ANTIBACTERIAL AND THERMAL PROPERTIES OF SEBS/PP BASED COMPOUNDS LOADED WITH ZINC OXIDE

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Abstract - Compounds based on styrene-ethylene/butylene-styrene (SEBS) copolymers are a class of thermoplastic elastomers (TPE), usually blended with polypropylene (PP), are recyclable and used in domestic appliances. In order to prevent microbial attack, antimicrobial additives, like zinc oxide (ZnO), can be added in TPE compounds. In that sense, the aim of this study was to evaluate the effect of ZnO (0, 1, 3 and 5 %wt) in antimicrobial and thermal properties of compounds based on SEBS/PP. Samples were aged in cleaning solution (3% neutral detergent) and characterized by thermal and antimicrobial properties against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). Additions of ZnO did not affect the thermal properties. In unaged compounds loaded with 3% zinc, antimicrobial assay showed a reduction over 42% in *E. coli* and over 49% in *S. aureus* population. In aged samples, there was a reduction of 49% of *E. coli* population and of 2% of *S. aureus*.

Keywords: *Antibacterial, home device, SEBS, TPE, zinc oxide*

Introduction

A range of thermoplastic elastomers (TPE) are applied in home use devices [1,2]. TPE compounds based on block copolymer poly(styrene-b-(ethylene-co-butylene)-b-styrene (SEBS) should be used in blends with polypropylene (PP), plasticizers and fillers to facilitate processing and reduce costs. Besides that, the absence of C-C double bond makes this polymer resistant to aging [3].

These materials can be applied in products such as toothbrush cable, bath mats, which are submitted to contact with skin and high humidity conditions [4-7] and for this reason are susceptible to microbial attack. To inhibit the growth of microorganisms antimicrobial additives can be loaded in the polymer matrix [7]. The most commonly used inorganic antimicrobial additives are silver, zinc and copper based. Inorganic biocidal additives, as zinc oxide (ZnO) have higher heat resistance than organic ones [8]. They can withstand degradation during processing of the thermoplastic polymers (~ 200 °C) [9] and, once incorporated into the polymer matrix, remains in matrix for a long period of time [9,10].

This study aims to evaluate the antibacterial efficiency and thermal performance of SEBS/PP based compounds loaded with zinc oxide after ageing test that simulate conditions in bath mats and sink squeegee.

Experimental

Preparation of the Compounds

The compounds (SEBS/PP/oil/calcite) were prepared using a co-rotating double screw extruder with L/D ratio of 40 and screw diameter of 16 mm, model AX 16DR (AX Plásticos). The processing parameters were 226 rpm of screw rotation rate, with temperature profile from 150 to 190 ºC. After mixing, the materials were injection-molded using the Haitan (PL 860/260 - B) at 190 ºC. These parameters were kept for all compositions since changes in processing may interfere with the properties of the compounds [11]. The additive used in this study was zinc oxide supplied by

Perrin S.A. in portions of 0%, 1%, 3% and 5%. A sample without additive (standard) was used to compare changes on antibacterial efficiency and thermal performance. The compounds were named as shown in Table 1:

Table 1 ZnO content of prepared compounds

Compounds	*ZnO content*
Standard	0%
C-ZnO1	1%
C- ZnO3	3%
C- ZnO5	5%

Ageing test

In order to simulate the use of compounds under specific conditions, ageing tests were performed based on ASTM D 471. To this aim test specimens were immersed in a cleaning solution (3% neutral detergent) at 70 °C for 168 h.

Characterization

The thermogravimetric analysis (TGA) were performed on a thermogravimetric analyzer (TA Instruments, model Q500), according to ASTM D 6370, in an inert atmosphere of nitrogen conducted in the temperature range from 20 °C to 550 °C, with a heating rate of 20 °C/min.

The melt temperature and degree of crystallinity in the compositions were determined by differential scanning calorimetry (DSC) analyzed according to ASTM D 3418, in a differential scanning calorimeter (TA Instruments, model Q-100). The analyses were performed using around 6.3 ± 0.5 mg of sample. The samples were subjected to heating from -30 °C to 180 °C at a heating rate of 10 °C/min. The temperature of 180 °C was maintained for 5 min and cooled to -30 °C, at the same rate and reheated again, under a nitrogen atmosphere. Melting temperature (Tm), enthalpy of fusion (ΔH_f), crystallization temperature (Tc) and degree of crystallinity (Xc) were obtained in the second cycle. As the melting enthalpy of the sample considers the heat of fusion of the sample with all its constituents, the value obtained was corrected considering only the content of polypropylene in the composition. The degree of crystallinity was calculated using Eq. 1:

$$\text{Crystallinity } (\%) = \Delta Hf / (w.\Delta Hf^{\circ}) .100 \qquad (1)$$

Where:

ΔHf = sample enthalpy of fusion per gram (J/g);

w = weight fraction of the PP found in the composite;

ΔHf° = enthalpy of fusion per gram of 100% crystalline PP (209 J/g)[12].

Japanese industrial standard (JIS) Z 2801 was applied to evaluate antibacterial efficiency of samples against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) bacterial strains. The result was expressed as a percentage value calculated from the difference between the numbers of colony forming units per square centimeter (CFU/cm^2) in the initial incubation period and final incubation period.

Results and Discussion

Thermal stability of compounds were evaluated by thermogrevimetric analysis. Fig. 1 shows TG and DTG curves of TPE compounds with different concentrations of ZnO additive. It was observed that in the concentration of additive used ZnO did not cause significant changes in the material decomposition profile. The maximum decomposition temperature remained constant in each

thermal event of both, unaged (Fig. 1a) and aged (Fig. 1b) samples. The maximum degradation temperatures are presented in Table 2. Aged samples shown lower thermal stability than unaged samples in onset and event 1 temperatures.Catto [13] showed that samples subjected to weathering lose thermal stability in relation to unaged samples due to photooxidation and degradation by hydrolysis .

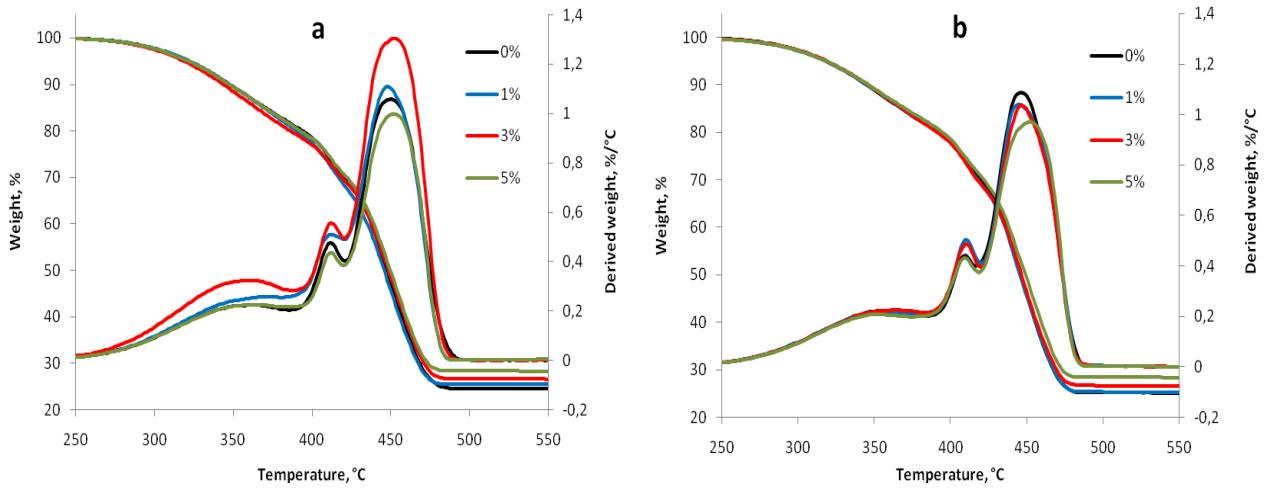

Figure 1 TG and DTG curves of a) unaged and b) aged ZnO loaded compounds

Table 2 Temperatures in maximum degradation rate of beginning of degradation (onset), first event (e1), second event (e2) and third event (e3) obtained by TG/DTG analysis.

Sample	T_{onset} (°C)		T_{e1} (°C)		T_{e2} (°C)		T_{e3} (°C)	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Standard	301	294	362	356	412	409	450	446
C-ZnO1	302	294	365	357	413	410	448	445
C- ZnO3	300	293	362	363	412	410	452	447
C- ZnO5	301	294	364	351	412	410	453	453

Table 3 shows the results of Tm, ΔH_f, Tc and Xc of the PP present in TPE compounds. The addition of ZnO did not change the Tm and Tc values of the compounds. Thus, it can be concluded that low amounts of this additive did not interfere in the crystalline structure of the PP in this composition. Modifications in ΔH_m and Xc values were not significant and are within the margin of error expected in the analysis [14].

Table 3 Melting (T_m) and Crystallization (T_c) Temperatures, Fusion Enthalpy (ΔH_f) and Crystallization fraction (Xc)

	T_m (°C)		T_c (°C)		ΔH_f (J/g)		X_c (%)	
Sample	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Standard	154	154	112	112	14.7	13.5	47	43
C-ZnO1	154	154	112	111	14.3	14.1	46	46
C- ZnO3	154	154	112	111	13.6	14.1	45	47
C- ZnO5	154	154	111	112	14.3	13.5	48	45

Antibacterial properties of zinc loaded compounds were evaluated against *S. aureus* and *E. coli* bacteria and were compared to standard samples. Fig. 2 shows the variance in bacterial populations in the standard and loaded samples.

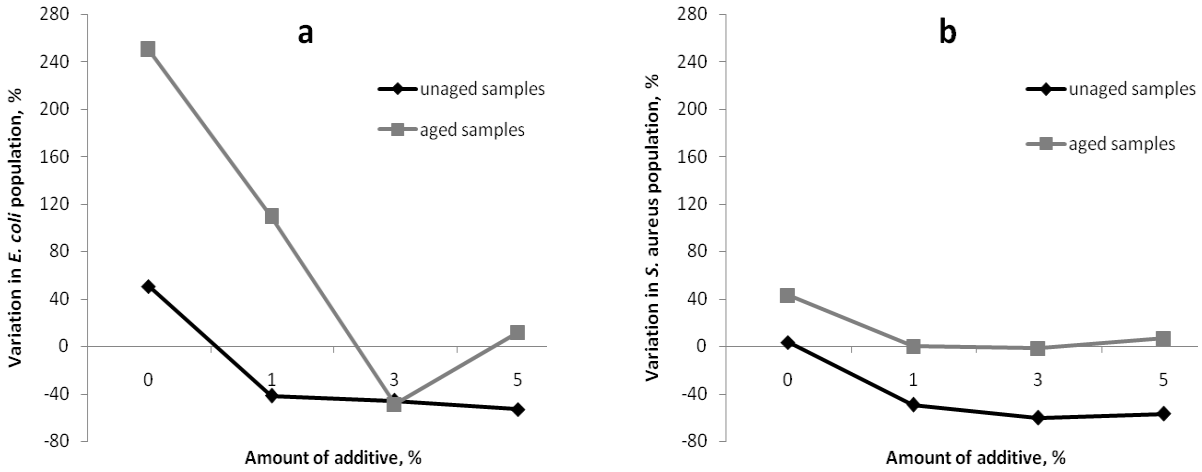

Figure 2 Variation in a) *E. coli* and b) *S. aureus* population in aged and unaged ZnO loaded TPE compounds.

It was observed that unaged standard samples were susceptible to the growth of both bacterial species, showing an increase of 50% and 4% of *E. coli* and *S. aureus*, respectively. The ZnO loaded TPE compounds showed an antimicrobial action, with a reduction between 42% and 53% of *E. coli* population (Fig. 2a), and between 49% and 60% of *S. aureus* population (Fig. 2b). The bactericidal activity increased according to the amount of ZnO added in the composition. Many hypotheses have been formulated to explain ZnO antibacterial property. Saway and colleagues [15,16] found evidences of reactive oxygen species (ROS), such as hydrogen peroxide (H_2O_2) and single oxygen (O_2^-), on particle surface; Pasquet and colleagues [17] found evidence of zinc ions (Zn^{2+}) and zinc complexes liberation. All this phenomena can cause cell wall damage and bacteria death.
It was noted that *E. coli* was more resistant to the biocidal action of ZnO. This behavior is in agreement with previous reports, showing Gram negative bacteria as more resistant to ZnO action [18, 19]. When submitted to aging in cleaning solution, ZnO loaded compounds reduced their antimicrobial action, showing values of reduction of 49% and growing of 109% against *E. coli* (Fig. 2a) and reduction of 2% and growing of 7% against *S. aureus* (Fig. 2b). It has been reported that polymer degradation can cause changes on antimicrobial TPE surface, such as modifications on topography, on surface free energy and the appearance of carbonyl groups, which reduces additive efficacy and favor bacterial development [20].

Conclusion

Thermogravimetric analysis and differential scanning calorimetry showed that ZnO additive do not change the thermal stability in TPE compounds based on SEBS/PP/oil/calcite. Moreover, ZnO did not interfere on cristanility of materials, verified by the DSC.
Microbiological assay showed the potential of ZnO to be used as an antibacterial additive in TPE compounds, however, it decrease this propertie when subjected to humid and warm conditions for a long period of time.

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References

1. J. G. Drobny *Handbook of thermoplastic elastomers*, William Adrew Publishing, New York, 2007.
2. R. Shanks; I. Kong in *Termoplastic Elastomers*, A. Z. EL-Sonbati, Ed.; InTech, 2012, 137-154.
3. M. B. Medienta-Gárcia; U. Páramo-Garcia; N.P. Díaz-Zavala; J.G. Robledo-Muñiz; J.L. M. Sugimoto; K. Sakai; Y. Aoki; T. Taniguchi; K. Kiyama; T. Ueda *J. Polym. Sci. Pol. Phys*. 2009, *47*, 955.
4. N. Karakaia; O. G. Ersoy; M. A. Oral; T. Gonul; V. Deniz *Polym. Eng. Sci*, 2010, *50*, 677.
5. W. G. F. Sengers, Ph.D. Thesis, Delft University of Technology, 2005.
6. P. Sengupta; J. W. M. Noordermeer *J. Elastom. Plast.* 2004, *36*, 307.
7. D. Nichols *Rapra Technol*. 2004, *15*, 14.
8. W. N. Schirmer; L. B. Pian, M. S. E. Szymanski; M. A. Gauer *Ciên. Saúde Coletiva*. 2001, *16*(8), 3583.
9. A. Jones *Plast. Addict. Comp*. 2009, *26*.
10. H. Palza *Int. J. Mol. Sci.* 2015, *16*, 2009.
11. D. Tomacheski; M. Pittol; C. E. Ermel; D. N. Simões; V. F. Ribeiro; R. M. C. Santana, *Polym. Bull*. 2017, *74* (5).
12. S. V. Canevarolo, *Técnicas de Caracterização de Polímeros*, Artliber, São Paulo, 2003.
13. A. L. Catto, Ph. D. Thesys, Universidade Federal do Rio Grande do Sul, 2015.
14. H. M. Tiggemann, Sc. M. Thesys, Univesidade Federal do Rio Grande do Sul, 2012.
15. J. Sawai; E. Kawada; F. Kanou; T. Kokugan; M. Shimizu. *J. Chem. Eng. Jpn.* 1996, *29* (4), 627.
16. J. Sawai; S. Shoji; H. Igarashi; A. Hashimoto; T. Kokugan; M. Shimizu; H. Kojima *J. Ferment. Bioeng.*1998, *86* (5), 521.
17. J. Pasquet; Y. Chevalier; J. Pelletier; E. Couval; D. Bouvier; M-A. Bolzinger. *Colloid Surface A.* 2014, *457*, 263.
18. R. Brayner; R. Ferrari-Iliou; N. Brivois; S. Djediat; M. F. Benedetti; F. Fiévet *Nano. Lett*. 2006, *6* (4), 866.
19. A. D. Erem; G. Ozcan; M. Skrifvars *Text. Res. J.* 2013, *83*(20), 2152.
20. D. Tomacheski; M. Pittol; D. N. Simões; V. F. Ribeiro; R. M. C. Santana. *Appl. Surf. Sci*. 2017, *405*, 137.