EVALUATION OF THE EFFECT OF FLAME RETARDANT ADDITIVES AND PHOTOSTABILIZERS ON POLYPROPYLENE COMPOSITES

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Abstract: Polypropylene (PP) is the most widely used thermoplastic with potential applications in many fields, but its high flammability and photosensitivity limit its applications. The objective of this study is to compare the performance of two flame retardant additives and investigate the influence of photostabilizers on the mechanical and rheological properties of PP composites. Flammability tests indicated an increase in the flame-retardant action of the composite when a combination of halogenated and non-halogenated flame retardants was added. Mechanical tests showed an increase in the stiffness of the composites compared to the base polymeric matrix. These studies are relevant to assist in the development of formulations with improved properties.

Keywords: Flame Retardants; Photostabilizer; Polypropylene; Mechanical Properties.

AVALIAÇÃO DO EFEITO DE ADITIVOS RETARDANTES DE CHAMA E FOTOESTABILIZADORES EM COMPÓSITOS DE POLIPROPILENO

Resumo: O polipropileno (PP) é o termoplástico mais amplamente utilizado, apresentando potencial aplicação em muitos campos. Porém, as altas flamabilidade e fotossensibilidade limitam suas aplicações. O objetivo deste trabalho é comparar o desempenho de dois aditivos antichama e estudar a influência de fotoestabilizantes nas propriedades mecânicas e reológicas de compósitos de PP. Ensaios de flamabilidade indicaram aumento na ação retardante de chama do compósito ao qual foi adicionado uma combinação de antichamas halogenados e não-halogenados. Ensaios mecânicos evidenciaram um aumento na rigidez dos compósitos em comparação à matriz polimérica base. Os estudos são relevantes para auxiliar o desenvolvimento de formulações com melhores propriedades.

Palavras-chave: Retardantes de Chama; Fotoestabilizante; Polipropileno; Propriedades Mecânicas.

1. INTRODUCTION

Polypropylene (PP) is a polymeric material derived from polyolefin with numerous desirable attributes, including excellent mechanical properties such as high impact resistance and molding flexibility. Also, it is non-toxic and more cost-effective than polyethylene [1, 2]. PP stands as the predominant thermoplastic, showing considerable potential across various industries, including packaging, automotive, and building construction [3]. However, its widespread use is hindered by inherent characteristics, such as high flammability and photosensitivity. [4, 5], as well as specific mechanical property constraints, which limit its applications.

In this context, researchers have been exploring methods to enhance fire performance and reduce the photodegradation rate of polymers in general. The use of flame retardant additives and photodegradation stabilizers during processing has proven to be a highly effective and economically viable method [6], and it is reported as an alternative to improve the stability of PP composites [3,7].

Commercially, the most commonly used flame retardant additives for PP are halogenated, whose action involves the neutralization of free radicals released during the polymer pyrolysis stage, interrupting the mechanism that sustains the combustion process [3, 4]. Halogen-free flame retardants are also reported; however, their efficiency requires a higher dosage, making the final product less competitive [6]. Thus, it is suggested to use non-halogenated flame retardants incorporated with halogenated flame retardants in order to promote a synergistic effect that guarantees greater efficiency of the formed flame retardant compound.

Among the classes of photostabilizers, sterically hindered amines (HALS) have been widely used for PP due to their high efficiency and action through more than one mechanism [7]. Aspects of the use of HALS in conjunction with halogenated flame retardants have been pointed out as antagonistic, since the performance of the anti-UV is reduced in an acid medium [6]. Therefore, new formulations of photostabilizers that present low interaction with acidic species from halogenated products are being studied in this work.

The aim of this work is to investigate the influence of flame retardant and photostabilizing additives on the flammability and mechanical properties of polypropylene composites. In this sense, a comparative study of the efficiency of halogenated (decabromodiphenyl ether and antimony trioxide) and non-halogenated (triazine derivatives) flame retardant agents on the flammability of polypropylene was carried out, in addition to the analysis of the interference of anti-UV agents (HALS) on the mechanical and rheological properties of PP composites.

2. METHODOLOGY

Formulations F1 and F2 were developed using Braskem's CP295 polypropylene resin, which is a heterophasic copolymer with high melt flow index (20 g/10 min) and impact resistance, with a secant flexural modulus corresponding to 750 MPa. These formulations were extruded with a combination of the photostabilizers UNIVUL 4050 FF and UNIVUL 5050 H, along with the flame retardant additives Decabromodiphenyl Ether ($C_{14}H_4Br_{10}$) and Antimony Trioxide (Sb_2O_3). Both formulations contain 10% by weight of Calcium Carbonate ($CaCO_3$) as a reinforcing agent and 10% of recycled PP, also by weight. The percentage choices were based on values from the literature [8] and supplier recommendations. All values can be seen in Table 1.

Table 1. Formula compositions, in percentage.

	PP CP295	Recycled PP	$CaCO_3$	$C_{14}H_4Br_{10}$	Sb_2O_3	Flamestab®	Univul 4050FF	Univul 5050H
F0	100	-	-	-	-	-	-	-
F1	50	10	10	22	7,5	-	0,25	0,25
F2	64	10	10	12	3	1	-	-

The formulations were processed using a co-rotating twin-screw extruder, KraussMaffei model ZE 30RX50D-UTX-UG, with a screw diameter of 30 mm and a length-to-diameter ratio (L/D) of 40/30, and a total length of 1200/1500 mm. The processing parameters adopted were a screw speed of 300 rpm, and the temperature settings for the heating zones were as follows: Z_1= 30ºC, Z_2= 175ºC, Z_{3-4}= 180ºC, Z_{5-7}= 185ºC, Z_{8-9}= 190ºC, Z_{10-11}= 195ºC, Z_{12}= 200ºC.

The pelletized composites were dried in a conventional oven for 4 hours at 100°C. Subsequently, the materials were dehumidified and then injected to obtain the test specimens according to ASTM standards. The ROMI injection molding machine, model PRIMAX 100R, was used for the injection process, and the injection process parameters can be found in Table 2.

Table 2. Injection process parameters.

Pressure [bar]	Speed [m/s]	Holding pressure [bar]	Dosage Volume [cm³]	Backpressure [bar]	Feeding speed [mm/s]
950	110	700	55	10	350
Real Temperature [°C]		**Heating**			
		Nozzle	**Zone 3**	**Zone 2**	**Zone 1**
		210	180	190	200

For the analysis of mechanical properties, impact and flexural tests were conducted. The flexural test was performed according to ASTM D790 standard, using a universal testing machine (Emic, model DL 2000) at a crosshead speed of 2 mm/min and a support span of 51 mm. The impact resistance test, on the other hand, was carried out using a CEAST INSTRON 9050 machine at 23°C, following ASTM D256 standard.

To evaluate the influence of fillers on the viscosity of PP and PP composites, melt flow index (MFI) tests were performed on samples F0, F1, and F2. The MFI analysis was conducted according to ASTM D1238-2013 standard using a KAYANESS INC. model 7050 apparatus. The test parameters were set at a temperature of 230°C and a load of 2.60 kg.

The flammability test was conducted in accordance with the Underwriters Laboratories (UL94) standard, with five replicates, following the vertical flame test procedure. For this purpose, five test specimens with dimensions of 125 ± 5 mm × 13 ± 0.5 mm × 10 ± 0.5 mm were clamped at a distance of 300 mm from the base of the combustion chamber. The specimens were exposed to a controlled flame for two 10-second intervals, and the flame extinction time was recorded. A piece of cotton was placed at the base of the combustion chamber, parallel to the test specimen, to check for the presence of flaming particles.

The injected samples were characterized based on these tests, and the analysis of the obtained data is presented below.

3. RESULTS AND DISCUSSION

3.1. Flammability Tests

The flammability of PP CP295 (reference), F0, and the PP composite formulations F1 and F2 was evaluated according to the UL94 standard, with five replicates for each sample.

The flame duration times for each specimen after the first flame application (t1) and after the second application (t2) were recorded, and the results for F0, F1, and F2 can be found in Table 3.

Table 3. Flammability Test Data (UL 94) for F0, F1, and F2.

Formulation	Rating	Burning time (t1+t2)	Flame hit clamping claw	Cotton was burnt
F0 (reference)	Failed for V0	>50 s	Yes	Yes
F1	Failed for V0	>50 s	No	Yes
F2	Approved for V0	<10 s	No	No

According to the data from Table 3, both the reference sample (F0) and F1 did not meet the V0 classification according to the UL94 standard. After 10 seconds of flame application, the F0 and F1 test specimens continued to burn for over 60 seconds, melting and igniting the cotton. This result was expected for F0 since polypropylene is a hydrocarbon derivative and, as such, is known to exhibit flammability and a high dripping rate. The F1 sample, with additives, did not demonstrate the expected fire resistance and extinction, indicating the need for adjustments by increasing the additive content.

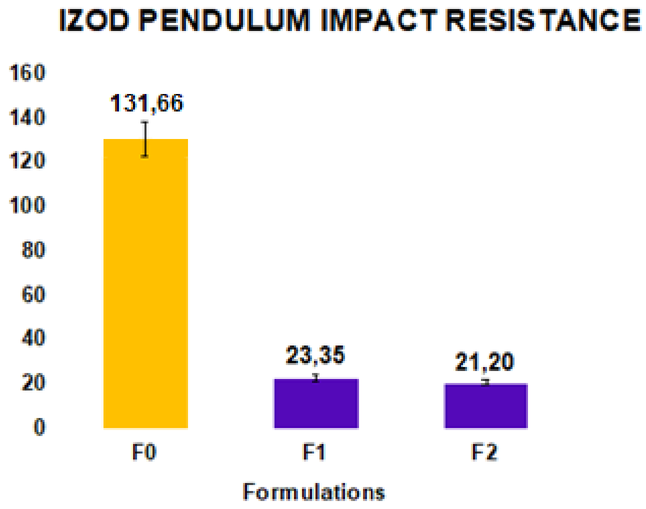
On the other hand, for F2, although there was dripping onto the cotton, it did not ignite, and the flame extinguished shortly after removing the flame source. Thus, the data obtained for F2 comply with the V0 fire behavior classification (UL94-V). This result suggests the higher efficacy of the additive combination (halogenated + non-halogenated) when compared to using only halogenated flame retardants. However, a more thorough comparison requires analyzing formulations with different additive levels, as well as formulations without halogenated flame retardants in their composition, which should be considered in future studies.

3.2. Mechanical Tests

3.2.1. Impact Test

Based on the results of the impact resistance test at 23°C (Figure 1), comparing formulations F1 and F2 with the base copolymer CP 295, a drastic reduction in impact resistance was observed. This can be attributed to the addition of $CaCO_3$, flame retardant additives, and UV stabilizers, which contribute to decreasing the toughness of the material. Additionally, the incorporation of fillers and stabilizers provides the matrix with additional rigidity. As a consequence, there is an increase in the resistance of the material to deformation under stress, leading to a higher susceptibility to fractures. It was also observed that the samples from F0 did not break during the tests, confirming the no-break characteristic of CP 295 [9].

Figure 1. Impact resistance data.

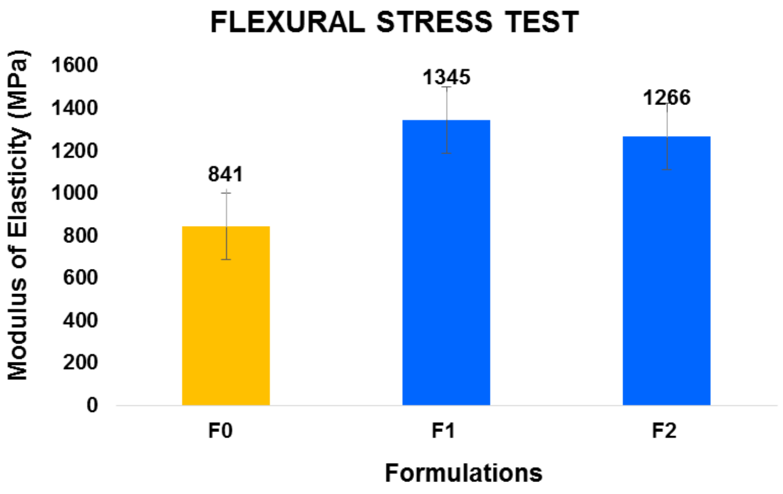


3.2.2. Flexural stress test

From the data obtained in the flexural test (Figure 2), a significant increase in the modulus of elasticity was observed for formulations F1 and F2 when compared to the base copolymer CP 295. These results are consistent with the addition of $CaCO_3$ to the polymer matrix, resulting in increased rigidity of the composites compared to the precursor due to the interaction between the filler and the matrix. This indicates that both formulations have the potential for applications in systems that require higher strength and rigidity, such as construction materials [9].

F1 showed an approximately 6% increase in the modulus of elasticity compared to F2. Despite containing only 0.5% of UV stabilizer, F1 has a higher percentage of stabilizers added to the matrix compared to F2. This difference in additive content may have contributed to the observed variation.

Figure 2. Data obtained from the flexure stress test.

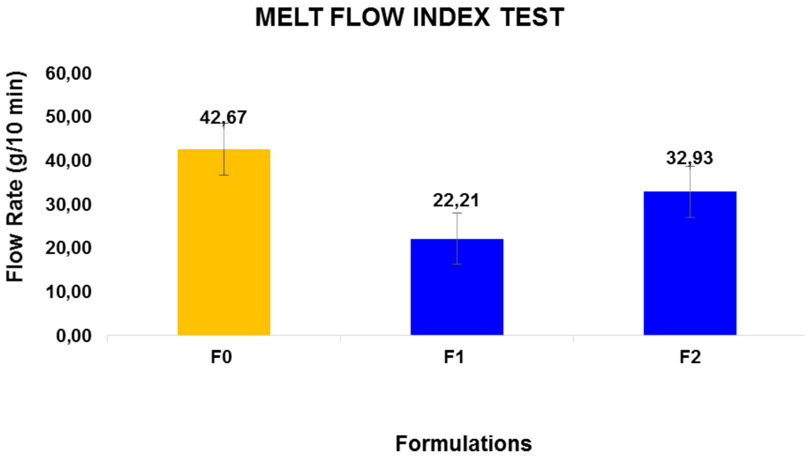


3.3 Ensaios de índice de fluidez

Figure 3 presents the results obtained for the melt flow index (MFI) of the analyzed formulations. In the formulation containing only halogenated flame retardant (F1), a decrease of 48% in the MFI was observed compared to the standard (F0). On the other hand, in the formulation containing both halogenated and non-halogenated flame retardants (F2), a decrease of 24% was observed compared to F0. This indicates that the presence of filler ($CaCO_3$) and additives (flame retardant and UV stabilizer) significantly influences the reduction of the MFI. According to [10], the presence of solid fillers in the polymer matrix, combined with the addition of stabilizers, restricts the mobility of the free polymer, resulting in increased material viscosity and consequently reducing the flow of the polymer in the molten state (lower melt flow index).

The formulation F1 contains 14% more additives in its composition compared to formulation F2 (F1 = 30% and F2 = 16% of additives). This contributes to explaining the difference in melt flow index values between formulations F1 and F2.

Figure 5. Melt index data.



4. CONCLUSION

In this study, the efficiency of the combination of halogenated and non-halogenated flame retardant additives in the flame resistance of composites manifested in the flammability process was confirmed. All flame retardant additions, mainly the non-halogenated base, combined with UV additives, influenced the influence to reduce the impact resistance of the PP compounds. However, an increase in their safety was evidenced by the higher modulus of elasticity compared to the base polymeric matrix. As a future perspective, it is intended to evaluate the properties of sensitivity to ultraviolet light through accelerated aging experiments.

Acknowledgments

Our sincere acknowledgment to SENAI CIMATEC for providing their facilities, which were instrumental in conducting this study. Additionally, we extend our appreciation to the Brazilian agencies EMBRAPII for financial support.

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