

## Evidence of Ionic Crosslinking in Natural Rubber Latex by ESI/TEM.

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Natural rubber is miscible in many solvents including toluene, but there is an insoluble gel fraction, which swells without dissolving, and its content increases with storage [1]. The gel phase formation is hypothetically assigned to chemical reactions between groups such as aldehyde [2] or epoxide[3], but there is not yet direct evidence for the presence of these groups in natural rubber [1]. Recent ESI-TEM results showed [4] that natural rubber latex films display a variety of distribution patterns for many elements, beyond the rubber C and H. Calcium ion maps differ from those of the other elements, showing that Ca has a unique behavior, as compared to other naturally occurring metal ions. Thus, microchemical data suggests that ionic crosslinking is another possibility to explain gel formation in natural rubber.

In this work, rubber was dissolved in toluene, and the resulting solution and gel phases were separated, cast on carbon thin films and subjected to microanalysis by transmission electron microscopy associated to electron energy-loss spectroscopy (EELS-TEM). Figure 1 shows bright field and elemental images from a sub-monolayer cast from rubber solution (top). Carbon is obviously prevalent and oxygen shows a similar pattern distribution. Nitrogen, silicon and calcium (not shown) are present and widespread. The examination of submonolayers from the gel reveals a much more complex morphology, and the elemental maps follow different patterns. First, there is not a good match between the bright-field image and the C map, evidencing that there are significant contributions from other elements to the electronic density in this sample. Second, the N, O, Si (not shown) and Ca elemental maps all show similar images in the central region, that does not appear very bright in the C map. Consequently, there are domains containing many non-carbon elements, both interspersed with polymer or isolated (see the dark spots in the C map, which appear very bright in one or more of the other maps). Relative EELS spectra intensities of C, Ca, O and N (not shown) are in Table 1. The results show that Ca/C and Ca/O ratios are higher in the gel relative to the soluble fraction, but N/C ratio is almost the same in both fractions. Thus, the protein content seems to have a limited effect in gel formation, but the higher Ca/C ratio in the gel is strong evidence in favor of ionic crosslinking, probably by  $\text{COO}^- \text{Ca}^{2+} \text{OOC}^-$  bridges.

The lability of ionic bridges explains the variations in the solubility of the gel in different solvents, which is an intriguing feature of natural rubber.

### References

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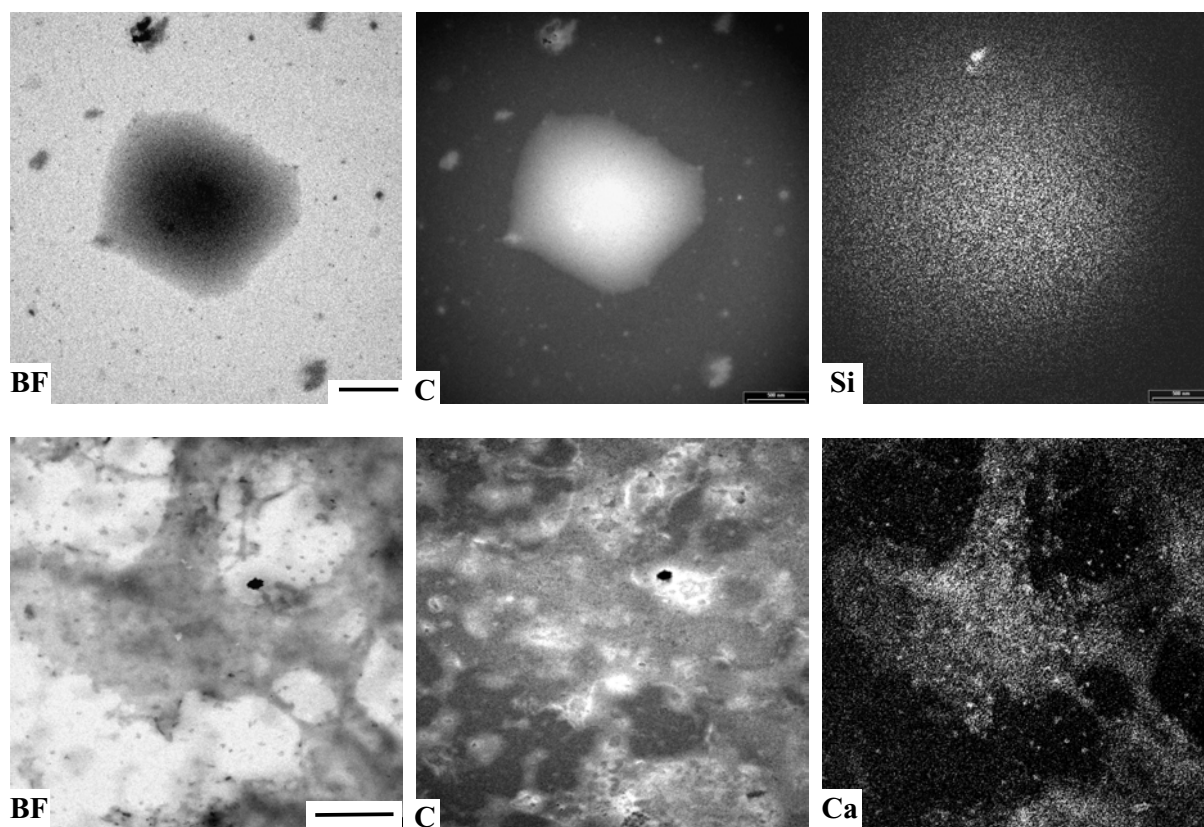


FIG. 1. Bright field images and elemental maps from soluble fraction (top) and gel (below) of dry rubber dissolved in toluene. Scale bar: 500 nm.

TABLE 1. EELS spectral intensity ratios for calcium, oxygen, carbon and nitrogen in the sol and gel films cast from toluene.

Sample	Ca/C	Ca/O	O/C	N/C
Sol	0.031	0.30	0.10	0.023
Gel	0.064	0.50	0.13	0.022