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The Reaction of Chlorinated Polyethylenes and Amines*

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Synopsis

The reaction of chlorinated polyethylene and amines, the chemical changes accompanying the heat treatment of the aminated product, and the changes of some practically important properties of the resulting product have been studied. It was found that during amination nitrogen is incorporated in the macromolecules; during the applied heat treatment this nitrogen is eliminated from the polymer and the product becomes practically insoluble. The anticorrosive properties of the resulting product are significantly better than those of chlorinated polyethylene, and this is a very important result from the practical point of view.

INTRODUCTION

Chlorinated polyethylene may be used for preparing corrosion-resistant coatings. The properties of the product depend largely on the chlorine content and on the structure of the polymer. The crosslinking has a favorable effect on the properties of the product. For this reason several methods have been developed for obtaining a crosslinked chlorinated polyethylene. The industrially most widely employed method consists in introducing sulfochloride (SO_2Cl) groups into the macromolecule, with the crosslinks formed by the reaction of the sulfochloride groups. This product is known as Hypalon, produced by du Pont from high pressure polyethylene.

The present work has been performed to study the changes produced in the properties of chlorinated polyethylene by treatment with amines and to find out whether the crosslinks could be formed in the product in this way or not.

EXPERIMENTAL

The investigation was carried out on the chlorinated Hostalen GM 5050-type low pressure polyethylene with 38.2% chlorine content (being therefore an elastic product). The chlorination of PE was carried out in solution with light catalysis. Monoethanolamine, diethanolamine, and

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triethanolamine as well as butylamine, diethylamine, and triethylamine were used for amination. Amination was carried out in an autoclave at 120°, 140°, and 160°C for 0.5, 2, and 4 hr, respectively. The amount of amine used was the stoichiometric quantity relative to chlorine. After the completion of the reaction, the product was shaken with distilled water and separated by centrifugation. This operation was repeated three times. In this way the unreacted amine and the amine salts formed with the hydrochloric acid were removed from the system. Finally, the product was dried and subjected to heat treatment.

In the course of our work we measured the changes in chlorine content of chlorinated polyethylene as a result of amination and of the above-mentioned heat treatment. Infrared spectroscopy was used to follow the chemical changes, and the changes of the mechanical and anticorrosion properties of the product were also investigated.

Results and Discussion

Amination of Chlorinated Polyethylene and Investigation of Chemical Structure of Product

Figures 1 and 2 show the effect of treatment with butylamine and ethanolamine, respectively, on the chlorine content of chlorinated polyethylene as a function of time and temperature. As can be seen from the figures, the curve of reduction in chlorine content flattens out as a function of time as well as of temperature, and there is no practical difference between the effects of the treatment with ethanolamine and with butylamine. This is also characteristic of treatment with the other tested amines, as shown in Table I, column 1. Chlorine content was determined by the combustion of a known weight of the substance above an alkali and subsequent argentometric determination of the Cl.

The aminated chlorinated polyethylene was also studied by means of infrared spectroscopy for determining the chemical structure. Figure 3 shows the spectra of the original chlorinated polyethylene (A), the chlo-

TABLE I

Amine	Chlorine lost in reaction, %	Chlorine lost in alkali leach during 6 days	Total chlorine abstracted from backbone, %	Nitrogen equivalent to total chlorine, abstracted %	Nitrogen found, %
Monoethanolamine	2.74	0.58	3.32	1.32	1.24
Diethanolamine	2.23	0.62	2.85	1.14	1.12
Triethanolamine	1.98	0.57	2.55	1.02	0.94
Butylamine	2.88	0.66	3.54	1.42	1.32
Diethylamine	2.32	0.66	2.98	1.19	1.08
Triethylamine	2.06	0.61	2.67	1.06	1.04

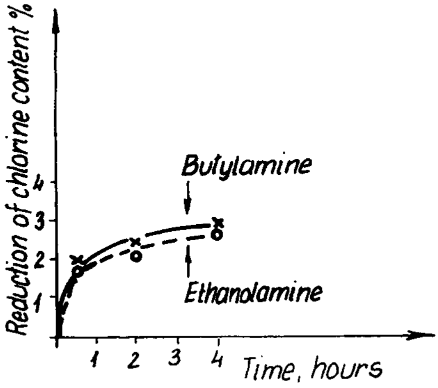


Fig. 1 Decrease in the chlorine content of chlorinated polyethylene during treatment with ethanol- and butylamine, respectively, at 160°C as a function of time.

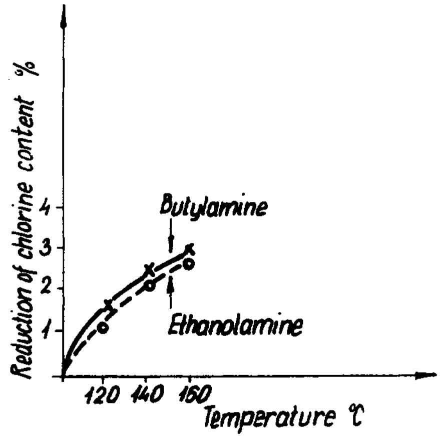


Fig. 2. Decrease in the chlorine content of chlorinated polyethylene during treatment with ethanol- and butylamine respectively for 4 hr as a function of temperature.

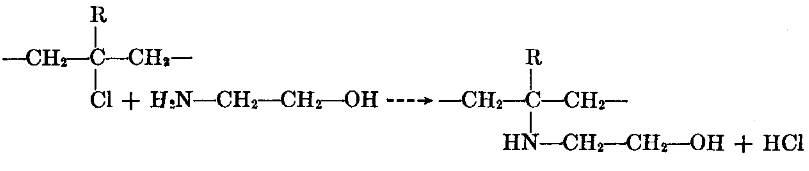
rinated polyethylene treated with monoethanolamine (B), and the chlorinated polyethylene treated with monoethanolamine and heat treated for 30 min at 160°C (C) (spectrum C will be discussed later).

In the spectrum of the aminated chlorinated polyethylene, the most pronounced changes were observed during amination with monoethanolamine and butylamine. In the infrared spectrum of the chlorinated polyethylene aminated with monoethanolamine, new bands appear at 1620, 1510, 1090, 1070, and 990 cm^{-1}. In the range 3300–2700 cm^{-1}, absorption is observed in the shape of a wide band which fuses with the bands of the stretching vibrations of the CH_2 groups. We have assigned this wide band to the stretching vibrations of the associated NH and OH groups.[1] The band of the stretching vibration of the NH_2^+ group (2700–2250 cm^{-1}) probably also fuses with this absorption band.[2]

The absorption around 1620 cm^{-1} belongs to the deformational vibration of the secondary amine group (1650–1550 cm^{-1}), as does also the band at 1510 cm^{-1}.[3] The absorption around 1620 cm^{-1} includes the absorption of the hydrochloride of NH_2^+ which absorbs in the range 1620–1560 cm^{-1}.[2]

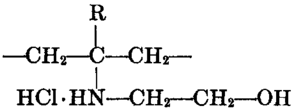
The absorption at 1090 cm^{-1} may be assigned to the stretching vibration of C—O in the ethoxy group; the band at 1070 cm^{-1} to stretching vibration of C—N bond; however, the band at 990 cm^{-1} belongs probably to the stretching vibration of C—N^+.[4]

One of the modes of formation of the C—N bond may be as follows:



$$-CH_2-\underset{Cl}{\overset{R}{C}}-CH_2- + H_2N-CH_2-CH_2-OH \dashrightarrow -CH_2-\underset{HN-CH_2-CH_2-OH}{\overset{R}{C}}-CH_2- + HCl$$

However, the hydrochloric acid salt of the system may be formed also:



$$-CH_2-\underset{HCl\cdot HN-CH_2-CH_2-OH}{\overset{R}{C}}-CH_2-$$

This conclusion is supported, aside from the infrared spectrum, also by the fact that, during the soaking of the product at room temperature in an alkali after it has been washed to neutral with distilled water, hydrochloric acid leaves the system. This is shown in the Table I, column 2.

We also measured the nitrogen content of the aminated products. The results are shown in Table I, column 5. Thus we were able to demonstrate analytically the presence of nitrogen in the macromolecules.

Nitrogen was determined by the Kjeldahl method; the product was boiled in concentrated sulfuric acid, with the formation of $(NH_4)_2SO_4$ from the fixed nitrogen. After alkalizing the solution, the liberated NH_3 was distilled into a known amount of acid, and the excess acid was determined by titration. $CuSO_4$ and K_2SO_4 were used as catalysts in the destruction.

When the total content of chlorine abstracted from backbone (Table I, column 3) is expressed in terms of nitrogen equivalent (Table I, column 4), it can be noticed that rather good agreement is found between the calculated (Table I, column 4) and the analytically determined nitrogen content (Table I, column 5). This fact also supports the suggested mechanism of the amination reaction.

In our opinion, the replacement reaction takes place at the branching points where there are labile tertiary chlorines on the polymer molecule's backbone. This conclusion is further supported by the following consideration: In case of 38% chlorine content in chlorinated polyethylene, there is approximately 1 chlorine atom per 5 carbon atoms. In our chlorinated polyethylene, thus, there are 200 chlorines per 1000 carbon atoms. According to Willbourn,[5] in Hostalen-type polyethylene there are 7 branches per

1000 carbon atoms. Thus, in our chlorinated polyethylene, about 3.5% chlorine atoms may be tertiary. Indeed, about 3.5% polymer chlorine is replaced in case of amination by monoethanolamine and butylamine.

Heat Treatment of Aminated Chlorinated Polyethylene and Investigation of Chemical Structure of Product

The aminated products are soluble in hydrocarbons and suitable for film formation. A film was prepared from the product for practical application and heat treated for 30 min at 160°C. During heat treatment, a further reduction of the chlorine content is observed as compared to the aminated products, as shown in Table II for the products treated with monoethanolamine and butylamine.

TABLE II
Reduction of Chlorine Content During Amination and Heat Treatment

Product	Reduction of chlorine content, %, during	
	amination	heat treatment
Chlorinated polyethylene	—	0
treated with monoethanolamine	2.74	5.37
treated with butylamine	2.88	6.08

After six days, alkali leach of the heat-treated product, only traces of chlorine may be detected in the soaking medium, which points to the disappearance of amine-HCl groups.

The same conclusion may be drawn from spectrum C in Figure 3: the bands mentioned in spectrum B have disappeared and the spectrum characteristic of the original chlorinated polyethylene are obtained.

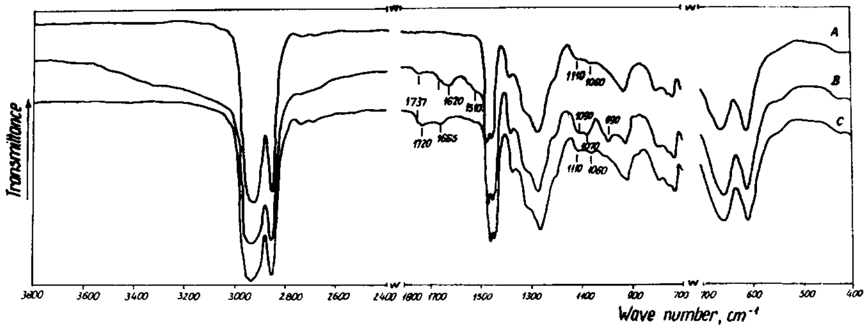


Fig. 3. Infrared spectra of chlorinated polyethylene (A), aminated chlorinated polyethylene (B), and heat-treated aminated chlorinated polyethylene (C).

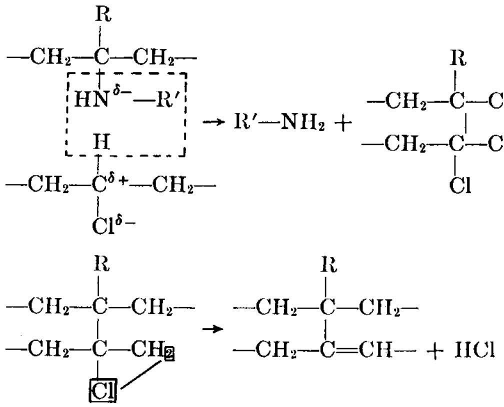
The new bands at 1737 and 1720 cm^{-1} are the results of oxidation; the band at 1655 cm^{-1}, however, probably belongs to an unsaturation which is a result of a dehydrochlorination formed during amination and subsequent heat treatment.

TABLE III
Nitrogen Content of Aminated Chlorinated Polyethylene After Heat Treatment[a]

Amine	Nitrogen content of aminated and heat-treated product, %
Monoethanolamine	0.35
Diethanolamine	0.24
Triethanolamine	0.43
Butylamine	0.33
Diethylamine	0.16
Triethylamine	0.27

[a] For 1/2 hr at 160°C.

Table III shows the nitrogen content of the aminated and heat-treated products. A comparison with the data in Table I, column 5, shows that the nitrogen content has been greatly reduced. The suggested reaction may be as follows:



The first part of the suggested mechanism of crosslinking reaction is supported also by the fact that the heat-treated polymer becomes insoluble; the second part is supported by the further reduction of the chlorine content during heat treatment.

Changes in Protective Properties Against Corrosion

Other properties are also changed, e.g., the tensile strength increases and the protective properties against corrosion improve. Chlorinated polyethylene has a tensile strength of 55 kg/cm^2, that of the product treated with monoethanolamine for 4 hr at 160°C is 52 kg/cm^2, and that

TABLE IV
Protective Properties Against Corrosion of Aminated and Heat-Treated Chlorinated Polyethylene Coatings

Amine	Trivalent Fe, g/liter	
	water	0.01*N* HCl
Original product (no amine)	0.0527	0.1536
Monoethanolamine	0.0440	0.1386
Diethanolamine	0.0456	0.1498
Triethanolamine	0.0472	0.1544
Butylamine	0.0382	0.1174
Diethylamine	0.0450	0.1460
Triethylamine	0.0468	0.1502

of the heat-treated film is 68 kg/cm^2; i.e., the increase of tensile strength is about 25% as compared with the original value.

The changes in protective properties against corrosion may be seen in Table IV. The tests were carried out by coating steel specimens with chlorinated polyethylene aminated at 160°C for 4 hr, taking care to have equal coating thicknesses on all specimens (the average coating thickness was about 50 microns). The specimens were heat-treated at 160°C for 30 min and subsequently placed for 20 days into distilled water or 0.01*N* hydrochloric acid. The iron content of the corrosive medium was measured.

It may be seen from the table that in each aminated case the iron content of the corrosive medium was lower as compared with the specimen coated with the original product, that is to say, the anticorrosive ability improved. The highest improvement was observed with the butylamine and ethanolamine specimens: the reduction of corrosion was about 25–30% as compared with the specimen coated with untreated chlorinated polyethylene.

The increase in tensile strength and the higher anticorrosive ability are important and welcome phenomena from the point of view of practical application, and theoretically they support our assumption concerning the formation of crosslinks.

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