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Chlorination of low-molecular-weight *Euphorbia lactiflua* natural rubber

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SUMMARY

The chlorination of low-molecular-weight natural rubber isolated from *Euphorbia lactiflua* latex (LMWER) was accomplished. The reaction was performed by using $Cl_{2(g)}$, and CH_2Cl_2 or CCl_4 solvents. Different temperatures, reaction times and Cl_2 to isoprene ratio were used. The products were characterized by elementary analysis, infrared spectroscopy (FT-IR), ^1H nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The maximum chlorination reached was 59.9%. The properties were found to be comparable with chlorinated rubber obtained from liquid natural rubber (LNR).

INTRODUCTION

Euphorbia lactiflua, a wild shrub that grows in arid regions in Chile, has been selected as a potential renewable source of natural rubber (NR); it has only *cis*-1,4 isoprene units and its molecular weight (MW) is 8.4 x 10^4 (1,2). This low molecular weight rubber (LMWER), although highly stereospecific, is unsuitable for high-performance applications such as *Hevea brasilensis* or guayule (*Parthenium argentatum*) rubber whose MW is 1.2 x 10^6 (3). On the other hand, the LMWER is soluble in common organic solvents and is of low viscosity. Therefore, it could find direct use as a plasticizer or processing aid (4,5). Alternatively, LMWER could serve as a feedstock for production of high value speciality polymer derivatives analogous to those produced from NR.

Chlorinated natural rubber (Cl-NR) is an important industrial product and it is commercially available under several trade names like, e.g., Pergut and Alloprene. It is a thermoplastic powder that is nonflammable and is resistant to attack of both acid and basic solutions up to 100°C (6). It is mainly used in the formulation of chemical- and heat-resistant paints and coatings, Cl-NR is also used in the formulation of adhesives and printing inks (7,8).

A major impediment in the manufacture of Cl-NR is the gel content of raw NR, which makes the preparation of solutions difficult. This procedure could be improved to a great extent by using depolymerized liquid natural rubber (LNR) which can be dissolved in CCl_4 to obtain solutions that can be stirred and homogenized during the chlorination (9). Since MW of LMWER is similar to the MW of LNR, the chlorination of LMWER could be performed in homogeneous solutions in apolar solvents.

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The objective of the present research is to study reaction conditions such as time, temperature, ratio of $Cl_{2(g)}$ to isoprene units, effect of UV light, to find conditions that lead to polymers with high Cl content and with similar properties to those used in industry. We report here the formation and characterization of chlorinated low-molecular-weight *E. lactiflua* rubber (Cl-LMWER) with different percentages of chlorination. To prevent the presence of residual solvent in the product, CH_2Cl_2 has been used instead of CCl_4, except when the temperature was above 35°C. The thermal properties of the Cl-LMWER were evaluated by means of TGA and DSC.

EXPERIMENTAL

Materials

LMWER: Fresh latex from *E. lactiflua* was mixed with perchloroethylene. After removing the azeotrope, the solid was dried at 50°C for 12 hours. Dry latex was dissolved in CH_2Cl_2, then filtered, and the solution was added drop by drop to methanol. The precipitate was centrifuged, dried at 50°C for 12 hours, then in a vacuum dryer at room temperature for 2 hours and weighed. The characterization was done by FT-IR, NMR spectroscopy (^{13}C and ^{1}H), GPC and DSC.

$KMnO_4$ Merck p.a.; HCl (37%) Merck p.a.

All other reagents and solvents were of analytical grade and were used as supplied.

Chlorination

a) Preparation of $Cl_{2(g)}$

$16\ HCl + 2\ KMnO_4 \text{ ---> } 5\ Cl_2 + 2\ MnCl_2 + 2\ HCl + 8\ H_2O$

A two neck 100 mL round bottomed flask, fitted with a separatory funnel provided with a pressure equalizer, was charged with a desired amount of $KMnO_4$ and placed on a magnetic stirring device. The funnel was charged with the desired amount of HCl (37%) (Table 1) and was added drop by drop over a 30-60 min. period under stirring. The flask was also fitted with an outlet gas tube.

b) Chlorination of LMWER

A 100 mL round bottomed flask fitted with an inlet gas bubbling tube was charged with a molar amount of LMWER dissolved in CH_2Cl_2 or CCl_4 (4% w/v solution) (Table 1). The mixture was placed in a bath at 30 or 50°C and stirred continuously with a magnetic device. A tygon connection was placed between the $Cl_{2(g)}$ outlet gas tube and the inlet gas bubbling tube, and the $Cl_{2(g)}$ was flow during 30-60 min. The reaction was maintained at 30 or 50°C under continuous stirring for 2 to 20 hours. The reaction vessel was also provided with a gas outlet tube immersed in a trap with saturated solution of NaOH and connected to a vacuum system, which was operated according to the $Cl_{2(g)}$ pressure, to maintain constant flow. In some runs after finishing the Cl_2 flow, the reaction mixture was poured in a quartz flask and placed under UV light for 6 hours. At the end of the reaction the solution was degassed, the solvent was evaporated and the polymer was dried at 50°C for 12 hours, then in a vacuum dryer at room temperature before analysis.

Analysis

The molecular weight of *cis*-1,4-polyisoprene from *E. lactiflua* was determined by gel permeation chromatography (GPC). Analyses were run in tetrahydrofuran (THF) solution (0.5% w/v) at room temperature on a Bruker L 21B GPC apparatus equipped with Bruker 4000-40000, 40000-400000, 1000 Å columns and refractive universal index detector, using polystyrene calibration.

Infrared analyses were performed on a Nicolet System Magna-IR 550 spectrometer, using films cast on NaCl windows. ^{1}H-NMR spectra were obtained on a Bruker AC 250 P 250 MHz nuclear magnetic resonance spectrometer using deuterated chloroform as solvent with tetramethylsilane as internal reference.

Thermogravimetric analysis and differential scanning calorimetry (DSC) were performed at 30°C/min under nitrogen flow on a STA 625 Polymer Laboratories Series 451 System, from 50 to 500°C.

RESULTS AND DISCUSSION

Isolation and characterization of E. lactiflua rubber

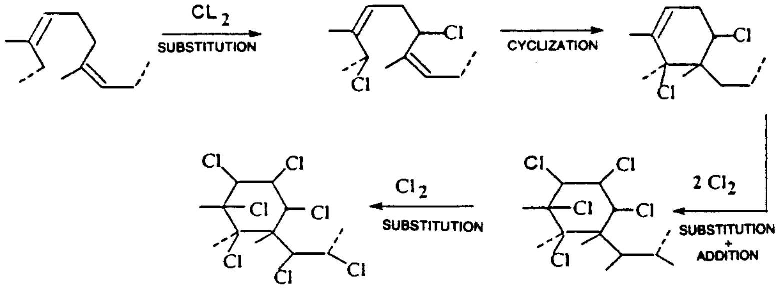
LMWER was isolated from *E. lactiflua* latex following the fractionation method given in the Experimental section. The yield from different samples were from 12.6 to 20.8% on dry weight basis.

FT-IR, ^{1}H and ^{13}C-NMR spectra agreed with those given in the literature (5-9) for *cis*-1,4-polyisoprene. The presence of -OH, -CO and >C=O groups, that generally are found in variable amounts in raw NR, were not found in the ^{13}C or ^{1}H-NMR spectra. Nevertheless, the FT-IR spectrum shows a medium intensity peak due to OH stretching at 3200-3400 cm^{-1} and weak signals in the >C=O stretching region, 1750 cm^{-1}, and C-O stretching, 1100 cm^{-1}. Therefore it could be concluded that these groups are present in the LMWER in small quantities.

GPC analysis gave Mw = 83570 and Mn = 48300, with a MWD (Mw/Mn) of 1.7. The intrinsic viscosity of LMWER was 0.58 dl g^{-1} which is suitable for industrial purposes.

Chlorination

The chlorination of NR is a highly complex substitution, addition and cyclization process (11-16). The mechanism is not fully understood, and the ultimate structure of Cl-NR remains unknown (14). The proposed cyclic structure is consistent with a cationic mechanism (scheme 1) (11-16). The formation of 5-membered rings during the last stage of chlorination, $Cl/C_5 < 1$ has also been suggested (1).



Scheme 1. Chlorination of NR

TABLE 1. Chlorination conditions and characteristics of Cl-LMWER.

	Reaction conditions			Cl-LMWER			
Run Nº	Time[b] (hours)	T °C	Mol ratio[d] $Cl_2/C{=}C$	% Cl[e]	Tg[f] (°C)	TDT-10[g] (°C)	TDT-50[g] (°C)
1	0.5+2	30	4	36.91	62.9	226	414
2	0.5+7	30	4	49.37	61.3	262	416
3	0.5+14	30	4	49.93	61.9	255	324
4	0.5+20	30	4	57.50	61.6	271	331
5	1.0+7	30	8	56.63	62.1	287	328
6	1.0+20	30	8	59.77	65.6	285	334
7	0.5+14	50	4	43.33	85.4	-	375
8[a]	0.5+20	50	4	46.72	88.9	226	333
9[a]	0.5+20	50	8	48.45	92.7	262	412
10	0.5+6[c]	36	4	38.03	59.1	237	398
11[a]	0.5+6[c]	36	4	54.02	60.3	256	329

a: Solvent CCl_4, all the other solvents CH_2Cl_2

b: The first value is the time of $Cl_{2(g)}$ bubbling, the second is the time of reaction.

c: Under UV light

d: Theoretical molar ratio of $Cl_{2(g)}$ to isoprene units

e: Obtained from elementary analysis

f: Obtained by DSC

g: Obtained by thermogravimetric analysis (TGA); TDT-10 = temperature at 10% of weight loss; TDT-50 = temperature at 50% of weight loss.

The extent of chlorination and product characteristics depend on the reaction conditions and type of rubber utilized (12, 14). The conditions and results are given in Table 1. The reactions were carried out in CH_2Cl_2 solutions (4% w/v) to facilitate the separation of the residual solvent in the polymer (12); when the reactions were carried out at higher than 35°C, CCl_4 was used.

Effect of the reaction conditions

It was found (Table 1) that the percentage of Cl incorporation depends on the time and the ratio of Cl_2 to isoprene units used. In the early stage of the reaction, Cl incorporation was relatively fast (run 1) and after it was rising slowly (runs 2 to 4). This is in agreement with previous results based on kinetic and spectroscopic studies which had proposed during the first stage of chlorination fast Cl incorporation exclusively by substitution (11, 15).

The results in Table 1 show that an excess of $Cl_{2(g)}$, maintaining the temperature and time, leads to a higher chlorine level in the final product (runs 5 and 6 vs. runs 2 and 4).

On the other hand, it was found (Table 1) that the extent of chlorination was lower at 50°C than at 30°C, maintaining the reaction time and Cl_2/C=C ratio (runs 3, 4 and 6 vs. runs 7, 8 and 9). This could be explained by side reactions due to hydroxyl or epoxy groups (detected in small quantities in LMWER) with the hydrochloric acid formed and/or to crosslinking. The Cl-LMWER obtained at 50°C showed reduced solubility in common organic solvents.

When UV light was used and CCl_4 (run 11), a higher extent of Cl incorporation was obtained at similar reaction time and Cl_2/C=C ratio than in the reaction in the absence of UV light (run 2); the corresponding mechanism is shown in scheme 1, which proposes a final stage of substitution. When UV light was used and CH_2Cl_2 (run 10), a lower incorporation of Cl was obtained. This could be explained by assuming that the heat generated by the UV light did not allow, under the experimental conditions, to maintain the temperature below 36°C, which caused partial evaporation of CH_2Cl_2 (bp = 40.1°C) and therefore of the dissolved $Cl_{2(g)}$.

Characterization of Cl-LMWER

As the level of chlorination increases, the FT-IR of the chlorinated polymers shows a progressive enhancement of the bands, between 690 and 788 cm^{-1}, due to stretching vibrations of C-Cl groups (17). Moreover, the strong band at 830 cm^{-1} present in the starting polymer (Figure 1) which is due to *cis*-C-H bending, progressively diminished as the chlorination level increased. Nevertheless, even in the Cl-LMWER with 59.9% of Cl, this band did not completely disappear, showing that there are still some >C=C< groups remaining; this has been confirmed by the bands at 1630 cm^{-1} present in this polymer (Figure 1).

The ^{1}H-NMR spectra of chlorinated rubbers of composition $Cl/C_5 > 1$ are very complex because of overlapping of olefinic signals and those due to various >CHCl, $-CH_2Cl$, and $-CHCl_2$ protons; thus a reliable interpretation of NMR spectra would need an excessively large number of model compounds (11). In the spectra of the polymers obtained there are multiple signals in the δ = 2.5 to 4.0 ppm range, corresponding to different -H-CCl and H-C-Cl protons, and a signal at δ = 5.1 ppm (H-C=C-) which confirms the presence of remaining unsaturated groups in the chlorinated polymers.

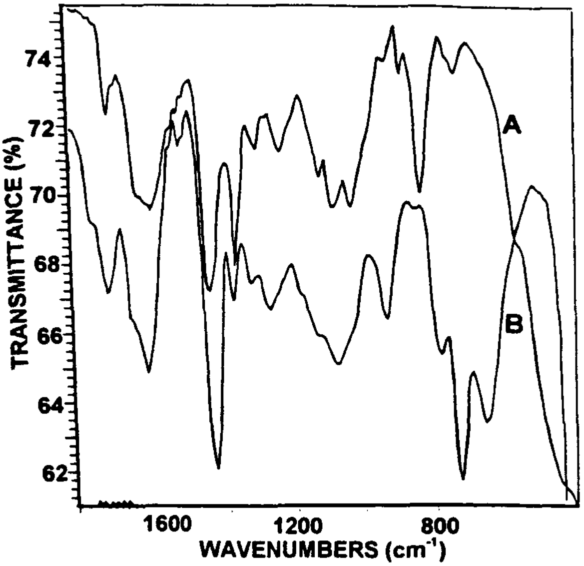


FIGURE 1. FT-IR spectra of A: LMWER, B: Cl-LMWER with 59.8% of Cl.

It has been proposed (18) that the compositional heterogeneity of chlorinated rubbers could be caused by the activation of neighbouring units after a chlorine enters a macromolecule, so that extremely fast chlorination proceeds along the chain. This acceleration causes both high rate and compositional heterogeneity of the product (15).

Thermal properties of Cl-LMWER

All chlorinated LMWER obtained at 30°C show similar thermal properties (Table 1). Typically, their glass transition temperatures (Tg) were between 59 and 63°C (Tg = - 65.9 for LMWER). Complete decomposition occurs at ~300°C where an exotherm has been recorded. Other chlorinated polymers like Cl-NR obtained from *Hevea* or polybutadiene also show similar behavior, with the exception of the Tg, that is lower in Cl-LMWER.

From the thermograms obtained for Cl-LMWER, decomposition is seen to begin at ~130°C, reaching about 10% weight loss (TDT-10) between 230 to 280°C. At about 300°C the main decomposition begins and a plateau is reached at about 400°C with a total weight loss of about 60%. The thermogram of Cl-LMWER with 59.8% Cl, is shown in Figure 2. Assuming that only hydrochloric acid is evolved in the first step, it is found that about 0.5 molecules of hydrochloric acid are lost for each isoprene unit and, after the main decomposition, the value of 60% of weight loss corresponds to the total chlorine content of Cl-LMWER plus the chlorinated side methyl groups.

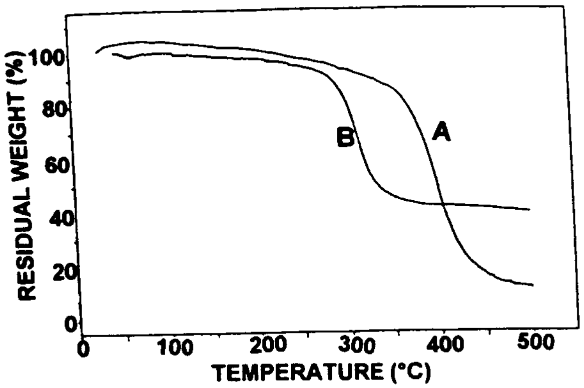


FIGURE 2. Thermogram of A: LMWER, B: Cl-LMWER with 59.8% of Cl.

The Cl-LMWER obtained at 50°C shows Tg values between 85.4 to 92.7°C, similar to those of chlorinated hydroxyrubbers. It has been reported that these values from 71.9 to 104.9°C depend on the percent of OH groups in the rubber and polymerization degree (14). This, besides the lower contents of Cl in the polymers obtained at 50°C, confirms the possibility of side reactions or crosslinking.

CONCLUSIONS

Cl-LMWER has been obtained by chlorinating LMWER in CH_2Cl_2 solution with $Cl_{2(g)}$. Characterization of the polymers has been done by FT-IR and ^{1}H-NMR. The extent of chlorination was determined by elementary analysis. At 30°C, with ratio Cl_2/C=C =8 and 20 hours of reaction, a maximum of 59.9 % of Cl in the product was obtained. Remaining C=C bonds in the product were detected by FT-IR and ^{1}H-NMR spectroscopy.

The catalytic effect of UV light and hence the proposed mechanism of substitution in the last stages of the reaction was confirmed.

The thermal properties of the Cl-LMWER are similar to those reported previously for other chlorinated polymers.

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