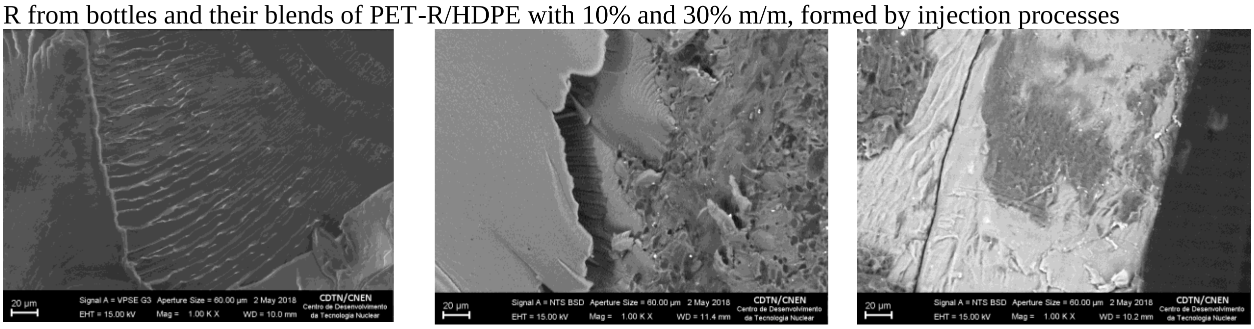
System	E (MPa)	TS (MPa)	BS (MPa)	Elongation to failure (%)
PET-R100%	(7 sps) 1443,84 ±144,40	(7 sps) 15,49 ±1,74	(5 sps) 15,10 ±1,29	(6 sps) 2,60 ±0,14
PET-R/PEAD10%	(4 sps) 1628,89±130,36	(6 sps) 17,64 ±3,14	(6 sps) 16,62 ±3,64	(3 sps) 2,43 ±0,07
PET-R/PEAD30%	(5 sps) 1410,43 ±179,45	(4 sps) 18,22 ±2,82	(4 sps) 16,12 ±1,64	(3 sps) 2,38 ±0,34
P value	0,11	0,13	0,73	0,08

E=Elasticity modulus - TS=Limit of tensile strength – BS Breaking strength. The values reported are the means +/- 1 experimental standard deviation, according to the number of specimens tested (sps)

The digital SEM images showed that the PET-R samples with added HDPE, in all concentrations, had phase segregation revealed by phase contrast images, where one can attribute the smoother phase to the PET-R and the rougher phase to the HDPE. These images confirm the formation of a physical blend between the polymers PET-R and HDPE The fracture surfaces of the PET-R/HDPE blends showed a brittle fracture with uniform propagation.

Table 3 presents the results obtained from the thermal transmittance of the samples, considering as reference the typology and materials (fiber-cement roof tile and pine lining) of ABNT NBR 15220-2:2005 example C.6 [3], together with the value of the thickness adopted and the total thermal resistance (Equation 1). The results of the evaluation of the thermal performance of the samples investigated by the simplified method were compared the values established as reference.

Figure 1 - Digital SEM images obtained on the fracture surface of samples processed in this investigation based on PET-R from bottles and their blends of PET-R/HDPE with 10% and 30% m/m, formed by injection processes



(a) PET-R (5 kx) (b) PET-R/PEAD-10% (5 kx) (c) PET-R/PEAD-30% (5 kx)

As can be observed in Table 3, there was practically no change in the value of the total thermal transmittance, for the different types of materials, ranging from 1.10 to 1.12 $W \cdot m^{-2} \cdot K^{-1}$, when compared with the value of the reference (1.11$W \cdot m^{-2} \cdot K^{-1}$). This result can be explained with fact that the largest contributor in the calculation of the total thermal resistance is the resistance of the air layer between the tile and liner (Rar = 0.61 $m^2 \cdot K \cdot W^{-1}$) which is a function of the thickness of the air layer, the surface emissivity and the direction of heat flow (horizontal, ascending or descending), as presented in table B.1 ABNT NBR 15220-2:2005 [5]. It can also be seen that the materials tested meet the maximum permissible value for thermal transmittance criteria.

Table 3 - Thermal Transmittance Comparison

Material	Thickness (m)	Total thermal resistance ($m^2 \cdot K \cdot W^{-1}$)	Thermal transmittance ($W \cdot m^{-2} \cdot K^{-1}$)
Fiber cement ABNT NBR 15220-2:2005	0,008	0,90	1,11
PET-R/PEAD-0%	0,003	0,90	1,12
PET-R/10% PEAD (1)	0,003	0,90	1,12
PET-R/10% PEAD (5)	0,003	0,90	1,12
PET-R/30% PEAD (1)	0,004	0,90	1,12
PET-R/30% PEAD (2)	0,003	0,90	1,12

Special mention should be made to the performance of the samples when inserted in bioclimatic zones 3, 4, 5 and 6, because they reach two levels of minimum and intermediate requirements in terms of thermal performance [4]. These bioclimatic zones are critical and require superior thermal performance from buildings, because they are mainly comprised in the Brazilian southeast and mid-west regions, where transitions occur between hot low-latitude climates and mild mid-latitude temperate climates, with both seasonal and daily air temperature variations [15], that presents a long dry period without rainfall and a short wet rainy period, with intense solar radiation and low relative humidity indexes [6].

These characteristics require higher thermal performance levels than in other regions, especially when materials with high absorbance levels, higher than 0.6, are used on the external surface of the roof. These results confirm that PET-R roof tiles are potential materials that can be used on building roofs as an engineering solution for thermal comfort and, as a consequence, reducing the environmental impact. The results obtained for all test materials meet the minimum mandatory thermal performance requirements for any bioclimatic zone and are similar when compared to the reference example.

Conclusions

The results confirm that PET-R is a promising material to be used in building roofing as an engineering solution to replace traditional materials, with characteristics that can improve thermal and mechanical performance, according to the architectural design, including in terms of innovation. Additionally, it can also imply in an improvement in the industrial production process with standardization practices and rationalization of production and also in the covering mass reduction and possibility to be made using innovative shapes and dimensions.The incorporation of HDPE in the polymer blends (PET-R/HDPE) increased the thermal conductivity when compared to the result of the PET-R samples. No difference between the thermal conductivity values were detected between the (PET-R/HDPE) blends. The similar results of thermal transmittance in a prototype roofing of ABNT NBR 15220-2:2005, points to a potential use of the blends and the necessary parameters of thermal performance to be applied in building roofing,

Acknowledgments

To Universidade Fumec, Universidade Federal de Minas Gerais, and the Centro de Desenvolvimento de Energia Nuclear.

References

1. C. Michels; R. Lamberts; S. Güths. Energy and Buildings, v. 40, p. 445-451, 2008.
2. International Organization For Standardization. ISO 7730:2005.
3. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. *ABNT NBR 15220-2:2005.*
4. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. *ABNT NBR 15575-5:2013.*
5. S. M. Franchetti; J. C. Marconato. Química Nova na Escola. n18. Nov. 2003.
6. D. H. Guimarães, et al. In: Anais do 11º Congresso Brasileiro de Polímeros, Campos do Jordão - SP, Out 2011.
7. J. Marconcini; FILHO, A. Filho. Polímeros: Ciência e Tecnologia, vol. 16, nº 4, p. 323-331, 2006.
8. C. Iñiguez; E. Michel; R. González; R. Nuñez. Polymer Bulletin. v. 45, n. 3, p. 295–302, 2000.
9. AMERICAN SOCIETY FOR TESTING AND MATERIALS. ASTM D638, 2014.
10. A. Degiovanni, A. Maillet, D. André, S. Bastsale, J. C. Moyne**.** John Wiley & Sons, Ltd, 2000.
11. F. Pacheco, S. Cota, T. Silva, M. Senne. Artigo. Química Nova. Volume 32, No. 9, 2294-2298, 2009.
12. Y. Pietrasanta, J. Robin, N. Torres, b. Boutevin. Macromolecular Chemistry and Physics 200(1):142 – 149. 1999.
13. Z. Chen. University of Birmingham, 2012.
14. S. Paszkiewicz. Journal - The Royal Society of Chemical, n7, p. 41745-41754. 2017.
15. T. A. L. Martins; BL. S. Bittencourt; C. M. L. B. Krause. Ambiente Construído, v. 12, n. 2, p. 59-75, 2012.