INFLUENCE OF COPPER MICROPARTICLES ON THE THERMAL AND ANTIBACTERIAL PROPERTIES OF SEBS/PP BASED COMPOUNDS

Vanda F. Ribeiro[1,3*], Erton Cardoso Jr.[2,3], Douglas N. Simões[1], Michele Pittol[1], Daiane Tomacheski[1,3] and Ruth M. C. Santana[3]

1 – Softer Brasil Compostos Termoplásticos, Campo Bom, RS, Brazil
vanda@softerbra.com.br
2 - BRUTT Indústria Metalúrgica, Cachoeirinha, RS, Brazil
3 – Departamento de Materiais, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil

Abstract -This study evaluated the adoption of copper microparticles as antimicrobial agent in thermoplastic compounds based in styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS) and polypropylene (PP). Copper is historically known to have biocide qualities and its addition into polymeric matrices can be a good option for producing thermoplastic elastomers (TPEs) with antimicrobial properties. In this work was evaluated the interference of the addition of copper microparticles on the thermal behavior and antimicrobial properties of compounds based SEBS/PP against *Escherichia coli* and *Staphylococcus aureus*. The results from antimicrobial tests showed a reduction of 99.99% in counts of both bacteria tested. The addition and concentration of copper microparticles in compounds did not cause significant variations in thermal properties of the compounds.
Keywords: *SEBS, PP, TPE, copper, antibacterial properties.*

Introduction

Thermoplastic elastomers (TPEs) based on styrene-(ethylene-butylene)-styrene (SEBS) are used in a variety of general-purpose rubber items by its versatility in processing, design, recyclability and lower cost. The SEBS is blended with polypropylene (PP) to make stiffer compounds and to improve processability [1]. These characteristics promoted the use of SEBS/PP based compounds in a variety of applications, such as hygiene articles with soft touch surface, household items and automotive components, including parts of heating, ventilation and air conditioning systems (HVAC).

HVACs can be source of contamination, which can bring serious health issues and unpleasant smell to the environment [2,3]. The main contaminants of biological origin in the air of indoor environments are bacteria, fungi, pollen, mites and spores [4].

HVAC filters with antimicrobial agents are widely available on the market, which does not occur with other plastics components where the use of SEBS/PP blends is a raw material option. Once this family of compounds does not have inherent antimicrobial properties, the main form to obtain antimicrobial materials is the incorporation of biocidal additives into the compound in a molten state. Inorganic antimicrobial additives are thermally more stable than the organic ones [5]. This inorganic antimicrobial agents, does not suffer degradation under standard processing conditions of thermoplastic polymers (~200°C) [6] and, once incorporated in the polymer matrix, the metal ion does not lose its biocidal effect and remains in the polymer, ensuring effect for a long period of time [7,8]. The most used inorganic antimicrobial additives are based on silver, zinc and copper.

Several studies make reference to efficiency of copper against pathogenic bacteria, fungi, algae and viruses. The biocidal effect of copper can be related to its direct contact with the metal followed by damage of numerous key components in bacterial cells membrane or viral protein structure [8,9].

The purpose of the present study was to verify the action of copper microparticles as antimicrobial agent in SEBS/PP/oil/calcite compounds predicting its use in parts of heating, ventilation and air conditioning system of automotive vehicles. In addition to antimicrobial assays, all loaded compositions were evaluated on their thermal properties.

Experimental

Materials and Methods

The matrix of thermoplastic compound used in this study was based on styrene-(ethylene-butylene)-styrene triblock copolymer with linear structure (styrene/rubber ratio of 30/70, molecular weight of 192.031 atomic mass units and Mw/Mn= 1.36) and polypropylene homopolymer with melt index of 1.5 g/10 min. The plasticizer used was a white mineral oil with a viscosity of 105 cST. Calcite with 15 µm average particle size was used as mineral filler. Copper microparticles, having density of 1.18 g/cm³ and 46 µm as average particle size, provided by Brutt Indústria Metalúrgica, was tested as antimicrobial agent.

The weight percentage copper microparticles (CuMP) in the compounds were 0%, 1 %, 2 % and 4 % and this was the only variable component in the compositions. The compounds were produced in a co-rotating double screw extruder (L/D ratio of 40 and 16 mm screw diameter) with temperature profile from 150ºC to 190ºC. The extrusion parameters were kept constant for all samples. Flat sheets for the cutting of test specimens were injection molded at 190ºC. The thermal analysis was carried out by Differential Scanning Calorimetry using a DSC Q100 (TA Instruments) under flowing nitrogen. The samples were heated from -30°C to 180°C at a heating hate of 10ºC/min. Thermogravimetric analysis (TGA) were performed using a TGA TA Q500 (TA Instruments) under flowing nitrogen from 20°C to 800°C. Heating rate was 20°C/min and the amount of sample was ~ 11 mg.

Morphological analysis of the samples was performed with scanning electron microscopy (SEM), where the samples were deposited in carbon type stuck to stub, metalized with gold, compounds were cryogenically broken in liquid nitrogen. For image acquisition, a SEM of field emission (SEM-FEG) (Inspect F50, FEI) was used with 20 kV, spot 3 and working distance (WD) of 10 mm.

Japan Industrial Standard (JIS) Z 2801: 2010 was applied to evaluate antibacterial abilities of the compounds against *Escherichia coli* ATCC 8739 (*E. coli*) and *Staphylococcus aureus* ATCC 6538 (*S. aureus*) strains. The condition of incubation was 24 h at 35 ± 1°C. The bacterial reduction was expressed as a microbial value calculated from the difference between the number of colony forming units (CFUs) per square centimeter, at zero hours (initial) and after 24 hours of incubation.

Results and Discussion

Thermal Properties

Thermogravimetric analyzes were performed to observe the modifications in the thermal stability of the compounds. As can be seen in DTG curves (Fig. 1) the addition of CuMP did not cause significant changes in the thermal degradation behavior of the compounds. All samples have three peaks of decomposition, the first and second being oil decomposition, and the third corresponding to SEBS and PP. Taking as reference the temperature of 415°C such as the final temperature of loss of plasticizer, is observed that in this initial phase of decomposition, the presence of copper microparticle caused a slight increase in the thermal stability.

The compounds without CuMP had a loss of 20% at a temperature of 376.2ºC and the compounds with CuMP presented this loss of mass at 378.9ºC (1%), 381.8ºC (2%) and 381.2ºC (4%). On the other hand, no significant effects were observed in the decomposition of the polymers, which can be observed in Fig.2 that shows the TGA curve of the composite with 2% of CuMP.

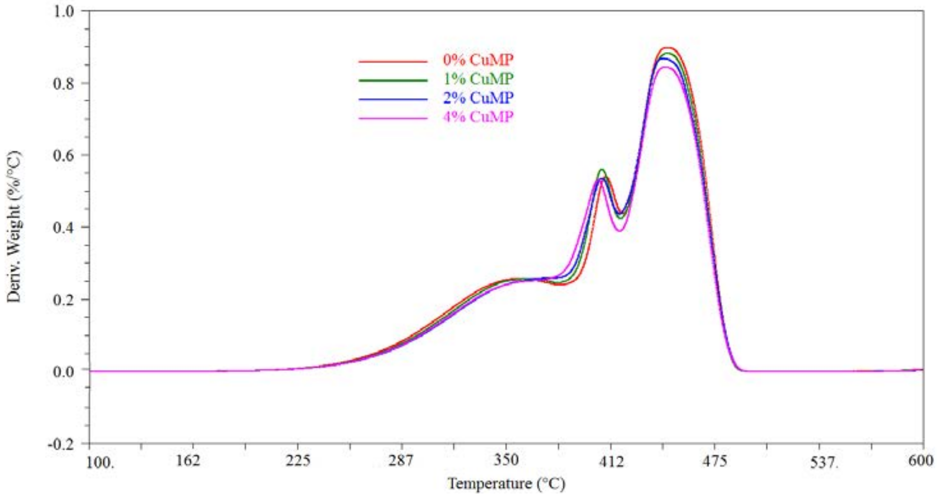

Figure 1 – DTG curves of the compounds.

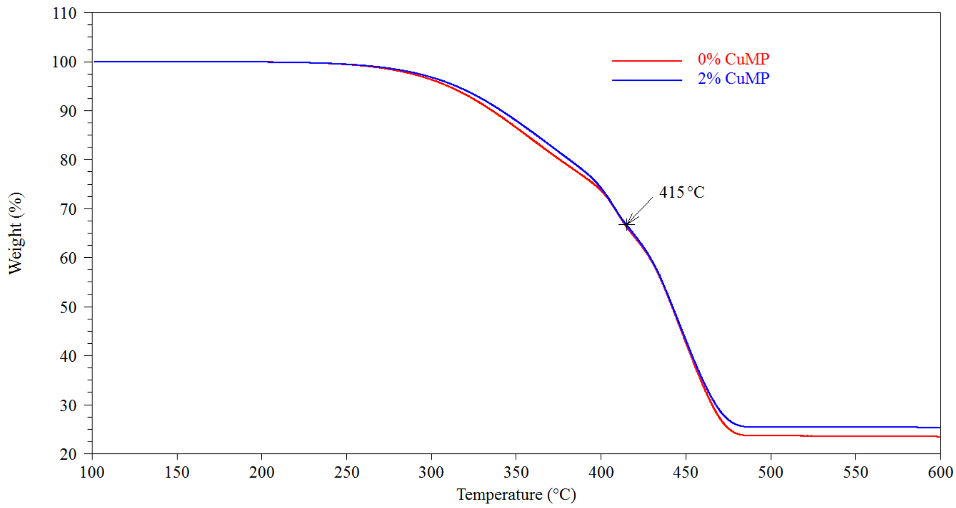

Figure 2 – TG curves of the compound without and with 2% of CuMP.

According to the literature, copper is a metal with high heat capacity and thermal conductivity and can promote or delay the thermal degradation of the organic phase at different rates [10], as can be verified in several studies [11,12,13]. The thermal conductivity performance of the polymers modified with the inclusion of metallic particles will vary according to the thermal conductivity of the metallic fillers, the particle shape and size, the volume fraction and the spatial arrangement in the polymer matrix [14].
Results of DSC are show in Table 1. It is observed that the temperature of crystallization (Tc) decrease with the increase of copper content. This suggests that the particles inhibit the crystallization of PP homopolymer, which is confirmed by reducing the degree of crystallinity (Xc).

Table 1 - Melting (T_m) and Crystallization (T_c) Temperatures, Fusion and Crystallization Enthalpy (ΔH_f) and degree of crystallinity of PP phase (X_c).

	T_m(°C)	ΔH_f (J/g)	T_c(°C)	ΔH_c (J/g)	X_c (%)
0 % CuMP	152.6	11.7	108.3	13.2	47.2
1 % CuMP	152.2	11.4	107.4	12.6	46.2
2% CuMP	152.4	10.9	106.8	12.4	44.5
4% CuMP	152.5	10.8	106.9	12.1	45.3

With the introduction of copper particles the fusion enthalpy (ΔH_f) decreases slightly, from 11.7 J/g (sample without copper) to 10.8 J/g (4% of copper content), not being observed significant influence on the melting temperature of the PP phase.

Morphology

The Fig. 3 shows the SEM image of the sample with 1% of CuMP, where the calcite particles are depicted in red and the copper particles are depicted in yellow. Although some points suggest small particle agglomerates, predominantly, the image shows that the copper particles are homogeneously dispersed in the compound matrix.

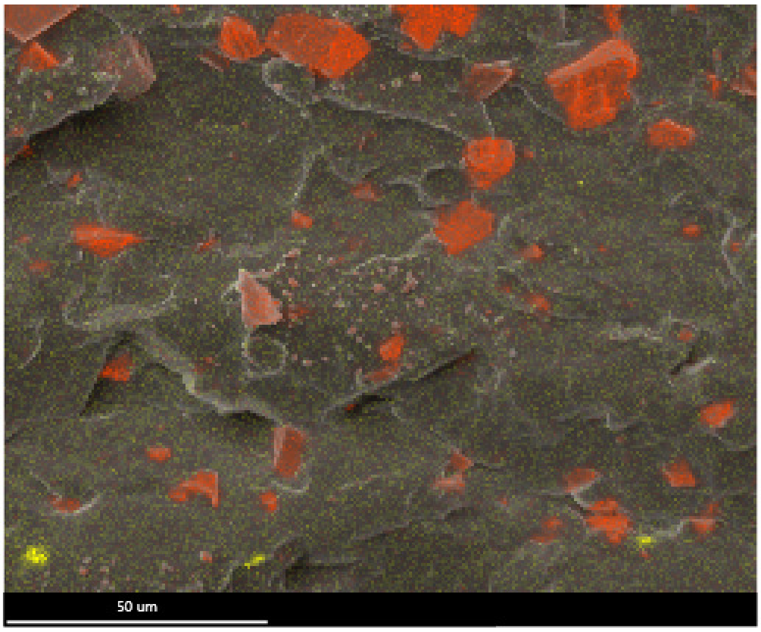

Figure 3 – SEM image of the compounds with 1% of CuMP (Copper are depicted in yellow).

Antimicrobial Activity

Polymers are a great source of carbon and hydrogen, so they are susceptible to action of microorganisms [15]. The activity of the compounds with copper microparticles was evaluated against Gram-positive bacteria (*S. aureus)* and Gram-negative bacteria (*E. coli).* As can be seen in Table 2, the compound without copper was susceptible to both bacteria action. On the other hand, in the concentrations tested, the addition of copper showed a biocidal action with a reduction of almost all bacterial colonies.

Table 2- Antimicrobial activity of the compounds

	E. coli		*S. aureus*	
	Reduction (%)	R	Reduction (%)	R
0% CuMP	No reduction	-	No reduction	-
1% CuMP	99.99	4.25	99.99	4.11
2% CuMP	99.99	4.40	99.99	4.07
4% CuMP	99.99	3.82	99.99	4.20

NOTE: R – logarithmic reduction of bacterial population. Effective if R ≥2.0.

Conclusion

The addition of copper microparticles by melting blending in the formulations of SEBS/PP/oil/calcite shown to be a promising means to obtain compounds with antibacterial properties with excellent inhibition results against *E.coli* and *S.aureus*. The metallic additive did not produce any significant variation in the thermal properties of the compounds. The incorporation of copper microparticles in SEBS/PP compounds can be used in industry to develop antimicrobial products, which can contribute to public health besides increasing the product shelf life.

Acknowledgements

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