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Publisher *Taylor & Francis*

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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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**To cite this Article** Ly, Pham Huu(1996) 'Reinforcement of Natural Rubber from Hydroxyl-Terminated Liquid Natural Rubber Grafted Carbon Black. I. Grafting of Acyl Chloride Capped Liquid Natural Rubber onto Carbon Black', Journal of Macromolecular Science, Part A, 33: 12, 1931 – 1937

**To link to this Article:** DOI: 10.1080/10601329608011017

**URL:** <http://dx.doi.org/10.1080/10601329608011017>

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# REINFORCEMENT OF NATURAL RUBBER FROM HYDROXYL-TERMINATED LIQUID NATURAL RUBBER GRAFTED CARBON BLACK. I. GRAFTING OF ACYL CHLORIDE CAPPED LIQUID NATURAL RUBBER ONTO CARBON BLACK

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## ABSTRACT

This paper deals with the grafting of acyl chloride capped liquid natural rubber (LNR—COCl) onto carbon black by the reaction of the acyl chloride group with the phenolic hydroxyl group on the surface. LNR—COCl was prepared by the reaction of hydroxyl-terminated liquid natural rubber (HTNR) with adipoyl dichloride. The percentage of grafting was estimated to be 18–21% depending on the grafting temperature and the molecular weight of HTNR used. It increased with an increase in the molecular weight of LNR—COCl. The LNR grafted onto carbon black was investigated by IR spectroscopy and by hydrolysis with a dilute THF solution of KOH. It was shown that LNR grafted onto the carbon black surface with ester bonds.

## INTRODUCTION

To improve dispersibility, compatibility of the inorganic powder-polymer composites, and to give various functions to reinforcement inorganic substances such as photosensitivity, bioactivity, crosslinking ability, amphiphilic properties, etc., the chemical and physical modification of inorganic powder surfaces has been extensively studied: for instance, the in situ technique (reinforcing particles in place [1-3], surface modifications by oxidation, treatment with surfactant, plasma treatment, and spattering, especially, by surface grafting of polymers onto inorganic substances [4].

In the present paper we report the grafting of liquid natural rubber (LNR) onto carbon black by the reaction of acyl chloride capped liquid natural rubber (LNR-COCl) with phenolic hydroxyl groups on the surface. In addition, the effects of the grafting temperature and of the molecular weight of HTNR on the grafting onto carbon black surface were also discussed.

## EXPERIMENTAL

### Materials

Hydroxyl-terminated liquid natural rubbers (HTNR) with  $M_n$  of 3,000-10,000 and  $F \approx 2$  (Table 1) were prepared by photochemical degradation of natural rubber (NR) (10% toluene solution) using  $H_2O_2/THF$  and sunlight [5]. All HTNRs were treated with 0.5% w/w Santowhite MK antioxidant and dried in vacuo before use.

The carbon black used was channel black Neospectra II (Columbian Carbon Co., BET specific area:  $906 \text{ m}^2/\text{g}$ ). The content of carboxyl, phenolic hydroxyl, and quinonic oxygen groups on the carbon black was 0.42, 0.26, and 0.90 mEq/g, respectively. The carbon black was dried in vacuum at  $120^\circ\text{C}$  before use.

Adipoyl dichloride (Fluka) was used without any purification. All other reagents and solvents were purified by the usual methods.

### Synthesis of Acyl Chloride Capped Liquid Natural Rubber (LNR-COCl)

Into a 250-mL flask equipped with a dropping funnel, a reflux condenser, and a nitrogen inlet, 0.01 mol HTNR dissolved previously in dry toluene was charged. Then 0.022 mol adipoyl dichloride was added dropwise to the flask under stirring with a magnetic stirrer. The reaction was carried out at  $45^\circ\text{-}50^\circ\text{C}$  in a stream of nitrogen. The solvent and excess of adipoyl dichloride were removed by vacuum distillation using a rotatory evaporator. The resulting LNR-COCl was dried in vacuo at  $45^\circ\text{-}50^\circ\text{C}$ .

### Grafting of LNR-COCl onto Carbon Black

Into a 250-mL flask, 0.40 g carbon black, 6.0 g LNR-COCl (for the control sample, HTNR was used instead) dissolved in dry toluene (100 mL), and 0.2 mL triethylamine were added. The reaction mixture was stirred at  $30^\circ\text{-}110^\circ\text{C}$  under

nitrogen for a definite period of time. After the reaction was completed, the dispersion was centrifuged at  $10^4$  rpm. The precipitated carbon black was extracted with THF until LNR—COCl was no longer detected in the extract. The percentage of grafting was estimated by the equation given in Ref. 6:

$$\text{Percentage of grafting (\%)} = \frac{\text{polymer grafted (g)}}{\text{carbon black used (g)}} \times 100$$

### Stability of Dispersion of LNR-Grafted Carbon Black

The stability was determined by the method described in Ref. 6.

LNR-grafted carbon black (0.30 g) was dispersed in 100 mL THF with a magnetic stirrer, and the dispersion was allowed to stand at room temperature. After a selected time, 5.0 mL dispersion liquid was removed with a pipet, and the content of carbon black dispersed in THF was determined. The stability of dispersion was estimated by the carbon black content of the dispersion:

$$\text{Content of carbon black in dispersion (\%)} = \frac{\text{carbon black dispersed after standing (g)}}{\text{carbon black dispersed before standing (g)}} \times 100$$

### Hydrolysis of LNR-Grafted Carbon Black

The hydrolysis of LNR-grafted carbon black was carried out using 5% THF solution of KOH at  $40^\circ\text{C}$  with stirring. After the hydrolysis was completed, the dispersion was centrifuged. The precipitated carbon black was extracted with THF until HTNR was no longer detected in the extract. Finally, the product was dried in vacuo at  $110^\circ\text{C}$  to constant weight.

## RESULTS AND DISCUSSION

Figure 1 shows the infrared spectra of HTNR and adipoyl chloride capped LNR (LNR—COCl). As seen from Fig. 1, the absorption of hydroxyl group of HTNR at  $3600\text{--}3500\text{ cm}^{-1}$  completely disappeared due to the reaction with adipoyl dichloride. Furthermore, the infrared spectra of LNR—COCl exhibited new absorptions at  $1800$  and  $1740\text{ cm}^{-1}$ , which are characteristic of the acyl chloride group and the ester bond, respectively.

Table 1 presents the molecular weight of HTNR and LNR—COCl, respectively, as determined by vapor pressure osmosis. These values relatively agreed with the theoretical molecular weight.

Figure 2 shows the infrared spectra of untreated carbon black and LNR-grafted carbon black (percentage of grafting  $\approx 21\%$ ). The infrared spectra of untreated carbon black exhibited a broad and weak absorption at  $1620\text{--}1610\text{ cm}^{-1}$ , whereas the infrared spectra of LNR-grafted carbon black possessed the absorption band at  $1740\text{ cm}^{-1}$ , characteristic of the ester bond. In addition to this, other absorption bands in LNR-grafted carbon black agreed with those of LNR—COCl.

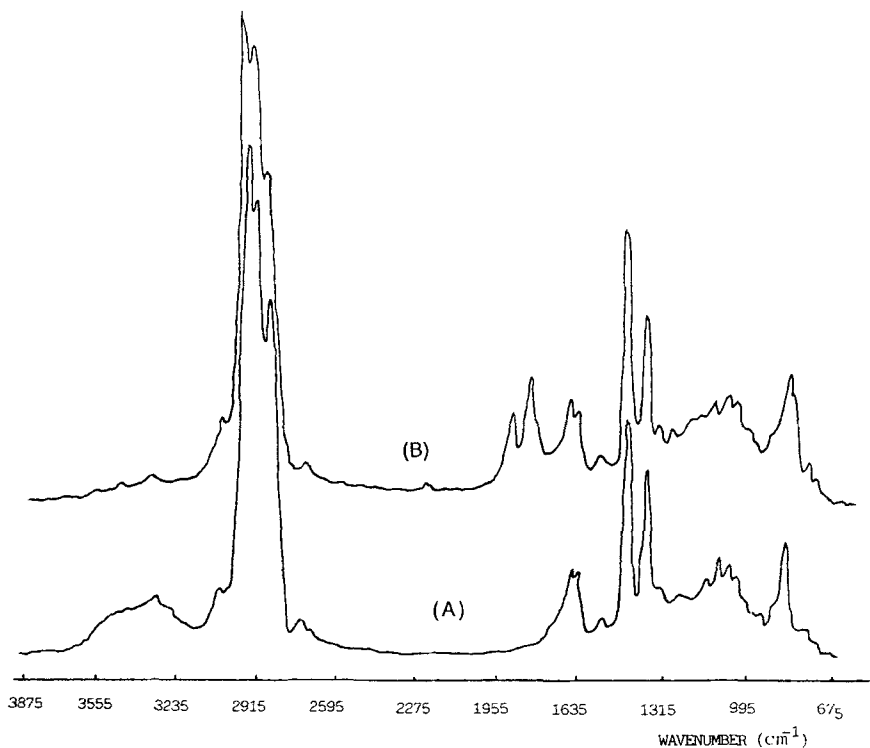


FIG. 1. Infrared spectra of HTNR (A) and of LNR-COCl (B).

Also, the infrared spectra of ungrafted carbon black and of that of hydrolyzed LNR-grafted carbon black by a dilute THF solution of KOH completely agreed. Based on these results, it was concluded that LNR grafted onto carbon black with ester bonds as shown in Scheme 1.

The LNR-grafted carbon black obtained from the reaction was completely dispersed in THF, and no carbon black-LNR gel was observed, indicating that the terminal acyl chloride group of the grafted LNR chain no longer reacted with

TABLE I. Characteristics of HTNR Used as a Starting Compound and of LNR-COCl

| No. | HTNR                   |      | LNR-COCl:<br>$M_n \times 10^{-3}^a$ |
|-----|------------------------|------|-------------------------------------|
|     | $M_n \times 10^{-3}^a$ | $F$  |                                     |
| 1   | 3.0                    | 1.94 | 3.3                                 |
| 2   | 4.0                    | 1.92 | 4.2                                 |
| 3   | 6.0                    | 1.89 | 6.4                                 |
| 4   | 8.0                    | 1.91 | 8.2                                 |

<sup>a</sup>Determined by vapor pressure osmosis.

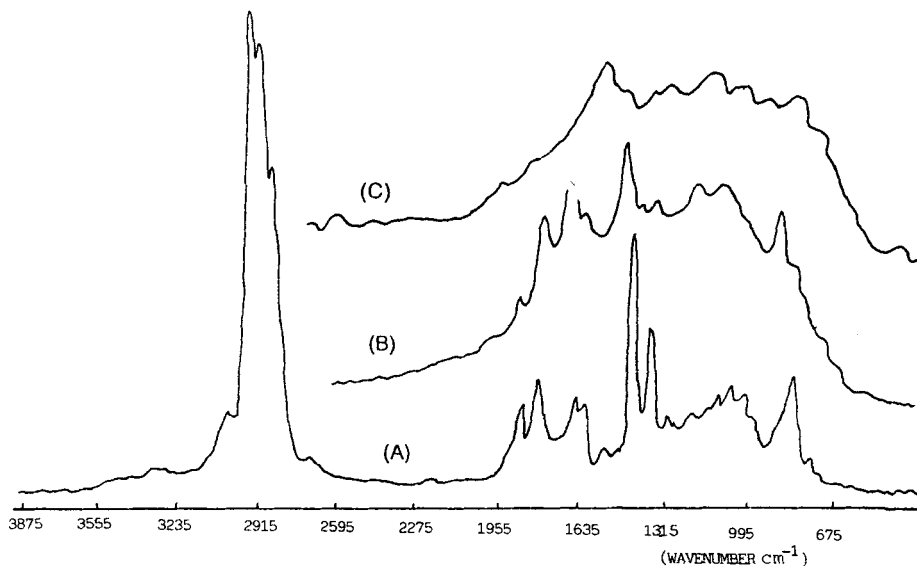
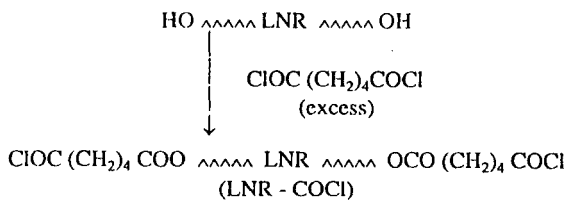
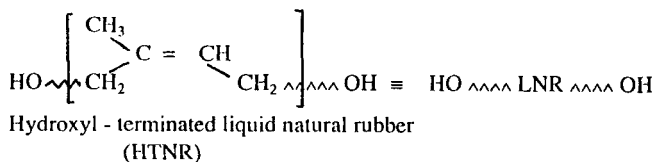


FIG. 2. Infrared spectra of LNR-COCl (A), LNR-grafted carbon black (B), and untreated carbon black (C).



SCHEME 1. Preparation of LNR-grafted carbon black.

TABLE 2. Influence of Temperature, Reaction Time, and Molecular Weight on the Grafting of LNR by the Reaction of LNR—COCl with Carbon Black

| No. | $T$<br>(°C) | $t$<br>(h) | Percentage of grafting     |                                    |                            |                                    |                            |                                    |                            |                                    |
|-----|-------------|------------|----------------------------|------------------------------------|----------------------------|------------------------------------|----------------------------|------------------------------------|----------------------------|------------------------------------|
|     |             |            | HTNR<br>( $M_n =$<br>3000) | LNR—<br>COCl<br>( $M_n =$<br>3300) | HTNR<br>( $M_n =$<br>4000) | LNR—<br>COCl<br>( $M_n =$<br>4200) | HTNR<br>( $M_n =$<br>6000) | LNR—<br>COCl<br>( $M_n =$<br>6400) | HTNR<br>( $M_n =$<br>8000) | LNR—<br>COCl<br>( $M_n =$<br>8200) |
| 1   | 30          | 10         | 5.6                        | 7.2                                | 7.0                        | 7.9                                | 6.9                        | 8.1                                | 7.2                        | 10.9                               |
|     |             | 20         | 6.2                        | 7.9                                | 7.5                        | 8.7                                | 7.2                        | 9.5                                | 7.9                        | 12.7                               |
|     |             | 30         | 6.3                        | 9.1                                | 7.3                        | 10.6                               | 7.5                        | 11.7                               | 8.1                        | 14.7                               |
|     |             | 40         | 6.8                        | 10.5                               | 7.9                        | 13.1                               | 8.0                        | 13.9                               | 8.7                        | 14.9                               |
| 2   | 50          | 10         | 5.9                        | 8.7                                | 7.2                        | 9.2                                | 7.5                        | 10.4                               | 7.6                        | 12.5                               |
|     |             | 20         | 6.5                        | 9.6                                | 7.9                        | 12.8                               | 7.7                        | 14.6                               | 8.2                        | 15.9                               |
|     |             | 30         | 6.8                        | 14.5                               | 8.1                        | 16.8                               | 8.1                        | 16.7                               | 8.7                        | 17.7                               |
|     |             | 40         | 7.1                        | 14.7                               | 8.3                        | 17.2                               | 7.9                        | 17.4                               | 9.0                        | 18.2                               |
| 3   | 70          | 10         | 6.2                        | 9.1                                | 7.6                        | 9.7                                | 7.4                        | 12.1                               | 8.0                        | 15.6                               |
|     |             | 20         | 6.7                        | 12.3                               | 8.3                        | 13.8                               | 8.1                        | 16.7                               | 8.5                        | 17.8                               |
|     |             | 30         | 7.3                        | 17.8                               | 9.1                        | 18.2                               | 8.6                        | 19.2                               | 9.1                        | 21.4                               |
|     |             | 40         | 7.9                        | 17.7                               | 9.8                        | 18.6                               | 9.2                        | 19.9                               | 9.6                        | 21.3                               |
| 4   | 90          | 10         | 7.0                        | 9.4                                | 8.1                        | 9.1                                | 7.9                        | 11.1                               | 8.2                        | 13.2                               |
|     |             | 20         | 6.8                        | 12.5                               | 8.2                        | 12.3                               | 8.0                        | 13.8                               | 8.7                        | 15.6                               |
|     |             | 30         | 6.5                        | 17.8                               | 7.8                        | 16.5                               | 8.1                        | 15.3                               | 9.0                        | 17.1                               |
|     |             | 40         | 6.4                        | 18.1                               | 7.6                        | 14.8                               | 7.8                        | 16.2                               | 9.0                        | 17.8                               |
| 5   | 110         | 10         | 6.6                        | 8.2                                | 7.2                        | 8.0                                | 7.6                        | 10.6                               | 8.6                        | 11.9                               |
|     |             | 20         | 5.8                        | 9.1                                | 6.7                        | 8.8                                | 7.0                        | 9.7                                | 8.1                        | 11.2                               |
|     |             | 30         | 5.1                        | 12.5                               | 6.2                        | 11.1                               | 6.8                        | 10.0                               | 7.2                        | 10.0                               |
|     |             | 40         | 4.7                        | 11.7                               | 5.6                        | 12.0                               | 6.1                        | 9.7                                | 7.0                        | 8.9                                |

Note. Neospectra II, 0.40 g; LNR—COCl, 6.0 g; Et<sub>3</sub>N, 0.2 mL.

carbon black; i.e., product (B) was not able to be formed. A small absorption band at  $1800\text{ cm}^{-1}$  (Fig. 2), characteristic of the COCl group, also confirmed the terminal acyl chloride group of the LNR-grafted carbon black. This might be due to a large excess of LNR—COCl used.

Table 2 shows the influences of the grafting temperature, the reaction time, and the molecular weight of polymers used on the grafting of LNR—COCl onto carbon black. The results indicate that HTNR was retained on the surface of carbon black even after extraction with THF. The gain in weight of treated HTNR was 6–10%. This is possibly due to the steric hindrance increasing with temperature, as reported in Ref. 6, and also due to the adsorption of HTNR onto a carbon black surface; i.e., this is the HTNR that finds itself in the internal void space of the structure aggregates of carbon black. The adsorption degree of HTNR onto the carbon black surface decreased with increasing temperature, especially at  $110^\circ\text{C}$ ,

which may be caused by thermal oxidative degradation of the occluded HTNR. The same tendency was observed in the grafting reaction of carbon black with LNR-COCl. However, the amount of HTNR retained on the carbon black surface was considerably less than that of LNR-COCl grafted onto the surface. Therefore the LNR-COCl was effectively grafted onto the surface by the reaction of the LNR-COCl with carbon black. It can be seen from Table 2 that the optimum temperature of the grafting reaction of LNR-COCl with carbon black is about 70°C, and that the percentage of grafting increased with an increase in the molecular weight of LNR-COCl. A similar result was reported previously [6].

The results on the stability of a dispersion of LNR-COCl-grafted carbon black in THF showed that untreated carbon black precipitated in THF after standing for 10–15 h. On the contrary, LNR-grafted carbon black was a very stable colloidal dispersion in THF for, at least, approximately 1 week.

### CONCLUSIONS

LNR was effectively grafted onto the surface through ester bonds by the reaction of LNR-COCl with phenolic hydroxyl groups on carbon black. The grafting reaction was accelerated by raising the reaction temperature up to 70°C. The percentage of grafting increased with an increase in the molecular weight of LNR-COCl and reached maximum values of 18–21% depending on the grafting temperature and the molecular weight of LNR-COCl used.

The use of LNR-grafted carbon black to improve NR vulcanizates is under investigation and the results will be published in the near future [7].

### ACKNOWLEDGMENTS

It is a pleasure to acknowledge the financial support by the National Program on Advanced Materials through Grant KC-05-16, and partial support by the National Fundamental Research Program KT-04.

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