

Synthesis, Characterization, and Coating Applications of Chlorinated Hydroxyrubber

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SYNOPSIS

Chlorinated hydroxyrubber has been synthesized via the chlorination of hydroxylated liquid natural rubber. The formulation examples and coatings properties of two-component chlorinated hydroxyrubber polyurethane coatings are described. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Chlorinated rubber has long been used to provide coatings with excellent chemical and water resistance, abrasion resistance, and flame retardancy. It is one of the better binders for use in harsh, corrosive environments, which include marine coatings, swimming pool coatings, and traffic paints.¹ However, chlorinated rubber is a nonconvertible binder of poor solvent resistance and thus its applications have generally been limited to solvent-based coatings of high volatile organic content (VOC). High VOC coatings are under attack by regulatory agencies and, thus, substitutes based on the newer technologies of water-borne, high-solid, and powder coatings are under development.

The chemical modification of chlorinated rubber has been a topic of extensive studies in recent years,²⁻¹⁵ most of which have focused on free-radical-initiated graft copolymerization with functional acrylate or styrene monomers. The initiators of choice include organometallic complexes²⁻⁵ and benzoyl peroxide.⁶⁻⁸ Copolymerization via thiolated chlorinated rubber has also been reported.^{9,10} Although direct modifications of chlorinated rubber are limited, due to the chemical inertness of chlorinated rubber, its amination with aminoester^{11,12} and polyamide¹³ was reported by Makani et al. They reported that side reactions such as polycondensa-

tion and elimination could not be avoided. Others have used functionalized chlorinated rubber in controlled-release antifouling coatings,^{2-5,9-14} water-dispersible coatings,¹⁵ and polyurethane coatings.^{7,8} However, to our knowledge, none of the reported modifications of chlorinated rubber have achieved significant commercialization.

Our investigation has focused on the synthesis of functionalized chlorinated rubber derivatives with emphasis on utilization in environmentally friendly, low VOC coatings and in controlled-release antifouling coatings. This work describes the combined synthesis of novel chlorinated hydroxyrubber, a versatile convertible binder, and a precursor for further modification. The spectroscopic characterization and thermal properties of chlorinated hydroxyrubber are reported. Moreover, the formulation and performance of chlorinated hydroxyrubber polyurethane coatings are described.

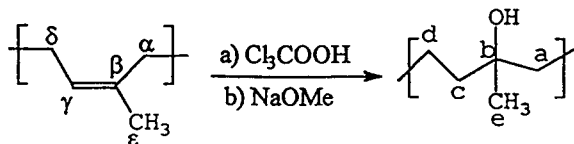
EXPERIMENTAL

Materials

Crude liquid natural rubber (DPR-40, MW ~ 40,000 and DPR-400, MW ~ 80,000) was supplied by Hardman Inc. and purified by dissolving in methylene chloride, filtering through a Gardco medium paint filter, and precipitating from methanol. Trichloroacetic acid, sodium methoxide (95%), and anhydrous toluene were purchased from Aldrich. Reagent-grade acetic acid was provided by Baker. Reagent-grade methylene chloride, chloroform, and methanol are all from Fisher Chemical. The sources

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Scheme 1 A schematic representation of the synthesis.

of the solvents and chemicals used in coating formulations are noted in Table IV.

Synthesis of Hydroxyrubber

To 350 mL of 5% rubber in anhydrous toluene in a 500 mL Erlenmeyer flask was added 56.8 g of trichloroacetic acid. The solution was stirred at 0°C under N₂ atmosphere. The solution was poured into a 1000 mL Erlenmeyer flask containing 60.7 g of sodium methoxide and 100 mL of methanol. After the mixture was continuously stirred for 20 h, 34.7 mL of acetic acid was added to neutralize the mixture. The mixture was stirred for an additional 15 min, after which it was poured into 650 mL of methanol and the pH adjusted to 5–6 with a few drops of acetic acid. The product was precipitated, washed with methanol and 50% (v/v) methanol in water, respectively, and dried in a vacuum oven. Additional purification of the hydroxyrubber was accomplished by dissolving in 100 mL methylene chloride and precipitating via the addition of 400 mL of methanol.

Synthesis of Chlorinated Hydroxyrubber

A solution of 5% hydroxyrubber (280 mL) in CHCl₃ was added to a three-neck flask fitted with a water condenser, gas inlet tube, and a glass stopper. The inlet tube was connected via Teflon tubes, through a gas trap, to a chlorine cylinder. The exit port of the condenser was connected to two traps filled with concentrated sodium hydroxide. The reaction flask was immersed in an oil bath for temperature control. Nitrogen was purged through the system for more than 15 min before introducing chlorine gas. The solution was allowed to reflux with constant agitation via a magnetic stirrer. A slight excess of chlorine was delivered into the reaction vessel while the liberated hydrogen chloride was trapped in the sodium hydroxide solutions. The product was precipitated with 600 mL methanol after the reaction was completed.

Characterization Methods

A Bruker 200 MHz NMR spectrophotometer and a Nicolet IR/42 FTIR spectrophotometer were used for nuclear magnetic resonance and infrared spectroscopic analysis, respectively. Thermal analyses were performed on a Mettler TA4000 unit while elemental analyses were conducted by the M-H-W Laboratory.

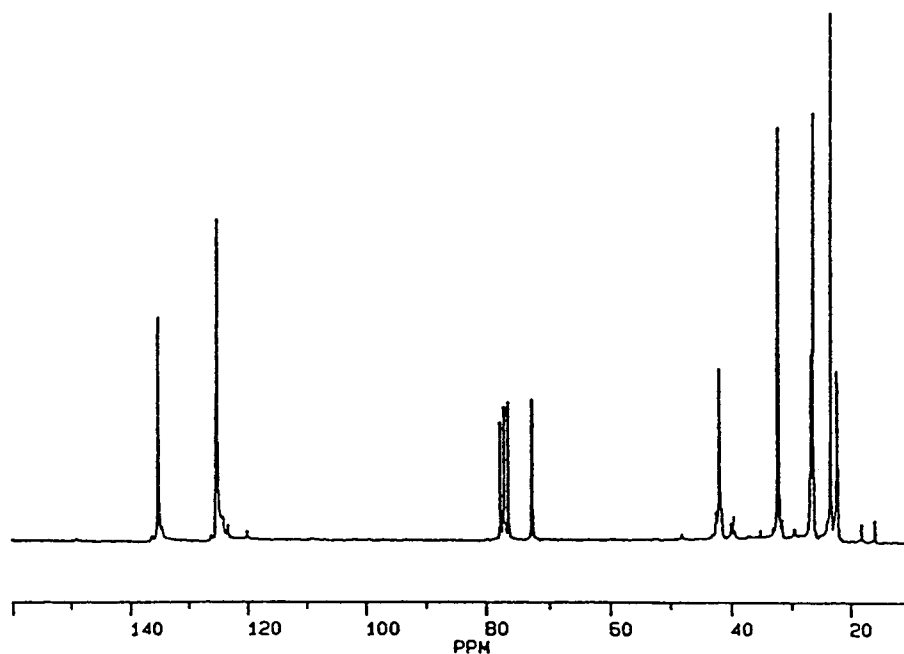


Figure 1 Typical ¹³C-NMR spectrum of partially hydroxylated rubber.

Table I ^{13}C -NMR Assignments of Partially Hydroxylated Rubber

	Carbons								
	α	β	γ	δ	ϵ	a, c	b	d	e
δ ppm	32.2	135.2	125.0	26.8	23.4	41.9, 42.4	72.7	22.4	26.4

Coating Formulations and Performance Tests

The coatings were formulated by dissolving additives, catalyst (Tone[®] 301), and chlorinated hydroxyrubber in solvent with shaking. The polyisocyanate (ca. 5–10% excess of hydroxyl equivalent) was added and the mixture was thoroughly stirred. The paint was applied with a draw bar at wet thickness of 2 mil. Standard aluminum Q-panels were used for all tests with the exception of impact evaluations, which used steel panels and free films that were obtained by using polyethylene panels.

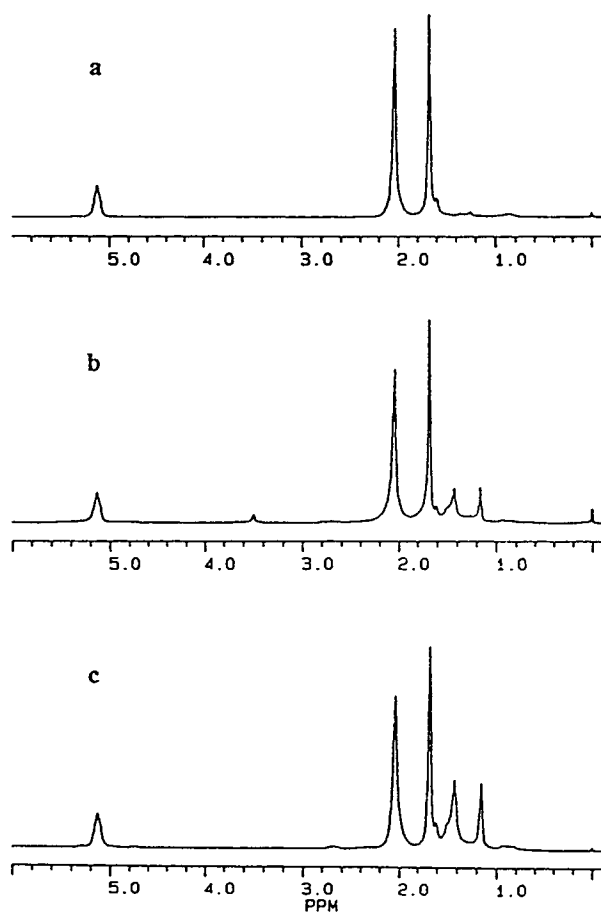


Figure 2 Typical ^1H -NMR spectra of partially hydroxylated rubber with different reaction times between rubber and trichloroacetic acid: (a) 0 h; (b) 23 h; (c) 48 h.

All tests were performed according to ASTM methods (with their ASTM # in Table IV) after the coatings cured for 7 days at ambient. The thickness of the tensile test samples was measured with a caliper having a sensitivity of 10^{-4} in.

RESULTS AND DISCUSSION

Synthesis

Chlorinated hydroxyrubber was synthesized via the chlorination of partially hydroxylated rubber, whereas the latter was prepared via the ester saponification of the adduct of natural rubber and trichloroacetic acid (Scheme 1).¹⁶ The reaction was carried out at 0°C under nitrogen atmosphere and the saponification was performed without isolation of the adduct. The process was straightforward and no interfering side reactions (e.g., cyclization of the rubber) were noted. The hydroxyl content of the product could be controlled by varying the reaction time.

Partial hydroxylation was confirmed with ^1H - and ^{13}C -NMR spectroscopy. The ^{13}C -NMR spectrum (Fig. 1) is consistent with the partially hydroxylated natural rubber as reported by Kim and Pandya.¹⁶ The ^{13}C -NMR assignments are listed in Tables I, while the ^1H -NMR is described in Figure 2. In addition to three major polyisoprene peaks (δ 5.13, 2.04, and 1.68 ppm, corresponding to vinyl, double-bond methylene, and double-bond methyl protons, respectively), two absorptions corresponding to methyl (δ 1.16 ppm), and methylene protons (δ 1.42

Table II Hydroxyl Content (wt %) of Hydroxylated Rubber vs. Reaction Time (RT) Between Rubber and Trichloroacetic Acid

RT (h)	Hydroxylated DPR-40	Hydroxylated DPR-400
23	3.7%	3.0%
48	6.0%	5.8%

Table III Properties of Chlorinated Hydroxyrubber

	RT = 23 h in Table II		RT = 48 h in Table II	
	CH Rubber			
	DPR-40	DPR-400	DPR-40	DPR-400
OH content (wt)	1.8%	1.5%	2.8%	2.8%
Cl content (wt)	51.7%	49.4%	52.7%	51.4%
T_g (°C)	77.9	71.9	104.9	91.9

ppm) are present. The fraction of hydroxylated isoprene units (**F**) can be determined from an integration of the areas representing the methyl ($S_{1.16 \text{ ppm}}$) and double-bond methyl protons ($S_{1.68 \text{ ppm}}$), i.e.:

$$F = S_{1.16 \text{ ppm}} / (S_{1.16 \text{ ppm}} + S_{1.68 \text{ ppm}}) \quad (1)$$

The hydroxyl content (**H**) of hydroxyrubber was subsequently calculated from **F** in the following manner:

$$\text{Hydroxyl content (wt \%)} \mathbf{H} = 17 \times \mathbf{F} / (68 + 17 \times \mathbf{F}) \quad (2)$$

The hydroxyl contents, as a function of reaction times, are listed in Table II.

Chlorinated hydroxyrubber was prepared via the chlorination of hydroxylated rubber with chlorine gas, leaving the remaining hydroxyl groups un-

changed. We did not detect side reactions under these mild chlorination conditions. FTIR analyses indicated that hydroxyl groups remained intact during the chlorination process. The product is a slightly yellow solid that forms clear, tough films. It is soluble in a variety of solvents including aromatic and chlorinated solvents (e.g., xylene, toluene, chloroform, and methylene chloride). Its chlorine content (**C**) was obtained from elemental analysis, whereas the hydroxyl content (**HC**) was calculated as follows and are included in Table III:

$$\mathbf{HC} = (1 - \mathbf{C}) \times \mathbf{H} \quad (3)$$

Spectroscopic Characterizations

The FTIR spectra of the chlorinated hydroxyrubber of varying hydroxyl content are shown in Figure 3. The presence of hydroxyl and chlorine is evidenced

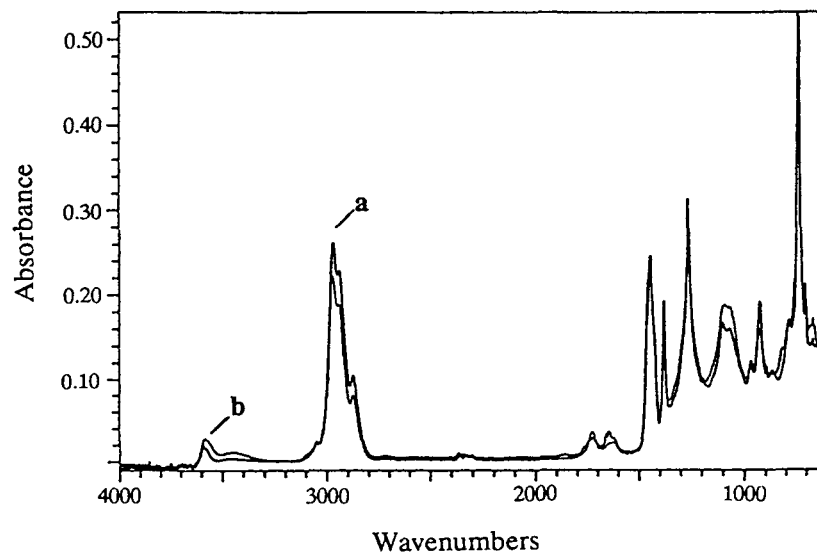


Figure 3 FTIR spectra of chlorinated hydroxyrubber with different hydroxyl contents (wt): (a) 1.8%; (b) 2.8%.

by characteristic absorption of O—H (near 3600 cm^{-1}) and C—Cl (738 cm^{-1}).¹⁶ The weak absorptions at 1648 and 1730 cm^{-1} confirm the presence of remaining vinyl groups and residual ester functionality, respectively.

The solid-state ^{13}C -NMR spectra of chlorinated hydroxyrubber, derived from lower molecular weight commercial rubber (DPR-40), are shown in Figure 4 and are very similar to those of higher molecular weight rubber (DPR-400)-derived chlorinated hydroxyrubber. The broad peaks ranging from 20 to 80 ppm indicate structural complexity. According to Makani and co-workers,¹¹ the broad peaks from 18 to 59 ppm are the contributions from methyl carbon ($-\text{CH}_3$), methylene carbon ($-\text{CH}_2-$), and methyl carbon linked to a single chlorine ($-\text{CH}_2\text{Cl}$). The broad peak at 66 ppm corresponds to the methylene carbon connected to a single chlorine ($-\text{CHCl}-$). The peak at 75 ppm is an overlapped peak consisting of contributions from the tertiary carbon connected to a single chlorine

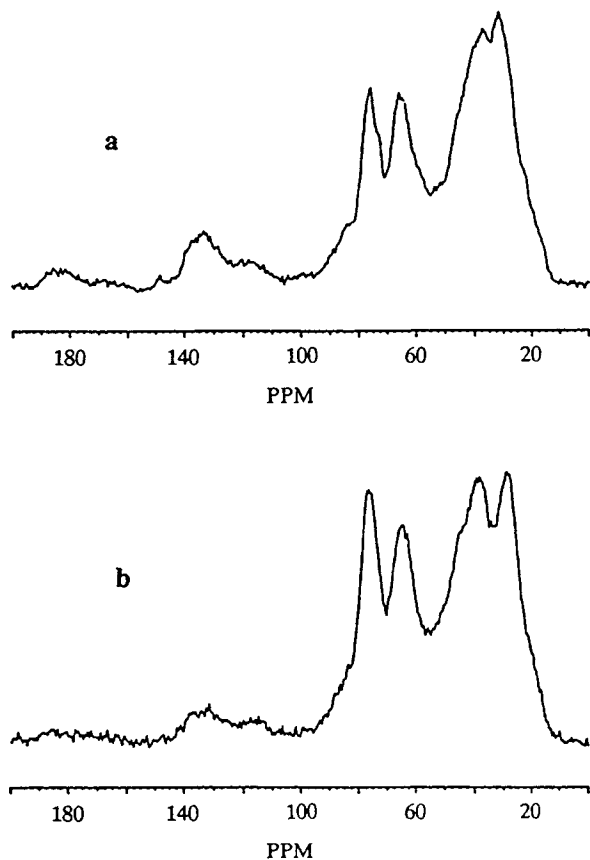
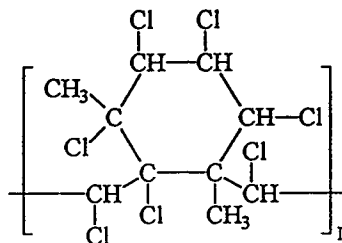


Figure 4 Solid-state ^{13}C -NMR spectra of chlorinated hydroxyrubber with different hydroxyl contents: (a) 1.8%; (b) 2.8%.



Scheme 2 Proposed structure of chlorinated rubber.

($\text{>CCl}-$, $74\text{--}77\text{ ppm}^{11}$) and from the tertiary carbon linked to the hydroxyl ($\text{>COH}-$, 73 ppm^{16}). It is clear that the relative intensity of the peak at 75 ppm depends on the hydroxyl content.

Some small amount of unsaturation, indicated by a broad, weak peak around $130\text{--}140\text{ ppm}$ in ^{13}C -NMR and the small peak at 1648 cm^{-1} in FTIR, exists in all the cases. However, less unsaturation exists in chlorinated hydroxyrubber of higher hydroxyl content.

Thus, spectroscopic characterizations confirm the chlorination and hydroxylation. The ultimate structure determination of chlorinated rubber is difficult, and its *exact* structure remains unknown. The proposed cyclic structure (Scheme 2), which is consistent with a cationic mechanism and a general for-

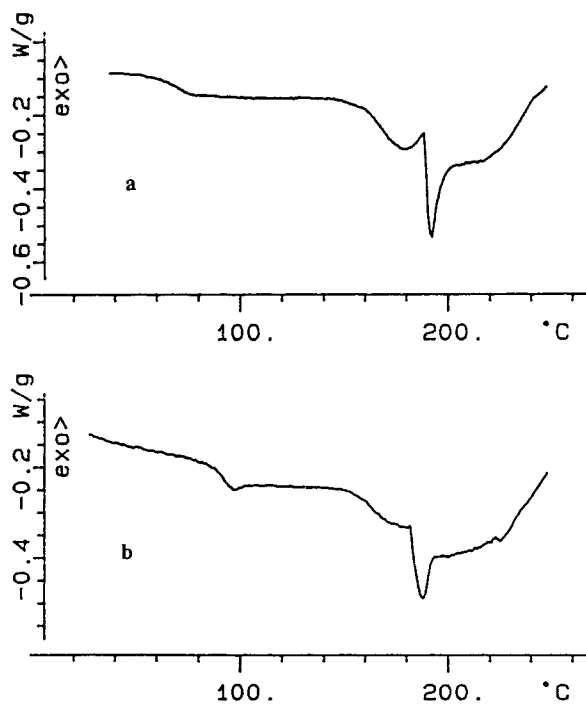


Figure 5 DSC thermograms of chlorinated hydroxyrubber with different hydroxyl contents: (a) 1.8%; (b) 2.8%.

mula ($C_{10}H_{11}Cl_7$), is generally accepted.¹⁷ However, the spectroscopic proof of this structure was reportedly difficult.¹¹ Regardless of its ultimate molecular structure, chlorinated hydroxyrubber shows excellent film-forming capability and promises to be a valuable raw material in a variety of film-forming technologies.

Thermal Properties

All chlorinated hydroxyrubbers (Table III) show similar thermal properties with the exception of their glass transition temperatures (T_g) (Fig. 5). Typically, at temperatures above 150°C, chlorinated hydroxyrubber undergoes an endothermal decom-

position characterized by a very broad endothermal absorption and results in an overlapping of the melting point and decomposition temperature.

The T_g of various chlorinated hydroxyrubbers are reported in Table III. Generally, increasing the hydroxyl content of the chlorinated hydroxyrubber results in higher T_g 's, a likely consequence of stronger interchain H-bonding interaction via the hydroxyl groups.

Chlorinated Hydroxyrubber in Two-component Polyurethane Coatings

Two-component chlorinated hydroxyrubber polyurethane coatings were prepared from chlorinated

Table IV Formulations of Clear Two-component Polyurethane Coatings with Chlorinated Hydroxyrubber (CHR)

	Formulation #		Suppliers
	1	2	
Materials			
CHR DPR-40	40.3 g		
CHR DPR-400		40.0 g	
Tone 301	9.7 g	9.7 g	Union Carbide
Ektapro EEP	20.0 g	20.0 g	Eastman
Xylene	25.0 g	25.0 g	Aldrich
Metacure T-120	0.15 g	0.15 g	Air Products
Byk 080	0.20 g	0.20 g	Byk
Byk 325	0.20 g	0.20 g	Byk
Desmodur N-100	35.0 g	35.1 g	Mobay
Properties			
Wet thickness	2 mil	2 mil	ASTM Method #
Drying time			D-1640
Set to touch	15 min	15 min	
Dust free	30 min	30 min	
Tack free	105 min	105 min	
Solid content by weight	65.5%	65.5%	
Pencil hardness	H	H	D-3363
Tensile strength (kpsi)	4.0	3.6	D-2370
Elongation at break	11%	13%	D-2370
Impact (in.-lb)			
Direct	140	120	Gardener Tester
Reverse	100	80	
Adhesion	5B	5B	D-3359
MEK (double rub)	200	200	D-4752
8 h spot tests ^a			D-1308
Water	5	5	
Concentrated NH_4OH	5	5	
10% NaOH	5	5	
20% H_2SO_4	5	5	

^a 5 = no effect; 4 = stain only; 3 = blistering; 2 = lifted film; 1 = failure.

hydroxyrubber, liquid polyol (Tone[®] 301), and polyisocyanate (Desmodur[®] N-100). The liquid polyol and polyisocyanate were used as reactive diluents to increase the solids content of the coatings. Chlorinated hydroxyrubber of 2.7–2.8% hydroxyl content, together with the polyol, was reacted with isocyanate in a hydroxyl/isocyanate ratio of 1.0/1.05–1.10. The coatings, thus formed, were cured at room temperature by an organotin catalyst. The formulation and coating performance are listed in Table IV. The cured coatings are insoluble in solvents known for their ability to dissolve chlorinated rubber (e.g., methylene chloride and xylene). The cross-linking of chlorinated hydroxyrubber and hexamethylene diisocyanate (HDI)-based polyisocyanate improves the solvent resistance of chlorinated rubber coatings. Furthermore, the use of a multifunctional alcohol as part of the formulation resulted in a significant increase in solvent resistance. Similar film properties were obtained for the chlorinated hydroxyrubber from DPR-40 and DPR-400. Overall, the coatings properties are very good; they are tough, high in gloss, and resistant to water, organic solvent, and most chemicals. The viscosity of the coatings is strongly dependent on the molecular weight of the hydroxyrubber. For instance, chlorinated hydroxyrubber from lower molecular weight DPR-40 gives a formulation of lower viscosity.

CONCLUSIONS

Chlorinated hydroxyrubber was synthesized via the chlorination of partially hydroxylated rubber derived from liquid natural rubber, and its spectroscopic and thermal characterizations have been completed. Chlorinated hydroxyrubber is a versatile convertible binder that has applications in a wide spectrum of coating needs. Two-component chlorinated hydroxyrubber polyurethane coatings show excellent chemical, water, and solvent resistance.

USDA is gratefully acknowledged for its financial support of this work (under Contract # 89-38200-4372). The assistance of Dr. Daniel Kugler and Mrs. Carmela Bailey is likewise acknowledged.

REFERENCES

1. S. Paul, *Surface Coatings*, Wiley, Chichester, 1985, pp. 248–260.
2. E. Marechal, in *IUPAC Macromolecules*, H. Benoit and P. Rempp, Eds., Pergamon, New York, 1982, p. 85.
3. P. Nogues, F. Dawans, and E. Marechal, *Makromol. Chem.*, **182**, 843 (1981).
4. P. Nogues, F. Dawans, and E. Marechal, *Makromol. Chem.*, **182**, 3481 (1981).
5. P. Nogues, F. Dawans, and E. Marechal, *Makromol. Chem.*, **183**, 549 (1982).
6. Y. P. Singh and R. P. Singh, *J. Appl. Polym. Sci.*, **29**, 1297 (1984).
7. K. Anbazhagan, C. R. Reddy, and K. T. Joseph, *J. Appl. Polym. Sci.*, **30**, 391 (1985).
8. K. Anbazhagan, C. R. Reddy, and K. T. Joseph, *Polym. Degrad. Stab.*, **15**, 109 (1986).
9. P. C. Deb and S. C. Sankholkar, *J. Appl. Polym. Sci.*, **43**, 1007 (1991).
10. S. Sankholkar and P. C. Deb, *J. Appl. Polym. Sci.*, **39**, 1681 (1990).
11. S. Makani, M. Brigodiot, and E. Marechal, *J. Appl. Polym. Sci.*, **29**, 4081 (1984).
12. S. Makani, M. Brigodiot, and E. Marechal, *J. Appl. Polym. Sci.*, **29**, 4091 (1984).
13. C. Bellorin, M. Brigodiot, and E. Marechal, *Eur. Polym. J.*, **22**, 611 (1986).
14. F. Dawans, M. Devaud, and D. Nicolas, U.S. Pat. 4,262,097 (1977).
15. C. J. Martinez and A. C. Chen, U.S. Pat. 4,439,587 (1984).
16. Y. H. Kim and A. Pandya, *Macromolecules*, **24**, 6505 (1991).
17. J. A. Brydson, *Rubber Chemistry*, Applied Science, London, 1978, pp. 178–179.

Received April 29, 1993

Accepted September 15, 1993