

Positron Annihilation Lifetime Spectroscopy of Carbon Black- and Silica-Filled Rubber

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Abstract Lifetime spectroscopy has been used to investigate different grades of carbon black (CB) and silica mixed into a variety of rubbers as a function of CB or silica loading. The spectra were analyzed into three lifetimes. The results show that: (1) The longest observed lifetime, τ_3 , attributed to ortho positronium formation depends on the rubber but not on filler loading or type of CB. The free volume size in the rubber is not affected by the addition of the filler. (2) The intensity, I_3 , of ortho positronium formation depends both on the loading and on the type of CB, but is less dependent on loading in the case of silica. (3) The intermediate lifetime, τ_2 , depends both on the loading of the filler and on the type of CB. For CB, this indicates that τ_2 is not simply the additive result of bulk annihilation in the rubber and CB. Rather the CB loading creates new trapping sites at the CB-rubber interface that depend on the type of CB.

Introduction While positron annihilation spectroscopy techniques have been extensively applied to the study of polymers, there has been much less study of rubber compounds filled with carbon black (CB) or silica [1,2,3,4]. When CB or silica is added to a rubber the principle effect is to strengthen the rubber compound. The purpose of this research was to investigate: (1) how the free volume measured by PAS changes when CB or silica is added to rubber; and (2) whether PAS is sensitive to the type of CB and to the CB-rubber interface.

Experimental Details The lifetime apparatus used is a typical fast coincidence system using plastic scintillation counters.[5] A Na-22 radioactive source, 10 – 50 μ Ci deposited on thin Kapton or nickel foil, is sandwiched between two identical pieces of the sample and placed between two scintillation counters, which are Hamamatsu photomultiplier tubes coupled to plastic scintillator. The timing resolution of the system is about 350 picoseconds.

Samples Carbon black (CB) is an industrial product of considerable economical and technological importance. For the tire industry, which uses as much as 80 % of the worldwide produced CB, the reinforcing properties of CB are essential. Several parameters of CB such as surface area and structure, which can be determined by today's available methods, can predict some properties of the CB-rubber compounds. However, other essential properties such as wear resistance and traction can not be directly correlated to CB and polymer chemical and physical characteristics. A detailed discussion of CB science and technology is given by Donnet *et al.* [7] and Gerspacher *et al.* [8].

Today, CB is produced mainly in the furnace process. In this process, the feedstock oil is burned in a non-stoichiometric reaction to form a very finely divided material composed of aggregates that are the CB monounits. These aggregates are typically submicron size objects of complex shapes. A typical CB aggregates size could range from 50 to 300 nm. The surface of these aggregates is tiled with turbostratic graphite crystallites and areas of disorganized and amorphous carbon. The specific surface area of CB is that which is accessible for interaction with the rubber molecules per unit of

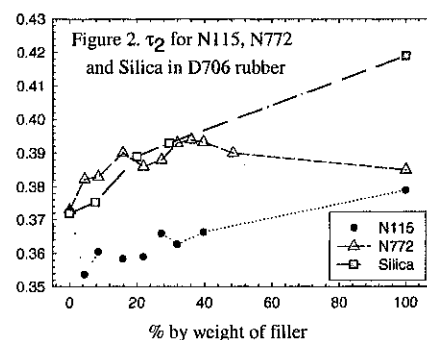
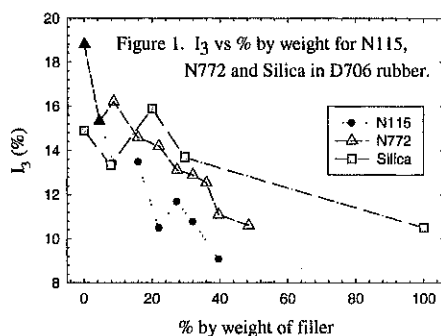
weight. Specific surface area for ASTM grade furnace CB can vary from 27 to 146 m²/g for CB types N772 and N115. As for structure, CB particles can be tightly clustered together, like a bunch of grapes, or the same number of nodes can be arranged in a more open fashion, giving greater bulkiness. High structure CBs give increased viscosity to uncured rubber stocks and increase smoothness of extruded stock. Increasing structure increases hardness, abrasion resistance and electrical conductivity, but decreases flex resistance in vulcanized compounds.

The Sid Richardson Carbon Co., Fort Worth, Texas, provided the samples. To prepare the samples, the rubber, vulcanizing additives and CB are mixed in an internal mixer (Haake Rheocord 90) according to the ASTM D3191 standard recipe. The samples were then cured in a mold at 160°C, which produced cylindrical samples with parallel surfaces of diameter 38 mm and thickness 15 mm. Two identical samples were used for each experiment. We studied nine polymers: natural rubber, polybutadene (BR), ethylene-propylene rubber (EPDM), butyl rubber, solution SBRs (Sn-SSBR, Duradene 706, Duradene 709, Duradene 711), and emulsion SBR (Copo 1500); six CB types: N115, N135, N326, N358, N772, and XLH82; and one silica type: ZeoSil 1165 MP.

Results and Discussion Over 300 lifetime measurements have been made on a wide variety of samples. Space permits the reporting of only a few typical results that illustrate the general conclusions. We analyzed the lifetime spectra into three components using the Kansy program, LT [6]. The shortest lifetime (τ_1) is fixed at the para-positronium lifetime of 125 ps to stabilize the non-linear fit. The longest lifetime (τ_3) is identified as due to the ortho-positronium (o-Ps) pick-off process. The intermediate lifetime (τ_2) is due to direct annihilation and trapping in the sample.

The o-Ps lifetime (τ_3) is found to be independent of both the % by weight of filler loading and the type of filler for both CB and silica in rubber. Regardless of filler, τ_3 just depends on the type of rubber. The addition of filler does not change the radius of the free volume in the rubber, which determines the o-Ps pick-off lifetime.

In Figure 1 the intensity I_3 of the o-Ps component is plotted versus % by weight of filler loading for two very different types of CB (aggregate size and surface area) and for silica. The errors in I_3 are typically $\pm 1\%$ and due to statistics, variation in fit, and variation in samples. I_3 decreases with



CB loading since CB acts as an inhibitor of positronium formation. This is expected because the amount of o-Ps formation in pure CB samples was less than 1% (not shown in the figure). Only N115 and N772 are shown in the plot, but a decreasing trend is observed for each type of CB studied. The decrease in I_3 is not simply additive, but depends on the type of CB. As CB is added to the rubber, some positrons will annihilate in the CB and thus the number available to form positronium in the rubber is reduced linearly with the % of CB added. While different CBs all have basically the same composition, the decrease in I_3 follows different trend lines. This indicates that the CB morphology (aggregate size and surface area, for example) plays an important role in the

decrease in the amount of positronium that traps in the rubber free volume. Only one silica sample was studied so we can not conclude anything about the dependence on grain size. However, the overall change is much less because there is substantial positronium formed in the pure silica, unlike the CB case. The difference in I_3 for the unfilled rubber samples is due to the different additive recipe used for vulcanization of the sample when either CB or silica is to be added.

Figure 2 shows the change in τ_2 as a function of % by weight of filler added. The errors in τ_2 are typically ± 1.5 %, or ± 0.006 ns. As CB is mixed into the rubber, the nature and number of available positron trapping sites changes affecting τ_2 value. In the case of N772, the τ_2 lifetime value increases, while for N115 the lifetime drops at small % loading and then tends to slowly increase. Both curves appear to converge to the pure CB value although it is not possible to produce samples with % loading greater than about 50%. This result demonstrates that τ_2 depends on the type of CB. The change in τ_2 suggests that the addition of CB creates new positron trapping sites, possibly at the surface of the CB aggregate or the CB-rubber interface. It is well known that particle or grain size plays an important role in positron lifetime for small metallic particles [9]. The aggregate size of CB is very small (from 50 to 300 nm) and certainly in the range where grain size is expected to significantly influence the intermediate lifetime. The addition of CB can change τ_2 depending on the type of CB. A large change occurs with small loading, suggesting that in future studies we look at loading less than 4%.

In contrast, for silica, the trend in τ_2 is more like what would be expected for a simple additive case where the change appears to be essentially linear from 0 to 100 % loading. This suggests that the positrons annihilate in the fraction of the sample they enter, either the rubber or the silica, and that trapping at the silica-rubber surface plays less role than in the CB case.

Conclusions The results presented here demonstrate that positron annihilation spectroscopy can discriminate among various types of CB added to rubber. The main conclusions are: (1) The lifetime of the o-Ps component is not changed as CB is added to the rubber. So, the addition of CB does not change the radius of the free volume in the rubber. (2) The intensity of the o-Ps component decreases with the addition of CB, and the decrease depends on the type of the CB. (3) The intermediate lifetime component τ_2 depends on the type of CB and on the loading. τ_2 is sensitive to the CB morphology and perhaps also to the CB-rubber interface. The value of τ_2 is due to a combination of positron annihilation in the bulk CB and bulk rubber and to new trapping sites created when CB is mixed into the rubber. The non-linear dependence of τ_2 as a function of CB load suggests that τ_2 is sensitive to trapping sites on the CB surface or the CB-rubber interface.

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