

THEORETICAL AND EXPERIMENTAL STUDY ON THERMAL CROSSLINKING OF POLYBUTADIENES

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Introduction

Crosslinking of rubbers is important because of the improvement on mechanical properties attainable by the polymer, with respect to non-crosslinked rubbers. Crosslinking or curing in rubbers can be promoted by conventional sulfur vulcanization, or by radical polymerization initiated by organic peroxides. The chemistry of sulfur vulcanization has been studied extensively. Regarding peroxide initiated crosslinking on rubbers, the assumed mechanism is attack to a proton in an allylic position, with respect to the rubber double bond. Direct attack to double bonds is considered to be negligible. One unsolved issue is the mechanism(s) for crosslinking, especially in the presence of peroxides, and a graftable monomer. Some researches argue that the prevailing mechanism leads to rubber-rubber linkages¹. Another school supports the idea that crosslinking results from bridges of graftable monomer, linking the rubber molecules. One goal of this study is to further investigate on the relevance of these two mechanisms. In this presentation we focus on the thermal crosslinking of polybutadiene rubbers, in bulk and solution. The motivation is the production of high impact polystyrene (HIPS). In HIPS production, grafting and crosslinking reactions can occur by a radical mechanism, due to thermal or peroxide-promoted initiation.

Experimental

In the first set of experiments, Taktene 1202 (Bayer) (high cis rubber), Ubepol (UBE) (high cis), and Solprene 200 (medium cis, Dynasol, Mexico) rubbers were heated on the center of a vacuum oven (to avoid temperature variation), at different temperatures. At this preliminary stage we have only used rubbers as received, without further purification. In a following stage purified rubbers, in which the effect of added antioxidants is not present, will be studied.

Gel content was measured by different experimental techniques, including Soxhlet extraction, the method ASTM D3616-88, and centrifugation. Figure 1 shows gel content versus time for the three studied rubbers, at different temperatures, in the interval 100-200 degrees Celsius. It is observed that below 140 degrees Celsius thermal crosslinking is not significant. Surprisingly, the rubber with higher vinyl content systematically shows a lower trend towards crosslinking. Although this result is in presence of antioxidants, it already has important practical implications.

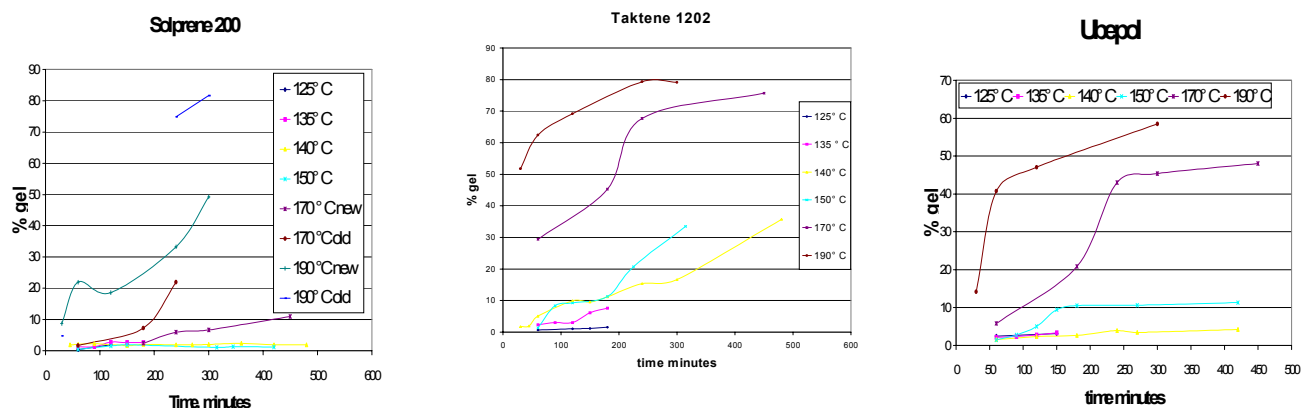


Figure 1. Thermal crosslinking of Solprene 200, Taktene 1202, and Ubepol rubbers.

Modeling

The crosslinking of polybutadiene is assumed to occur by thermal removal of a hydrogen atom, producing two radicals, a hydrogen radical and a polymeric radical. The polymeric radical will crosslink with a rubber molecule, producing a radical of a higher order generation. Radicals and stable molecules of different degrees of “size” (different generations) are thus produced. Termination by combination and reaction with the hydrogen radical are the radical killing reactions. Gelation is defined as the moment where a fifth order generation molecules is obtained. Gel content is calculated from the amount of sol (zero to fourth order polymer) and gel (fifth and higher order polymer). These ideas are an adaptation of the numerical fractionation technique of Teymour and Campbell², and will be explained in the presentation, besides some numerical simulations.

References

1. Keskkula, H.; Turley, S.G. *J. Polym. Sci. Lett. Ed.*, 7, 697, 1969; *Polymer*, 21, 466, 1980.
2. Teymour, F.; Campbell, D. *Macromolecules*, 27, 2460-2469, 1994.

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