

E.s.r. spectra of rubber-carbon black mixtures after mastication and extraction

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The investigation of the e.s.r. spectra of the product of the rubber-carbon black mixtures extracted with benzene was carried out. Spectra of the isolated rubber-carbon black gels are similar to those of the respective mixtures. Practically independent of filling and milling time, the narrowest spectral line intensity is specific for rubber-carbon black gel. Lack of lines specific for carbon black in the spectra of soluble part of mixtures even if the carbon black is found in the extract was confirmed.

INTRODUCTION

In a previous paper¹ the e.s.r. spectra of the plasticized rubber filled with various carbon blacks were described. The same type of spectra was found for the investigated mixture with all the carbon blacks. These spectra consist of three components: (a) a very broad line (~ 750 G) corresponding to the spectral line of plasticized rubber; (b) a narrower spectral line, specific for the carbon black used; (c) a very narrow line (~ 3 G) varying with the plasticization time and carbon black content. The narrow components (b and c) have been observed previously by Sullivan and Wise² in the mixtures of styrene-butadiene rubber with ISAF carbon black at liquid nitrogen temperature. Effect of the filling and the milling time on the narrowest spectral line intensity allows one to suppose, that this line results from the rubber-carbon black interactions¹. Waldrop and Kraus³ attribute this line to the radicals formed as a result of the the polymer macromolecules degradation, catalysed by interaction with carbon black particles and call it 'rubber spectrum'.

The rubber-carbon black interactions effect a reinforcement of rubber compounds. An important role in the reinforcement processes is attributed to the 'bound-rubber' isolated by extraction of the rubber-carbon mixtures. Investigations of the products of the rubber-carbon black mixtures extracted with benzene are described in this paper.

EXPERIMENTAL

A description of the rubber-carbon black mixtures prepared has been published earlier¹. The extraction of the samples was carried out in the generally accepted way^{4,5}. One gram specimens of the mixtures, cut into pieces of 2-3 mm dimensions, were placed in small metal baskets with tiny holes and immersed in 200 ml of benzene. Extraction was carried out for 72 h at room temperature. After extraction, samples (gel) were washed in benzene and dried in a vacuum drier at a temperature of 333K. For spectral studies of soluble parts of the mixtures the solvent was evaporated using a rotary vacuum evaporator. From these rubber-carbon black gels and the soluble parts of mixtures the specimens for e.s.r. tests were taken. The criteria for choosing the specimen mass and a detailed description of the spectrometer and the method of obtaining e.s.r. spectra

are given in the previous paper¹. All tests were carried out at room temperature (293K).

RESULTS

Studies were carried out for mixtures of the natural rubber filled with ISAF, HAF, SRF and TM-15 carbon blacks in amounts 10-90 phr for various milling times. For the mixtures containing 10 phr and in the case of TM-15 up to 50 phr carbon black, no stable gel was observed. The quantity of carbon black not forming gel and found in the extract decreases with carbon black content in the mixtures, and increases with the milling time. It influences the rubber-carbon black gel content, defined as a ratio of the mass after and before extraction, expressed as a percentage. Figure 1 shows, for example dependence of the gel content on the milling time and the SRF carbon black content in the mixtures. These data show that the gel content decreases with milling time and increases with the carbon black content in the mixtures.

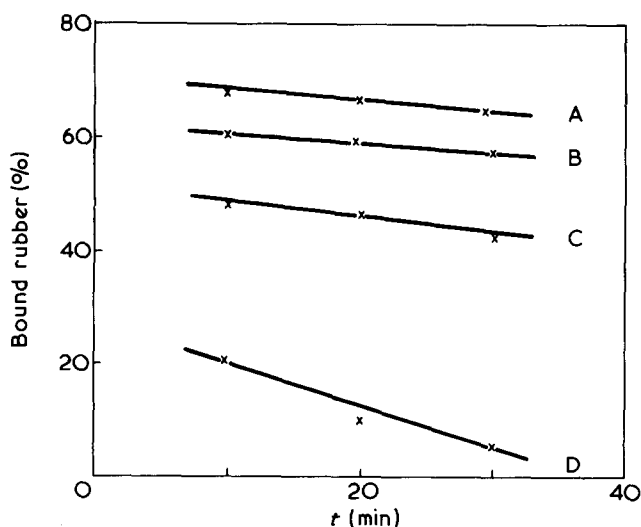


Figure 1 'Bound rubber' content vs. milling time of natural rubber with different admixtures of SRF carbon black. A, 90 phr; B, 70 phr; C, 50 phr; D, 30 phr

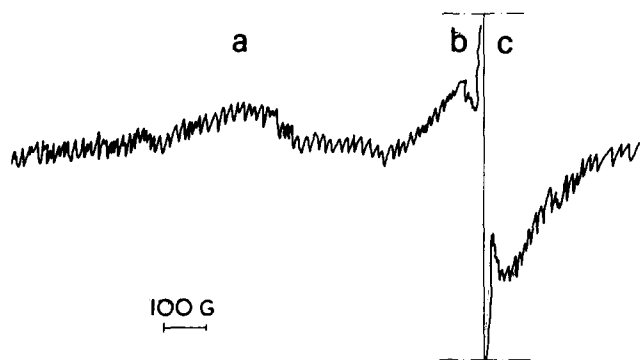


Figure 2 E.s.r. spectrum of natural rubber-SRF carbon black gel

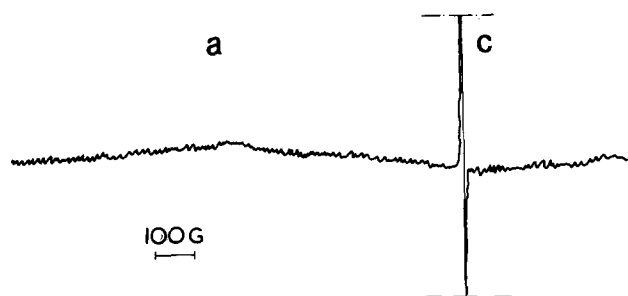


Figure 3 E.s.r. spectrum of soluble part of natural rubber-carbon black mixture

The e.s.r. spectra of rubber-carbon black gels (Figure 2) are similar to the one observed previously¹ for the respective mixtures. They consist of three lines a, b and c less well resolved than for mixtures. This is caused by the much smaller specimens (1-5 mg) necessary because of the large unresonant microwave absorption in gels. However, the effect of the type and content of carbon black, and the milling time on the intensity of gel spectral lines is quite different than for the respective mixtures.

We have confirmed that the intensity of the narrowest spectral line of gels is practically constant (within the limit of measurement errors) and independent of the filling and milling time.

The soluble parts of investigated rubber-carbon black mixtures display two kinds of e.s.r. spectra.

(1) When the extracts contain carbon black the spectra consist of two lines: broad (a) and the narrowest (c) (Figure 3). The narrowest line intensity depends on the carbon black content in the extract and the same changes with the filling and the milling time (Figure 4).

(2) When the extracts do not contain carbon black the spectra consist of only one line (a) corresponding to the line of plasticized rubber¹.

DISCUSSION AND CONCLUSIONS

The above mentioned data allow the concentration of free radicals ($\sim 4 \times 10^{17}$ sp/g) formed as a result of rubber-carbon black gel to be calculated from the intensity of the narrowest spectral line. The narrowest spectral line intensity is specific for the rubber-carbon black gel. The type and content of

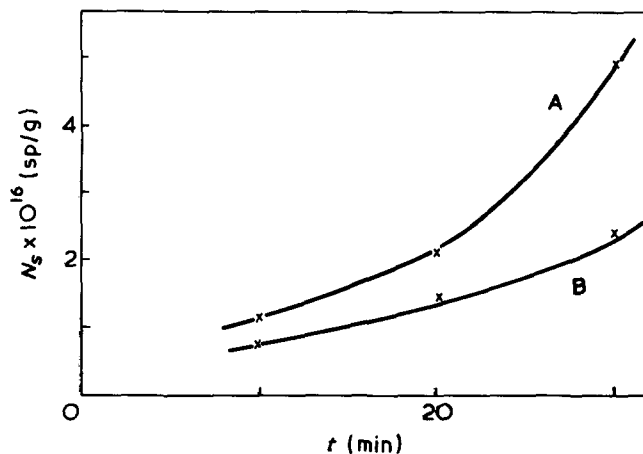


Figure 4 Unpaired spin concentration N_s vs. milling time for extract of natural rubber compounds with SRF carbon black

carbon black, and the milling time influence the quantity of gel only.

The lack of lines specific for carbon blacks (b) in e.s.r. spectra of soluble parts of mixtures, even when the extract contains carbon black proves that interaction between radicals of carbon black and macromolecules (macroradicals) occurs.

Our results confirm Meissner's⁶ theory of "bound rubber" which assumes, that the formation of rubber-carbon black gel relies on the absorption of some structural units of rubber on the reactive centres of filler particles. Each structural unit can form only one bond with the reactive centre. The constant concentration of free radicals formed as a result of rubber-carbon black interactions observed in the rubber-carbon black gel proves that the quantity of reactive centres, which make possible the formation of a stable gel, is constant. For the small content of carbon black and the small specific surface area all reactive centres on the particles surface are occupied by rubber macromolecules. For this reason and taking into account small quantity of reactive centres such systems do not form a coherent space lattice. The presence of the narrowest line and the lack of lines specific for used carbon black in spectra of extracts containing carbon black seems to point to the reasonableness of this argumentation.

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