Interfacial Reaction of Stannic Oxide in Silicone Rubber at 300°C

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ABSTRACT: The thermal stability of high-temperature vulcanized silicone rubber with stannic oxide as a heat stabilizer was investigated by heat aging at $300°C \times 24$ h in air. It was discovered that Sn^{+4} is reduced to Sn^0 during vulcanization and during heat aging in air by X-ray photoelectron spectroscopy (XPS). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2779–2781, 1999

Key words: silicone rubber; thermal stability; stannic oxide; XPS

INTRODUCTION

Silicone rubbers are known to exhibit excellent thermal stability over conventional carbon backbone rubbers. Siloxane bonds in the polymer main chain are resistant to cleavage, but methyl side groups undergo thermooxidative degradation above 250°C, forming crosslinked siloxanes. Methyl groups are first oxidized to hydroperoxides. These may either react with other methyl groups, making crosslinks between chains, or undergo formaldehyde elimination and silanol group formation. Silanol groups may react with siloxane bonds from the same or neighboring chains, forming cyclic and linear oligomers.[1–4] All these reactions may cause chain crosslinking and chain scission in heated silicone elastomers. Crosslinking plays a main role when silicone rubber is heated in air or oxygen, while chain scission plays a main role when heated in nitrogen or under a vacuum.

It has been known that the addition of metal oxides or hydroxides improves the thermal stability of silicone elastomers. This has been explained by the formation of stable complexes with the reactive center of siloxane molecules, as well as by radical elimination coupled to iron(II) reduction,[3] but the nature of the previously mentioned complexes has not yet been obtained. More recently, Wilson et al.'s results[4] showed that the stabilization of iron oxide on silicone rubber is attributed to the bonding of rubber chains to particle surfaces (in addition to the currently accepted mechanisms), which prevents the formation of volatile oligomers and adds stabilizing crosslinks to the network.

Stannic oxide is rarely used as a stabilizer in silicone rubber. In this work, it has been proved that Sn^{+4} is reduced to Sn^0 during vulcanization and during heat aging in air.

EXPERIMENTAL

XPS analyses were carried out in a Perkin–Elmer PHI-1600 X-ray photoelectron spectrometer in a vacuum of 10^{-8} Pa. For each specimen, a survey spectrum was recorded, together with high-resolution spectra of the region of interest (Sn3d5/2).

Table I   Effects of Stannic Oxide on the Thermal Stability of Vulcanizate

Effects	None	Filled with Stannic Oxide
Tensile strength (MPa)	8.3	8.4
Elongation (%)	780	630
Hardness, Shore A	49	54
After 300°C × 24 h heat aging in air		
Tensile strength (MPa)	—	3.8
Elongation (%)	—	210
Hardness, Shore A	Brittleness	61

(a)

(b)

(c)

Figure 1   XPS spectra of Sn3d5/2 obtained from (a) stannic oxide particle, (b) silicone rubber vulcanizate before heat aging, and (c) silicone rubber vulcanizate after 300°C × 24 h heat aging.
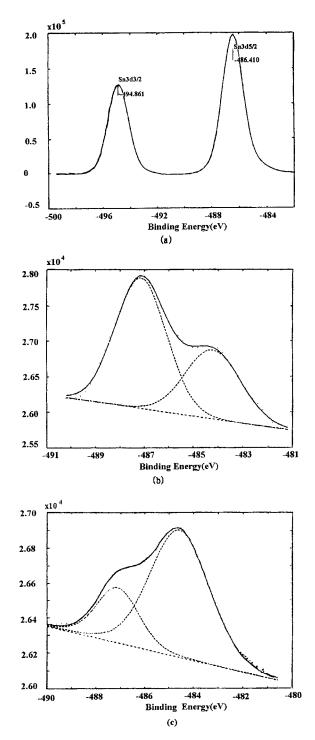
To obtain a new and fresh surface, 2-mm-thick silicone rubber samples were cut into halves for the XPS experiments.

RESULTS AND DISCUSSION

The effects of stannic oxide on the thermal stability of cured silicone rubber are described in Table I. Analysis of the data in Table I shows that stannic oxide is an effective heat stabilizer for silicone rubber vulcanizate.

XPS, a powerful tool to determine surface composition, is used in laboratories throughout the world to investigate surface/interface changes. A chemical shift in the core binding energy of elemental tin from Sn^{+4} to Sn^0 is above 2.50 eV, so it is easy to determine the chemical change of SnO_2. Figure 1 serves to illustrate the interactions between stannic oxide and polysiloxane in silicone rubber vulcanized at high temperature. The binding energy (BE) of Sn3d5/2 for SnO_2 powder and SnO_2-filled silicone rubber vulcanizate before and after heat aging are shown in Table II.

Figure 1 and Table II shows that there is only Sn^{+4} in the stannic oxide particle, but Sn^0 occurs in silicone rubber vulcanizate before and after heat aging. The rate of Sn^{+4}/Sn^0 (1.79) in silicone rubber before heat aging is greater than that (0.32) in silicone rubber after aging. These can be explained by the fact that Sn^{+4} is reduced to Sn^0 during vulcanization and during heat aging in air. It is suggested that the redox reaction prohibits the thermooxidation and increases the thermooxidative stability of silicone rubber, then protects the silicone rubber from thermal oxidation at high temperature.

CONCLUSIONS

The interfacial reaction of stannic oxide in silicone rubber was studied by heat aging and XPS. It is

Table II   Binding Energy of Sn3d5/2

Sample	Binding Energy (eV)	Changes of Binding Energy (eV)	Area (%)	% Gauss
SnO$_2$ Sn^{+4}	486.41	—	—	—
Before heat aging				
Sn^0	484.20	0	35.88	100
Sn^{+4}	487.14	2.94	64.14	100
After heat aging				
Sn^0	484.56	0	75.86	90
Sn^{+4}	487.11	2.56	24.14	80

revealed that stannic oxide is an effective thermal stabilizer for silicone rubber and Sn^{+4} is reduced to Sn^0 during vulcanization and during heat aging in air.

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