CURED ANTIBACTERIAL COMPOUND BASED ON SILICONE RUBBER AND TiO_2 AND ZnO NANOPARTICLES

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Vulcanizing elastomers is a main step, with a major impact on the final product properties. The amount and type of curing agent, curing time, temperature and pressure are important factors that control the degree of crosslinking and the final properties of the product. The vulcanization system used and required quantities of curing agents are selected based on the elastomer used and the envisaged characteristics. The uses of silicone rubber vulcanizates are vast, but they are preferred in medicine and food because relative to rubber mixtures based on other elastomers, they do not contain substances like antioxidants, accelerators, sulfur and other ingredients that are not permissible in terms of toxicology. The purpose of this paper is to develop a compound reinforced with TiO2 and ZnO nanoparticles based on silicone rubber having antibacterial properties determined by the nature and chemical structure of the matrix and the dispersed phase, processing conditions and curing, using innovative technologies for the development of competitive products for the food and medical industries. These advanced materials and technologies will help improve product quality, environmental protection, human health, antibacterial and antifungal sterilization of products, increased turnover for companies and technological competitiveness at international scale.

Keywords: siliconic rubber, antibacterial compound, nanoparticles.

INTRODUCTION

Lately, the field of polymer compounds has featured new improvements in synthesis of elastomers reinforced with nanopowders with antibacterial properties, offering the possibility of obtaining new advanced polymer structures, and the possibility of extending their area of application (Barton, 1990).

Reinforcement promotes physical, chemical and radicalic bonds between ingredient particles (nanoparticles, antioxidants, accelerators, stabilizers, plasticizers, active and inactive fillers, etc.) and macromolecules of silicone elastomer (silicone rubber) as a result of which a rubber-ingredient complex with special properties is formed (Zhou *et al*., 2012).

Due to the wide range of temperatures at which silicone elastomers may be used, from -100°C to +315°C, they can be applied in various fields (Petreus, 1999; Dobrinescu, 1971; Horn *et al*., 1997). They are used mainly in the development of products for the food and medical industry due to their high temperature resistance specific to sterilization, including the fact that they do not contain substances such as antioxidants, curing accelerators, etc. (Stelescu, 2010; Malcolm *et al*., 2003; Mashak, 2008; Mashak *et al*., 2006). They can also be used as insulating material in electrical industry, aircraft industry, textile industry, and machine building industry (Stelescu, 2010).

The antibacterial elastomeric compounds based on silicone elastomer, silicone rubber in this paper, nanometric reinforcing agents - ZnO (zinc oxide) and TiO_2 (titanium dioxide), crosslinking agents - PD (dicumyl peroxide) and fillers (chalk) were characterized physico-mechanically (Fallahi *et al*., 2003) for hardness, elasticity and tensile strength. The performance of antibacterial elastomeric structures depends on the development technology, processing parameters, the vulcanization system used and the curing agents used in compounding, etc. (Taghizadeh *et al*., 2004; Kajihara *et al*., 2003).

EXPERIMENTAL PROCEDURE

Materials

The following materials were used to develop the antibacterial compound based on silicone elastomer: (1) silicone rubber (Elastosil R701/70-OH: polydimethylsiloxane with vinyl groups, (dynamic) viscosity of over 9,000,000 mPa·s, in the form of paste, density - 1.32 g/cm^2, color - opaque); (2) stearin (white flakes, max 0.5% moisture, max 0.025% ash); (3) active zinc oxide (ZnO - 93-95% precipitate in the form of white powder, density - 5.5 g/cm, surface area - between 45 and 55 m^2/g); (4) zinc oxide nanoparticles (ZnO - white powder, 99.99% trace metals basis); (5) chalk (precipitated $CaCO_3$ - white powder, molecular weight 100.09); (6) di(tert-butylperoxyisopropyl) benzene, powder 40% with calcium carbonate and silica (PD) - Perkadox 14-40B (1.65 g/cm^3 density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

Procedure

Polymer nanocomposites based on silicone rubber, reinforced with zinc oxide nanoparticles and crosslinked with dicumyl peroxide were obtained by mixing on a laboratory roll of 1 Kg without heating, yielding formulations in the form of 3-4 mm thick sheets. Basic materials were added to the mixture in different proportions according to Table 1, respecting the order of mixing.

Table 1. Formualtions of polymer nanocomposites based on rubber, reinforced and crosslinked

Sample code	UM	CS_1	CS_2	CSZ_1	CSZ_2	CSZ_3	CSZT
Silicone Rubber	g	200	200	150	150	150	150
Stearin	g	10	10	7,5	7,5	7,5	7,5
ZnO	g	8	8	4,5	3	1,5	1,5
ZnO (nanoparticles)	g	-	-	1,5	3	4,5	4,5
TiO_2 (nanoparticles)	g	-	-	-	-	-	1,5
Creta	g	20	20	15	15	15	15
PD (Pekcadox)	g	15	30	11,25	11,25	11,25	11,25

For physical-mechanical characterization, plates were made by molding method using an electrically heated press. Antibacterial polymer nanocomposites based on silicone elastomer, reinforced with ZnO and TiO_2 nanoparticles and crosslinked with PD are placed in a mold specific to specimens used for finished products and physico-mechanical characterization with the following dimensions: l50mm x 2mm x l50mm; 70mm x 70mm x 6mm, forming in the press according to the established optimal parameters. Optimum curing time was determined using the Monsanto rheometer.

Figure 1. Electric press used to process specimens (for physical-mechanical testing)

RESULTS AND DISCUSSIONS

The resulting polymer composites were tested according to the physical-mechanical standards in force - normal state: hardness, °Sh A - SR ISO 7619-1:2011; elasticity, % - ISO 4662:2009; tensile strength, N/mm^2 - SR ISO 37:2012; elongation at break, % - SR ISO 37:2012. After conditioning for 24 hours at room temperature, samples were subjected to physico-mechanical measurements, in accordance with the above standards.

Physico-mechanical characterizations are shown in Table 2.

Table 2. Physical-mechanical characterisation

Symbol	CS_1	CS_2	CSZ_1	CSZ_2	CSZ_3	CSZT
Hardness ^{0}Sh D SR ISO 7619-1:2011	65	64	65	66	65	65
Elasticity, %, ISO 4662:2009	12	14	12	12	12	12
Tensile strength, N/mm^2, SR ISO 37:2012	3,4	3,8	3,4	3,8	3,8	3,8
Residual elongation, %, SR ISO 37:2012	36	36	37	39	42	43

The physical-mechanical analysis performed for these mixtures shows the following:

- *Hardness*. Antibacterial polymer nanocomposites based on silicone rubber, reinforced and cured with PD by adding ZnO and TiO2 nanoparticles, show no significant changes compared to control samples, CS_1 and CS_2.

- *Elasticity*. Similar to hardness, adding nanoparticles and crosslinking agent in different proportions keeps elasticity constant. Elasticity increases in the case of samples with a higher percentage of crosslinking agent, due to silicone rubber vulcanization (sample CS_2).

- *Tensile strength*. By introducing reinforcing agent (ZnO and TiO_2 nanoparticles) and crosslinking agent (dicumyl peroxide) into the formulations, tensile strength reaches values from 3.4 N/mm^2 to 3.8 N/mm^2. Therefore tensile strength increases compared to CS_1 and CS_2 control samples depending on the percentage of reinforcing agent introduced in mixtures.

- *Residual elongation* increases with the addition of reinforcing agent. The higher the proportion of reinforcing agent in the form of nanoparticles, the higher the elongation at break.

CONCLUSIONS

The aim of the work was the development of polymer nanocomposites based on silicone rubber, reinforced with ZnO and TiO_2, in the presence of curing agents - dicumyl peroxide (Perkadox - powder 40% with calcium carbonate and silica) and their physical-mechanical characterization determining hardness, elasticity, tensile strength, and elongation at break.

Polymer nanocomposites based on silicone elastomer, reinforced and crosslinked were processed using elastomer processing machinery and physical-mechanical characterization was performed according to the standards in force.

Adding ZnO and TiO_2 nanoparticles does not influence the hardness of antibacterial polymer nanocomposites. Also elasticity is not influenced by adding nanoparticles in the formulations.

Tensile strength increases compared to control samples CS_1 and CS_2 by adding reinforcing agent, and residual elongation increases as the percentage of reinforcing agent is higher.

From experimental data, we can say that antibacterial polymer nanocomposites based on silicone rubber, reinforced with ZnO and TiO_2 nanoparticles and crosslinked with dicumyl peroxide show feasibility of application in pharmaceutical and food industry.

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