Polymer Bulletin 2, 461–467 (1980)

Polymer Bulletin

Determination of Labile Chlorine Content in Polychloroprene, Chlorobutyl Rubber and Chlorinated Ethylene-Propylene Copolymer by Thermal Dehydrochlorination Combined with Me_3 Al Treatment

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Summary

The labile (allylic and/or tertiary) chlorine content of polychloroprene, chlorobutyl rubber, and chlorinated ethylene propylene copolymer has been determined by thermal dehydrochlorination combined with Me_3Al treatment. The difference between the extent of dehydrochlorination of virgin and Me_3Al-treated polymers yielded the labile Cl content of these rubbers.

Introduction

The concentration and nature of active or labile (tertiary or allylic) chlorines in chlorobutyl rubber (Cl-IIR), polychloroprene (CR) and chlorinated ethylene-propylene copolymer (Cl-EPM) importantly influence ultimate properties e.g., heat stability, cure versatility, of these rubbers. Since the concentration of these chlorines is very low (1-2%) their accurate determination is very difficult and conventional methods are not sufficiently sensitive for this purpose.

We have combined two quantitative methods developed in our laboratories i.e., thermal dehydrochlorination (TÜDŐS and KELEN 1973, IVÁN et al. 1980a,b) and substitution of labile chlorines by Me_3Al ($R\text{-}Cl^* + Me_3Al \longrightarrow R\text{-}Me + Me_2AlCl$, where $-Cl^*$ = labile chlorine) (KENNEDY 1970, KENNEDY et al. 1973, GUPTA et al. 1978) to determine active chlorine concentration in Cl-IIR, CR and Cl-EPM.

Experimental

Materials

Polychloroprene. An experimental CR sample 15894-79-2, E.I. DuPont de Nemours and Co., $ML^{2.5}_{100}$ =

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0170-0839/80/0002/0461/$01.40

25, $\overline{M}_n$ = 1.03 x 10^5 (by osmometry) has been used. The sample was prepared at ~65% conversion using a standard alkaline aqueous emulsion polymerization with rosin acid primary surfactant and an alkyl mercaptan chain transfer agent at ~40°C. The allyl chlorine content determined by pyperidine-method is 0.6 w% (BARNEY, 1979). The sample was repeatedly precipitated from toluene into methanol and once from methylene chloride into n-pentane under N_2, dried under vacuum in the dark at ambient temperature overnight.

Chlorobutyl rubbers, (Cl-IIR',) (HT-1066 and HT-1068 of Exxon Chemicals Co., ~1.1 w% Cl) were reprecipitated from n-pentane into acetone and vacuum dried.

Chlorinated ethylene propylene copolymer (Cl-EPM). (EPCAR 306, ML ~ 25 of B. F. Goodrich) was photochlorinated (SMITH 1973) and purified by repeated precipitations from freshly distilled peroxide-free THF into methanol and vacuum dried.

Trimethylaluminum (Me_3Al) (Texas Alkyls Co.) was distilled under reduced pressure.

Solvents were refluxed over CaH_2 overnight and distilled before use.

Treatment of rubbers by Me_3Al

Reactions of Me_3Al with rubbers were carried out under nitrogen in a dry box at 25°C. CR and Cl-IIR's were dissolved in methylene chloride, and Cl-EPM in 25/75 methylene chloride/chlorobenzene mixtures (~2 g rubber in 200 ml solvent were used). Reactions were initiated by adding 2.5 ml Me_3Al and terminated by methanol after 2 hrs of stirring with CR and Cl-IIR's, and 5 hrs with Cl-EPM. Untreated (control) samples were prepared by subjecting them to the same processes in the absence of Me_3Al. Aluminum-containing residues were carefully removed from Me_3Al-treated samples since the rate of overall HCl loss is extremely sensitive toward these impurities. In the presence of aluminum-containing residues in the samples, the initial rate of HCl loss will be unexpectedly fast (GUPTA et al. 1978). Thus samples were reprecipitated five-seven times, dissolved, centrifuged and filtered, and vacuum dried.

Thermal Dehydrochlorination

Dehydrochlorinations were carried out with samples prepared in form of thin films deposited on U-shaped glass tubes (6 mm id). The tubes were filled with THF solutions of the samples, the solvent was evaporated and the samples were dried to constant weight (0.02-0.04 g) under vacuum in the dark. Dehydrochlorination was carried out at 190°C as described earlier (IVÁN et al. 1980a). The evolved HCl was determined by conductivity and the method has been described in detail (TÜDŐS and KELEN 1973).

Results and Discussion

Our method for the determination of active or labile chlorine content in a polymer is based on two well established facts: 1) Me_3Al quantitatively and rapidly methylates labile C-Cl bonds (tertiary, allylic chlorines) and gives rise to relatively heat stable C-Me bonds (KENNEDY 1970, KENNEDY et al. 1973, GUPTA et al. 1978) and 2) Labile chlorine containing compounds readily and quantitatively lose HCl upon heating to relatively low temperatures (180-200°C) (MAYER 1974, IVAN et al. 1980a,b). Thus the labile chlorine content of a polymer can be obtained by determining the difference of HCl loss of a sample before and after treatment with Me_3Al.

Experimentally we plotted the extent of HCl loss as a function of time for untreated (control) and Me_3Al-treated CR, Cl-IIR and Cl-EPM samples at 190°C. The ξ_{HCl} versus time plots of the controls invariably exhibited two phases: an initial phase during which HCl evolution was rapid which was followed by a relatively slow HCl-loss phase. In contrast, the ξ_{HCl} versus time plots of Me_3Al-treated samples exhibited only a relatively slow rate. Importantly, the slopes of the slow phases were parallel indicating identical HCl loss kinetics. It is postulated that Me_3Al-treatment removes the thermally labile chlorines so that the rate of HCl-loss of treated and untreated samples becomes indistinguishable during the second phase of these dehydrochlorination experiments.

Thus the labile chlorine content is the difference Δ between these ξ_{HCl} versus time plots and can be readily obtained by substraction ($\Delta = \xi_{HCl\ untreated} - \xi_{HCl\ Me_3Al\text{-treated}}$). Figures 1-3 show experimental curves and Δ. Necessarily, Δ must become horizontal during the second stage of HCl loss and the labile chlorine content can be obtained by extrapolation to the ordinate (indicated by dotted lines).

According to the data in Figures 1-3, dehydrochlorination continues slowly for long times and the ξ_{HCl} versus time plots do not tend to become horizontal even after many hours of heating. Similar

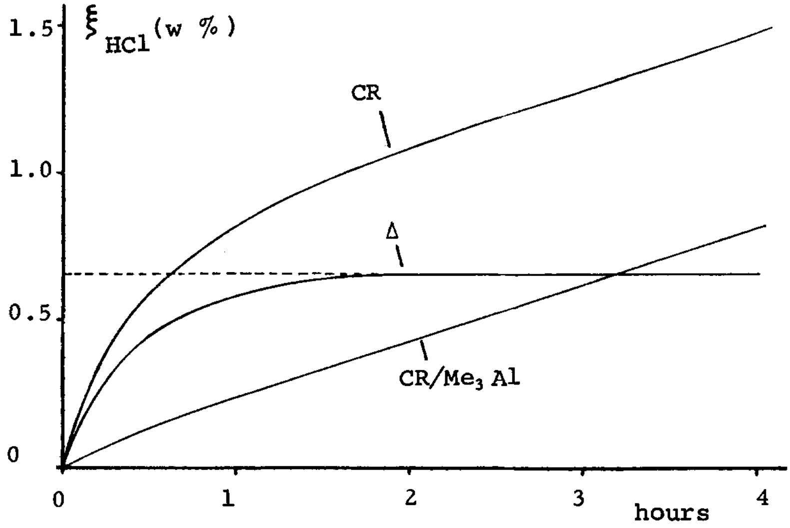

Figure 1. Extent of HCl loss as a function of time for CR, CR/Me$_3$Al, and the difference.

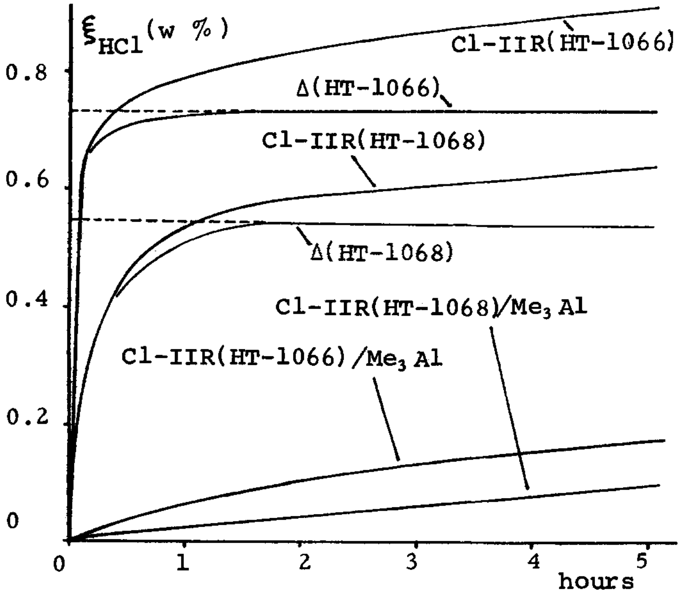

Figure 2. Extent of HCl loss as a function of time for Cl-IIR (HT-1066), Cl-IIR (HT-1066)/Me$_3$Al, and Cl-IIR (HT-1068), Cl-IIR (HT-1068)/Me$_3$Al, and the differences.

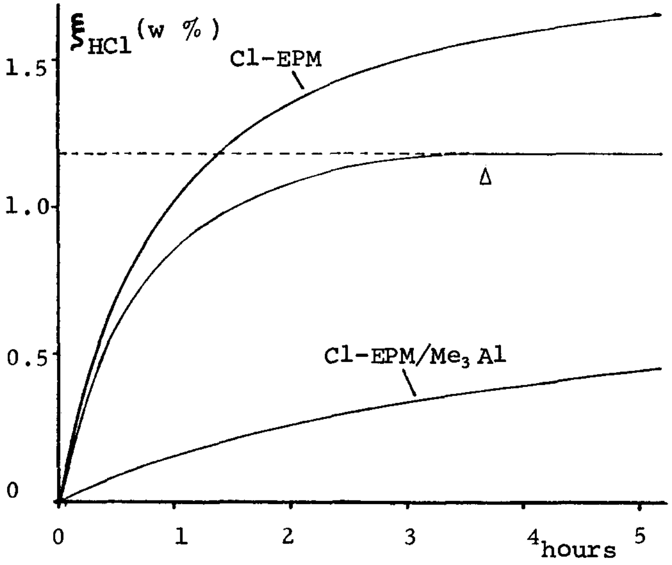

Figure 3. Extent of HCl loss as a function of time for Cl-EPM, Cl-EPM/Me$_3$Al, and the difference.

Table I. Labile chlorine content of rubbers determined by thermal dehydrochlorination combined with Me$_3$Al-treatment.

Rubber	Overall Chlorine wt.%	Labile Chlorine wt. %
CR(a)	40.1(b)	0.64
Cl-IIR(HT-1066)	1.12(c)	0.71
Cl-IIR(HT-1068)	1.1	0.54
Cl-EPM	9.34	1.15

(a) Allylic Cl content = 0.6 w % determined by pyperidine method.
(b) Theoretical value.
(c) See ref. (KENNEDY and CHARLES 1977).

phenomena have been observed for cationically modified CR's (IVÁN et al. 1980a). This slow and steady dehydrochlorination is most likely due to HCl loss from relatively heat stable primary, secondary, vinylic, etc. chlorines.

Polychloroprene

According to COLEMAN et al. (1977, 1978) CR contains a few percent of relatively unstable allylic chlorines $-CH_2-\overset{|}{C}(Cl)-CH=CH_2$, $-CH_2-\overset{|}{C}=CH-CH_2Cl$ in addition to the stable vinyl chlorines $-CH_2-C(Cl)=CH-CH_2-$ and $-CH_2-\overset{|}{C}H-C(Cl)=CH_2$. Significant differences in thermal dehydrochlorination rates of untreated and cationically modified (cyclopentadienylated and grafted) CR's have been found (IVÁN et al. 1980a; KENNEDY et al. 1980).

According to the data in Figure 1 the allylic chlorine content is 0.64 wt.%. This value is in excellent agreement with that obtained from the source (0.6 wt.%, BARNEY 1978, cf Table I).

Chlorobutyl rubbers

Cl-IIR is made by chlorination of butyl rubber containing ~1.5 mole % isoprene units. The allylic chlorines in Cl-IIR are predominantly $-CH_2-C(=CH_2)-CH(Cl)-CH_2-$ and smaller amounts of $-CH=C(CH_3)-CH(Cl)-CH_2-$ (YABLONSKII et al. 1973, BALDWIN et al. 1975).

According to the data in Figure 2, the two chlorobutyl samples contained 0.71 and 0.54 wt. % labile chlorines, respectively. According to manufacturer's specification the samples contained ~1.1 wt. % Cl (cf Table I). The discrepancy between our and the manufacturer's specifications values is most likely due to the fact that chlorination of butyl rubber not only results in allylic chlorines but also yields more stable, most likely primary, chlorines.

Chlorinated ethylene propylene copolymer

Photochlorination of ethylene propylene copolymer leads to ~20% labile tertiary chlorines $-CH_2-\overset{|}{C}(Cl)CH_3$ and ~80% relatively stable secondary and/or primary chlorines $-CH_2-CH(Cl)-$, and $-CH_2-\overset{|}{C}H-CH_2-Cl$ (BRUZZONE and CRESPI 1960).

According to the data in Figure 3, Cl-EPM contains 1.15 wt % labile tertiary chlorines (cf. Table I).

Acknowledgement

The authors are grateful to the E.I. DuPont de Nemours Co. for the experimental CR, to the Exxon Chemicals Co. for the Cl-IIR, to the B.F. Goodrich Co.

for the EPM, and to Mr. F. O. Grant of the Institute of Polymer Science for chlorinating the latter. Financial assistance by the Institute for Cultural Relations, Hungary, and the National Science Foundation (INT-78-27245), is acknowledged.

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Received March 24, 198o