TENSILE PROPERTIES OF POLYPROPYLENE COMPOSITES REINFORCED WITH ALUMINA NANOPARTICLES AND CARBON SHORT FIBERS

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ABSTRACT

The set of properties and the high productivity obtained through injection molding processing have promoted the use of composites reinforced with short carbon fibers in the production of automobile components. The low strength and stiffness, however, have limited the use of these materials in some applications. The incorporation of inorganic nanoparticles such as alumina (Al_2O_3) is a proposed solution to this problem. There is evidence that nanoparticles promote better interfacial interaction between the polymer and short carbon fibers, improving the mechanical performance of composites. The aim of this work was to develop polypropylene (PP) composites reinforced with alumina nanoparticles and short carbon fibers for the automotive industry. The composites were processed in a twin-screw extruder. The response surface methodology was used to define the content of nanoparticles in the composites and to evaluate the effect of the incorporation of the alumina and polypropylene grafted maleic anhydride (PP-g-MA) on the properties obtained. The hybrid composite that showed the best tensile properties was used as a matrix reinforced with different levels of carbon fiber. The tensile properties were determined by a standardized technique. The results showed that the materials obtained can be used in applications that require low density, high productivity, rigidity and resistance.

Keywords: *Polypropylene, Hybrid composites, Carbon fibers, Alumina.*

INTRODUCTION

Nowadays, there is an increasing use of polymeric thermoplastic composites in the automotive industry, as they make cars lighter and promote greater energy efficiency in the use of fuel(1). The cost, as well as the strength of these materials depend on the manufacturing process. Despite their high mechanical performance, continuous fibers cannot be processed through injection molding, which makes the mass production of these composites difficult(1). As a result, there is a growing tendency to use short fibers as reinforcing elements in thermoplastic matrices, due to the high productivity obtained through the injection molding process and the recyclability. However, these materials have low stiffness and strength, even when high strength fibers such as carbon fibers are used. The strength of these materials is a function of the fiber length and content, as well as the interfacial shear strength, which is very low between polypropylene and carbon fibers.

The addition of nanoparticles to composites filled with fiber-reinforced thermoplastic matrices is an interesting alternative to obtain superior properties without changing the processing conditions, as long as there is a good distribution and dispersion of the nanoparticles between the fibers. In addition to improving the properties of the matrix, nanoparticles also affect the interfacial adhesion between the filler and the matrix. There are reports in the literature indicating that the incorporation of nanofillers improves some properties of short fiber reinforced thermoplastic composites[(1)]. The incorporation of alumina nanoparticles in thermoplastic matrices is a strategy used to improve its properties. The use of low levels of compatibilizers, such as polypropylene grafted with maleic anhydride, can improve the interfacial adhesion between the polymer and the fibers[(1)].
The response surface methodology (RSM) provides an efficient means of determining the optimal formulation of a specific mixture. The measured response depends only on the relative proportions of the components in the mixture[(2-5)]. The objective of this work was to use the RSM methodology to develop hybrid polypropylene composites reinforced with alumina nanoparticles and carbon short fibers.

MATERIALS AND METHODS

Materials

Polypropylene (PP, H503), MFI = 3.5 g/10 min – ASTM D1238 was supplied by Braskem SA.
Polypropylene grafted with maleic anhydride (PP-g-MA, Polybond 3200), MFI = 115 g/10 min – ASTM D 1238, at 190 °C was obtained from Chemtura Industria Quimica do Brasil.
Calcined alumina (Al_2O_3) at the nanometer scale (13 nm) was purchased from Sigma-Aldrich.
Short carbon fibers from Toho Tenax America under the name Tenax®-A/J HT C804, with an average length of 6 mm, diameter (D) of 7 µm, specific mass of 1.8 g/cm³ were kindly donated by Parabor.
The antioxidant Irganox 1010 FF was supplied by BASF.
The calcium stearate compound, Atmer SA 1753, supplied by the company Ciba Especialidades Químicas Ltda, was used as a lubricant in the processing of materials in a single-screw extruder.

Methods

Experimental design of mixtures

The response surface methodology consists of fitting a polynomial mathematical model to a response surface that was obtained according to a specific experimental design, known as statistical mixture design. The content of each component of the mixture can vary between zero (0) and one (1), and the sum of all components is equal to one. The experimental region of a mixture consisting of three components is a triangle defined by the coordinates (0, 0, 1), (0, 1, 0) and (1, 0, 0). The vertices of the triangle correspond to each of the three constituents of the mixture. The sides of the triangle correspond to binary mixtures. The points located inside the triangle represent the ternary mixtures[(2-5)].
In this work, the Minitab 19 software was used for the experimental design of the mixtures. This software was also used to describe the tensile mechanical behavior of the samples. Polypropylene, alumina and PP-g-MA were represented by the input variables designated as PP, Al2O3 and PP-g-AM, respectively.
The mixture components were subjected to the following restrictions: $0.88 \leq PP \leq 1.0$, $0 \leq$ alumina ≤ 0.06 and $0 \leq$ PPg-AM ≤ 0.06. Figure 1 shows the project's region of interest. The circles represent 9 PP/PP-g-MA/Al_2O_3 mixtures, which must be prepared to give an adequate

response surface using an n-degree polynomial equation. Table I shows the composition of the materials under study defined by the Minitab software

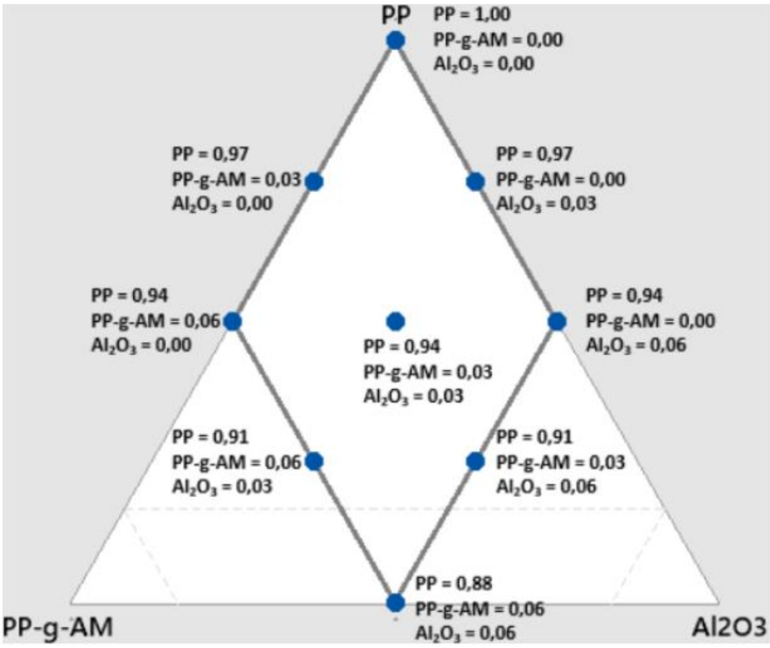

Figure 1: Planning extreme vertices design region.

Table 1: Composition of PP/PP-g-MA/Al_2O_3 composites

Samples code	PP (%)	PP-g-MA (%)	Al_2O_3 (%)
# 1	100	0	0
# 2	88	6	6
# 3	94	0	6
# 4	94	6	0
# 5	97	0	3
# 6	97	3	0
# 7	91	6	3
# 8	91	3	6
# 9	94	3	3

Preparation of PP/PP-g-MA/Al_2O_3 composites

A polypropylene concentrate filled with 8% alumina was prepared in an AX Plástico single-screw extruder, model 30:32 with a diameter of 30 mm and a length (L) / diameter (D) ratio = 32. An antioxidant (1 % w/w) and a lubricating agent (0.5% w/w) were incorporated into the masterbatch. The temperature profile adopted from the extruder feed to the die was 180/200/200/200/200 °C. The extruder speed was 35 rpm. The single-screw extruded material was placed in an oven at 60 °C and subsequently processed and diluted in a Leistritz co-rotating twin screw extruder, model ZSE18MAXX-40D, with a rotation speed of 500 rpm, feed rate of 5 kg/h and temperature of 200/210/190/190/190/190/200/220/220/230 °C. This dilution was required to achieve the proportion of components defined in the experimental mix planning (Table 1)

Determination of tensile mechanical properties

Tensile properties were determined using a Shimadzu universal testing machine, model AG-X Plus with a 5 kN load cell. The tests were carried out in accordance with ASTM D 638, using the dimensions of the Type I specimen. A movable crosshead speed of 20 mm/min was used in all determinations. The specimens for the mechanical tests were obtained by injection molding. The injection molding machine used was the Arburg (IMA/UFRJ), model Allrounder 270 S. The following injection conditions were used: temperature profile – 160/175/185/195/205 °C; injection pressure – 1200 bar; switching volume – 3 cm^3; injection speed - 15 cm^3/s; mold cooling time – 30 s; discharge pressure of 600 bar and discharge time of 2 s. Ten specimens for each sample were used to obtain the mechanical data. The modulus of elasticity was determined using the secant method applied at the point of 2% strain.

RESULTS AND DISCUSSION

Tensile mechanical properties of PP/PP-g-MA/Al_2O_3 composites

The tensile mechanical properties of polypropylene and PP/PP-g-MA/Al_2O_3 composites were determined. Table 2 presents the results obtained for the modulus of elasticity.

Table 2: Tensile Modulus of Elasticity of PP and PP/Al_2O_3 composites

Samples code (PP/PP-g-MA/Al_2O_3 (%))	Modulus of elasticity (MPa)	Standard deviation	Minimum value	Maximum value
#1 - (100/0/0)	881,38	± 38,84	842,54	920,21
#2 - (88/6/6)	961,46	± 69,08	892,38	1030,54
#3 - (94/0/6)	866,65	± 69,21	797,44	935,86
#4 - (94/6/0)	869,63	± 27,55	842,08	897,19
#5 - (97/0/3)	829,75	± 62,63	767,12	892,38
#6 - (97/3/0)	972,06	± 49,36	922,69	1021,42
#7 - (91/6/3)	982,99	± 16,16	966,83	999,16
#8 - (91/3/6)	1254,39	± 109,09	1145,30	1363,48

#9 - (94/3/3)	1025,51	± 80,15	945,36	1105,66

The results show that the tensile modulus increases only with alumina and maleic anhydride are jointly incorporate into the PP. This effect is more evident when the PP-g-MA content incorporated into the PP/Al_2O_3 composite was 3% (samples #8 (91/3/6)% and #9 (94/3/3)%). Alumina is a rigid mineral filler, which restricts the mobility of polymer chains. When added to the polymer along with the compatibilizer, it promoted the increase of stiffness. Similar results were found in other works[6-13]. The results obtained show that there is a synergistic effect on the modulus of elasticity, when PP-g-MA is incorporated into the PP matrix. This effect became more evident in sample #8, PP/PP-g-MA/Al_2O_3 (91/3/6)%, which showed a 42% increase in the modulus of elasticity. As the modulus is a function of the contact surface area between polymer and filler, the results indicate that maleic anhydride promotes the dispersion of alumina particles increasing this area.

Mechanical properties of hybrid composites

Due to the better mechanical properties, sample #8 (91/3/6)% was chosen as the matrix for composites formulated with 10 and 15% of carbon fibers, respectively. The composites obtained showed an increase in the tensile modulus of about 25% and 37% in relation to sample 8. In relation to polypropylene, this increase was 78% and 95%, respectively, and results from the greater stiffness of the carbon fiber.

CONCLUSIONS

The composite PP/PP-g-MA/Al_2O_3 – (91/3/6)% showed the best combination of mechanical properties and was adopted as a matrix for the development of hybrid composites. The composites obtained with incorporation of 10 and 15% of short carbon fibers to this matrix showed an increase in the tensile modulus of about 25% and 37%. In relation to polypropylene, this increase was 78% and 95%, respectively. Therefore, the materials obtained can be used in applications that require low density, high productivity, rigidity and resistance.

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REFERENCES

1. Arao, Y. et al. Mechanical properties of injection-molded carbon fiber/polypropylene composites hybridized with nanofillers. Composites Part A: Applied Science and Manufacturing, v. 55, p. 19–26, 2013.
2. Burlein, G. A. D. Avaliação das propriedades de polietileno de baixa densidade (PEBD),poli(3-hidroxibutirato) (PHB) e de suas misturas com torta de mamona. [s.l.] Universidade do Estado do Rio de Janeiro, 2010.
3. Barros Neto, B.; scarminio, I. S.; bruns, R. E. Como Fazer Experimentos: Pesquisa e Desenvolvimento na Ciência e na Indústria. 2. ed. 2007.

4. Coscione Aline Renée; Andrade, João Carlos de; May, Gyda Marie. O Modelamento Estatístico de Misturas: Experimento Tutorial Usando Voltametria de Redissolução Anódica Quim. Nova, Vol. 28, No. 6, 1116-1122, 2005.
5. Macedo Rose Meire P. R.; Aplicação da metodologia de experimentos para a formulação de massas cerâmicas para telhas. Tese doutorado, Ciências dos materiais. Universidade Federal do Rio Grande do Norte – Natal – RN, 2007.
6. Akil, H. M. et al. Effect of various coupling agents on properties of alumina-filled PP composites. Journal of Reinforced Plastics and Composites, v. 25, n. 7, p. 745–759, 2006.
7. Li, B.; Li, R.; Xie, Y. Properties and effect of preparation method of thermally conductive polypropylene/aluminum oxide composite. Journal of Materials Science, v. 52, n. 5, p. 2524–2533, 2017.
8. Pedrazzoli, D. et al. Thermal, viscoelastic and mechanical behavior of polypropylene with synthetic boehmite alumina nanoparticles. Polymer Testing, v. 35, p. 92–100, 2014a.
9. Pedrazzoli, D. et al. Mechanical and rheological response of polypropylene/boehmite nanocomposites. Journal of Reinforced Plastics and Composites, v. 33, p. 252–265, 2014b.
10. Shuai, X. et al. Mechanical properties and fracture morphology of Al(OH)3/polypropylene composites modified by PP grafting with acrylic acid. Journal of Applied Polymer Science, v. 80, n. 13, p. 2617–2623, 2001.
11. Silva, G. D. A. et al. Effect of alumina ceramic powder dispersion on mechanical properties of polypropylene polymers. Materials Science Forum, v. 727–728, p. 1729–1733, 2012.
12. Streller, R. C. et al. Isotactic poly(propylene) nanocomposites based upon boehmite nanofillers. Macromolecular Materials and Engineering, v. 293, n. 3, p. 218–227, 2008.
13. Zhao, H.; Li, R. K. Y. Crystallization, mechanical, and fracture behaviors of spherical alumina-filled polypropylene nanocomposites. Journal of Polymer Science, Part B: Polymer Physics, v. 43, n. 24, p. 3652– 3664, 2005.