Positron study of carbon black parameters: Structure and Surface Area

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Abstract Carbon black (CB) is essentially carbon in the form of extremely fine particle aggregates (100-200nm) having an amorphous molecular structure. Oil absorption or compressed dibutyl phthalate (CDBP) and iodine adsorption or nitrogen surface area (N₂SA) are parameters commonly used to describe CB morphology or structure and the surface area of CB available for reaction with rubber. We have used both positron lifetime and Doppler broadening spectroscopy to study these two parameters for a variety of rubber CB composite samples. The o-Ps pickoff lifetime depends only on the type of rubber and is independent of CDBP and N₂SA. However, the o-Ps lifetime intensity, I₃, and the S parameter decrease with both CDBP and N₂SA.

Introduction

Carbon black (CB) [2] is an industrial product. The main effect of adding CB into a rubber is to strengthen the rubber. Compressed dibutyl phthalate (CDBP) and nitrogen surface area (N₂SA) are two parameters that describe CB morphology and surface area of CB exposed for reaction with rubber [3,4]. The purpose of this research is to investigate the dependence of the positron annihilation lifetime spectroscopy (PALS) and Doppler broadening spectroscopy (DBS) on these two CB parameters for a variety of rubber CB composite samples.

Experimental details

The lifetime apparatus was a typical fast-fast coincidence system using BaF₂ scintillators, Photonis phototubes and Ortec 583 Constant Fraction Differential Discriminators. The data were collected with an Ortec Trump MCA in a PC computer. The timing resolution was about 350 ps. Two samples were sandwiched around a ²²Na₁₁ source, 50μCi deposited on 0.00125 cm nickel foil. No source correction was made since the source did not exhibit any long lifetime component, all the samples had the same average atomic number and thus the same source correction and we were only interested in relative values of the o-Ps pickoff intensity.

The Sid Richardson Carbon Co., Fort Worth, TX, provided the samples. For pure CB samples, the CB powder was pressed into a cylindrical aluminum sample holder of 50 mm diameter and 20 mm thickness. For composite samples the rubber, CB and vulcanizing additives were mixed according to ASTM D3191 and vulcanized in a mold to produce cylindrical samples of 38 mm diameter and 10 mm thick. All samples had a concentration of 50 g of CB to 100 g of rubber (50 phr). The rubber component included natural rubber, and two solution styrene butadiene rubbers, Sn-SSBR and D706 rubber. A variety of CB types were selected to have a range of CDBP and N₂SA. CB types are all the same composition, but differ in morphology. The CBs with lower number are more

branched while those of higher numbers are more spheroidal in structure. The CBs investigated included N110, N220, N326, N330, N339, N347, N358, N650, N660 and N772. (For more details: <http://www.sidrich.com/Products/Tire.htm>)

Results and discussion

The lifetime spectra were analyzed into three components using the LT program.[1] The shortest lifetime was fixed to 125 ps to stabilize the non-linear fit. The intermediate lifetime, Tau2, was attributed to annihilation in the bulk of both the rubber and the CB. The long lifetime component, Tau3, was attributed to ortho-positronium (o-Ps) pickoff.

In Fig. 1, the o-Ps pickoff lifetime, Tau3, is plotted versus CDBP of the CB in the samples respectively. A similar result is found for Tau3 vs N2SA. Tau3 is independent of both CDBP and N2SA; but it depends on the type of rubber. In the pure CB samples, there was less than 2% intensity for a long lifetime component, which was due to annihilation in the thin plastic covers and absorbed water in the CB and not to positronium formation in the CB itself. Thus in the composite samples, we attribute the o-Ps pickoff to the rubber and not to the CB.

Fig. 1 The O-Ps pickoff lifetime vs CDBP

Fig. 2(a) The o-Ps intensity vs. CDBP

Fig. 2(b) The o-Ps intensity vs. N2SA

In Figs. 2(a) and (b), the o-Ps pickoff lifetime intensity, I3, is plotted versus CDBP and N2SA respectively. I3 decreases with both CDBP and N2SA. Since there is no significant positronium formation in the CB material, the effect of adding CB to the composite is mainly to reduce the number of positrons available to form positronium in the rubber. A CB with a larger surface area (higher N2SA) or a more open, flat structure (higher CDBP) provides higher probability for the positron to stop in the CB particles so less positronium is formed in the rubber.

In Fig. 3, the S parameter is shown versus N2SA of the CB respectively. A similar result is found for S vs CDBP. Like I3, S decreases with both CDBP and N2SA. This is due mainly to the

fraction of positrons annihilating in the CB particles in the composite and therefore not being available to form positronium in the rubber. However, unlike I_3 , S is independent of the type of rubber. The three separated trend lines shown in Fig. 2(a) and (b), essentially collapse into one shown in Fig. 3. This is somewhat surprising since one would expect that the contribution to S due to para-Ps formation would correlate with I_3 . While that is true for typical polymers that are below the glass transition temperature [6], it has been found that for pure rubber samples, which have similar hydrocarbon composition but different morphology, S is essentially constant as o-Ps intensity I_3 varies with the type of rubber [7]. This behavior is like that of hydrocarbon liquids, and is due to the rubber being well above its glass transition temperature. With the addition of CB to form the composite, part of S comes from annihilation of positrons in the CB. Thus the CB changes the value of S , but the part due to the rubber remains independent of the type of rubber. The S parameter thus tends to reflect mainly the properties of the CB in the composite.

Summary

Both o-Ps pickoff intensity, I_3 , and the S parameter can be useful to characterize the rubber-CB composite materials with different CB properties. The o-Ps pickoff lifetime does not depend on the CB properties. The behavior of I_3 with CDBP or N2SA can be understood as due to an increase in the probability of positron annihilation within the CB in the composite and a corresponding reduction in positronium formation in the rubber that depends on surface area and structure or morphology of the CB particles. The S parameter, unlike I_3 , is independent of the type of rubber [7]. However, the part of the S parameter from the positron annihilation in the CB depends on the surface area and structure of the CB particles.

Fig. 3 The S parameter vs N2SA

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