Tensile Properties and Morphology of S$_2$Cl$_2$ Treated PVC-g-Butyl Rubber

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SUMMARY

We have grafted butyl rubber from PVC under a variety of conditions. The physical-mechanical properties of these graft copolymers have been examined both before and after extraction with hexane of the ungrafted butyl rubber. We have found a significant increase in the tensile strength of these materials upon S$_2$Cl$_2$ treatment (curing) in THF solution. This increase was observed even with unextracted copolymers. Electron micrograph studies suggest that curing causes an aggregation of the butyl rubber segments into crosslinked domains.

INTRODUCTION

Cationic grafting of PVC using alkylaluminum co-initiators has created much interest (KENNEDY, DAVIDSON, 1977, THAME, et al 1972, GAYLORD, TAKAHASHI, 1970, ABBAS, THAME 1975). It serves the dual role of thermally stabilizing PVC as well as modifying its physical-mechanical properties for its expanded use. While PVC grafting of isobutylene (i-C$_4$) has been extensively studied (KENNEDY, DAVIDSON, 1977), PVC-g-butyl rubber has also been synthesized by the same authors (KENNEDY, DAVIDSON, 1976).

The present study concerns itself with the preparation of PVC-g-butyl rubber and the evaluation of these cured copolymers.

EXPERIMENTAL

Isobutylene (Linde Div.) was distilled through a column packed with BaO (Fisher Chem.) and molecular sieves (4A, Linde Div.), prior to use. Isoprene and CH$_2$Cl$_2$ (Fisher Chem.) were distilled from CaH$_2$ and stored over it in a refrigerator. They were filtered under nitrogen atmosphere prior to use. PVC (FPC 9500) was dried in a vacuum oven at 50°C for at least two hours before use. Et$_2$AlCl (DEAC) (Ethyl Corp.) was used as received. S$_2$Cl$_2$ (Eastman Kodak) and THF...
(Fisher Chem.) were used as received.

Initial butyl grafting was carried out in a stainless steel dry box, equipped with a cooling bath, under nitrogen atmosphere (<30ppm moisture). The desired amount of PVC was suspended in 100ml of CH₂Cl₂ and the calculated amount of isobutylene. Isoprene added was 1/10th the isobutylene volume. Et₂AlCl was added last as a hexane solution (1.5M) and the grafting was stopped by adding 5ml of MeOH after a prescribed grafting time. The polymer was washed with excess MeOH, filtered and dried under vacuum at 60°C.

Butyl grafting was also carried out in a stainless steel reactor using 10 times the amounts used for the dry box runs. Reagents were charged using pop bottles and PVC was transferred using a bomb. At the end of the reaction, the entire batch was dropped into isopropanol, filtered and drum-dried at about 120°C. The products were characterized for the composition gravimetrically and by infrared spectroscopy. Grafting efficiencies (G.E.) were determined using hexane extraction in a soxhlet apparatus. Grafting efficiency is the ratio of butyl rubber grafted to the total butyl rubber formed and is reported as %.

The S₂Cl₂ treatment was carried out by first dissolving the graft product (unextracted) in THF, to give a concentration in solution of 5% (wt./vol.). The concentration of S₂Cl₂ was 1% (vol.) based on the THF charged. The reaction was carried out at room temperature for the desired time and under nitrogen atmosphere. Subsequently, the polymer was precipitated with excess MeOH, repeatedly washed, filtered, and dried under vacuum at 60°C. For evaluation, it was milled at 162°C with 2 phr barium-calcium laurate and 1 phr calcium stearate for up to 5 minutes and then molded into a thin sheet at 350°F for 5-7 minutes. The tensile properties and hardness were determined according to ASTM D-412-68 and D-785, respectively.

Films for the electron microscopy study were prepared by using a 1% wt./vol. THF solution and casting the film over mercury. The transmission electron micrographs were taken with a Phillips Model 300 Electron Microscope. Dark regions represent PVC since PVC has a higher electron density than the unstained butyl rubber segments.