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Tensile Properties and Morphology of S_2Cl_2 Treated PVC-g-Butly 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_2Cl_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 coinitiators 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-C4) 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_2Cl_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 9300) was dried in a vacuum oven at 50°C for at least two hours before use. Et_2AlCl (DEAC) (Ethyl Corp.) was used as received. S_2Cl_2 (Eastman Kodak) and THF

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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 CH_2Cl_2 and the calculated amount of isobutylene. Isoprene added was 1/10th the isobutylene volume. Et_2AlCl 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 S_2Cl_2 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 S_2Cl_2 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.

RESULTS AND DISCUSSION

In our preliminary study, we found that the mechanical properties were very poor for these graft products, if the ungrafted butyl rubber was not extracted. However, even after extraction of ungrafted butyl rubber, good properties were not obtained upon molding the graft products. This behavior was tentatively attributed to either small amounts of ungrafted butyl remaining in the sample or the decomposition of some grafted branches under sheer forces due to a great difference in the flow properties of butyl rubber branches and PVC backbone. By treating the graft product in solution with S_2Cl_2, we found that not only were mechanical properties vastly improved, but even the lengthy extraction step could be eliminated. This prompted us to undertake a detailed study of the S_2Cl_2 treatment of the graft product.

Table I provides the data obtained in the synthesis of some selected PVC-g-butyl rubber samples.

TABLE I

SYNTHESIS OF PVC-g-BUTYL RUBBER

PVC % Wt./Vol. Dry Box Runs	Mon.* Conc., M	DEAC, M $\times 10^3$	Mon. Conv., M	Butyl Content, Wt. %	G. E., %
26.5	9.9	20.9	8.5	18	40
15.0	7.5	16.4	11.3	26	10
Reactor Runs					
14.1	7.5	18.8	6.6	15	65
14.1	7.5	24.7	55.0	65	10

* Molar concentration of isobutylene and isoprene. Isoprene was always 10% of the isobutylene volume.

In general, in this suspension system, high grafting efficiencies were obtained only at low conversions. The conversions could be controlled by judicious choice of Et_2AlCl and/or isobutylene concentrations.

Table II gives the tensile data obtained on the graft copolymers treated with S_2Cl_2 for 56 hours. As the butyl content increases, both hardness and tensile strength decrease until a plateau is reached at the 50% butyl level. Such a decrease in both hardness and tensile strength is expected since the presence of butyl rubber flexibilizes the strong and rigid PVC matrix. The plateau in both tensile strength and hardness which occurs at high butyl rubber compositions is probably due to the increase in crosslink density of the copolymers as butyl rubber content increases. Such an increase in crosslink density apparently balances the plasticization effect butyl rubber has on PVC.

TABLE II

TENSILE PROPERTIES OF CURED PVC-g-IIR VS.% IIR

		Tensile Strength		Ult.
%IIR	Hardness*	MPa	psi	Elong.%
15	-	48.8	7070	40
		17.9	2600	115
18	40(R)	20.7	3000	23
		6.6	950	125
26	72(R)	26.2	3800	17
		13.0	1880	66
46	10(R)	31.0	4500	70
		6.0	870	230
55	54(D)	21.4	3100	95
		5.5	800	150
65	56(D)	24.1	3500	90
		7.6	1100	140

* Rockwell R or Shore D

(The second value of tensile strength and elongation refers to 100°C test temperature.)

Figure 1 depicts the significant increase in the tensile strength as a function of cure time for the graft products containing 18% and 35% butyl rubber. While the increase in tensile strength is linear in time for the graft containing 18% butyl rubber, it is more rapid initially, but quickly reaches a plateau for the graft product containing 35% butyl rubber. The initial faster curing in the sample containing 35% butyl rubber is due to the higher concentration of double bonds available as cure sites. It is not clear why the ultimate tensile strength remains so low for the latter product. A detailed explanation for the differences is not feasible since the nature and level of cure are not precisely known. Nevertheless, this study clearly proves the all important role of S_2Cl_2 treatment of the graft product if one wishes to obtain high tensile strengths.

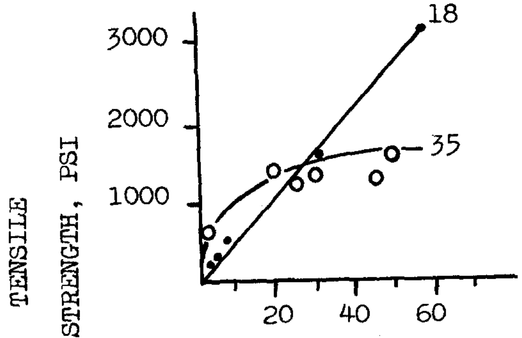

Fig. 1. Tensile Strength versus Cure Time for PVC-g-Butyl Rubber Copolymers

The high tensile strength and low elongation of samples described in Table II suggests a morphology consisting of a PVC matrix and butyl rubber domains. To investigate this possibility further, an electron microscopy study was carried out on the PVC-g-butyl rubber films (extracted samples) as well as on cured and molded samples. Figure 2 is a micrograph of an uncured film containing 55% grafted butyl rubber. It reveals a uniform dispersion of butyl rubber domains of the average size 600 Å in a PVC matrix. Figure 3 is a micrograph of an unextracted sample containing 65% butyl rubber molded and cured. Again, the matrix consists of PVC with butyl rubber making up the dispersed phase. In this case, however, domain sizes and shapes are highly irregular. Very large aggregates are present that were not seen in the micrograph of the uncured cast film. The elongated shape of these aggregates is probably due to the shear forces applied on molding. It seems likely that such aggregate formation can take place only upon curing since it is then that both grafted and ungrafted butyl rubber segments are joined together.

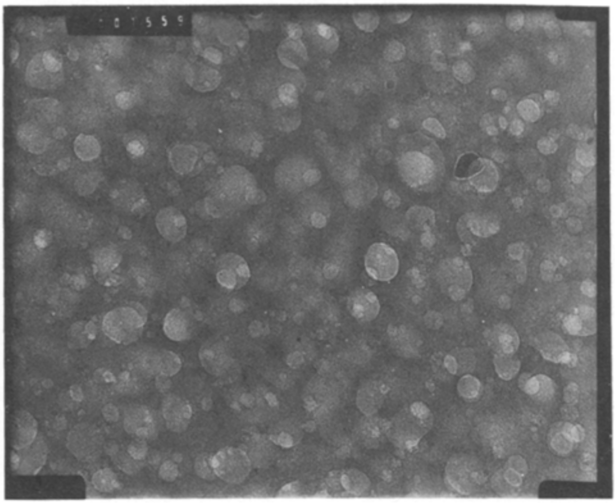

Fig. 2. Electron Micrograph of PVC-g-Butyl Rubber Film Containing 55% Butyl Rubber. Magnification 114,000.

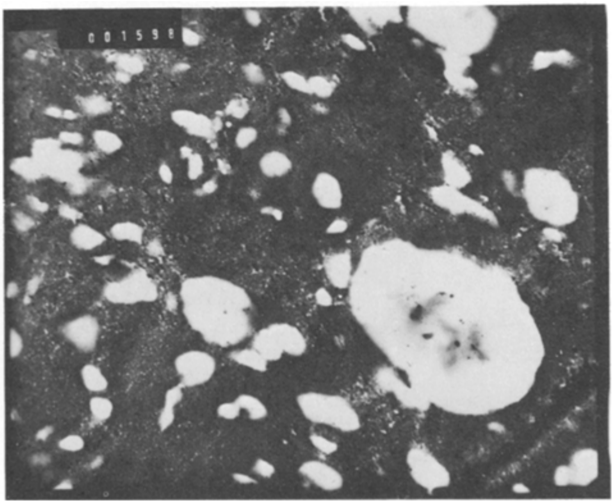

Fig. 3. Electron Micrograph of a PVC-g-Butyl Rubber Copolymer Containing 65% Butyl Rubber Molded and Cured. Magnification 4,500.

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