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Quantitative characterization of rubbery ethylene-propylene copolymers used in some commercial high impact Nylons

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Summary

An analytical method has been developed for the rapid quantitative characterization of maleinated EPR and EPDM rubbers in representative commercially available (DuPont, I.C.I.) high-impact nylons. The DuPont product is a nylon graft containing ∿ 20% (wt) maleinated EPDM whereas the I.C.I. product contains ∿20% (wt) maleinated EPR. The maleic anhydride residue attached to the rubber has been determined quantitatively. The rubber in both samples is partially crosslinked. The crosslink-density of the rubber in the I.C.I. product is much higher than that in the DuPont product. The rubbery phase in the DuPont and I.C.I. products contains a crystalline component.

I. Introduction

With the rapid development of rubber-toughened nylon technology a variety of high impact nylons have appeared on the market and attempts have been made to characterize these materials [1,2]. However, most of this work concerned physical properties and the morphology of the rubber-toughened nylons and virtually no attempt was made to study the details of the rubber phase. The present work concerns the structural characterization of the rubbery phase in high impact nylons and describes a quantitative analytical method for the characterization of rubber-toughened nylon-66.

II. Experimental

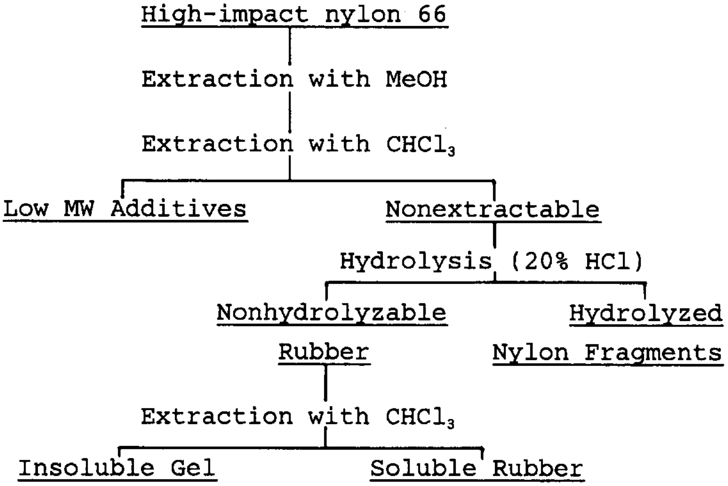
Materials and Instruments

The following high-impact nylons have been investigated: DuPont ST-801 and I.C.I. TA-510. The materials were received in the form of pellets which were ground into very small particles with a grinder at liquid nitrogen temperature. The solvents used for extractions were reagent grade and those for NMR and FTIR spectroscopies were spectro-grade. They were used without purification.

The following instruments were used: FTIR (Beckman FT2100), NMR Varian Assoc. XL-400 Broad Band Spectrometer), GPC (Waters 150-C) and DSC (DuPont 1090 Thermal Analyzer).

Separation Procedure

The rubber-toughened nylon particles were extracted and separated by the following procedure:



The acid hydrolysis of the nonextractable frction was designed to decompose the nylon phase and thus to allow quantitative recovery of the nylon grafted rubber.

All the fractions were characterized by FTIR, ^1H-NMR, GPC, and DSC. Two fractionations per sample were carried out and the results reflect the average of two determinations.

III. Results and Discussion

Sequential extractions with methanol and chloroform (Soxhslet, 20 hrs) yielded insignificant amounts (<0.5% and <1.0%, respectively) of viscous liquids (processing aids, stabilizers). Evidently all the rubber is chemically attached to the nylon phase.

The nonextractable fraction was hydrolyzed under stirring with 20% HCl at 85°C. After 40 hrs, the nylon was completely decomposed to diamine and dicarboxylic acid which remained in the HCl solution. The rubber, suspended in the acid solution in the form of small particles, was filtered off, washed three times with hot water, vacuum dried and its quantity was determined gravimetrically. Subsequently the rubber was extracted with $CHCl_3$ (Soxhslet, ∿20 hrs). Table I shows the results in terms of total rubber content, $CHCl_3$-soluble and $CHCl_3$-insoluble fractions.

Table I. Grafted Rubber Fraction

Sample	Rubber Content(%)	Insol.(%)	Sol.(%)
DuPont (ST-801)	18.9	64.2	35.8
I.C.I. (TA-510)	19.0	84.7	15.3

Analysis of the $CHCl_3$-Soluble Rubber Fraction

Figure 1 shows the infrared spectrum of the chloroform-soluble rubber fraction. Most of the bands are due to $-CH_2-$ and $-CH_3$ groups. The absorption at 1710 cm^{-1} suggests the presence of the carbonyl group in both samples. Carbon-carbon double bonds, as indicated by the absorption band at 980 cm^{-1}, may be present in the DuPont sample.

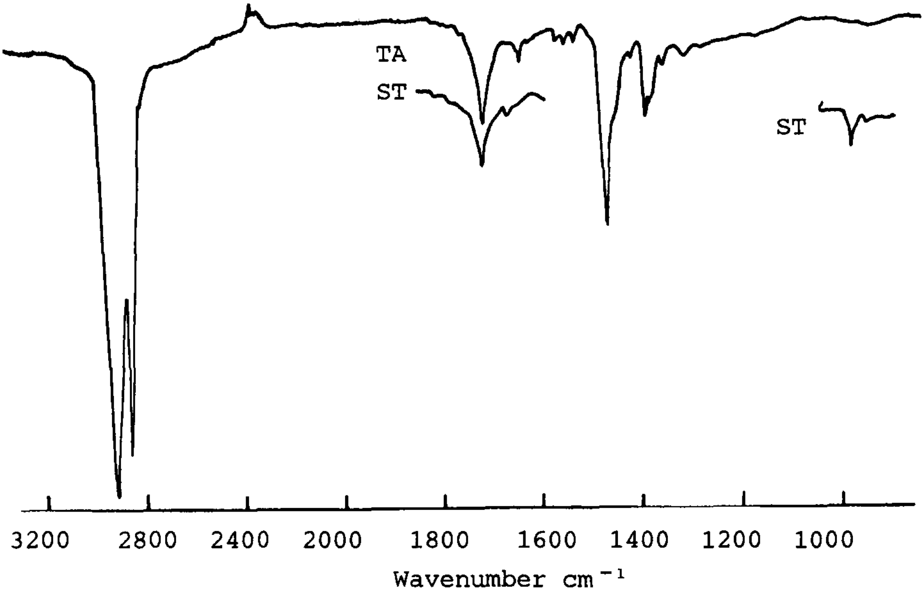


Figure 1. IR Spectra of $HCCl_3$-Sol. Rubber in ST-801 and TA-501

Figure 2 shows the ^{1}H-NMR spectrum of the chloroform-soluble rubbers. The two major resonances at 0.75 and 1.1 ppm are due to the protons of the $-CH_3$ and $-CH_2-$ groups, respectively. Spectroscopic information from IR and ^{1}H-NMR suggests that the rubbers in both samples are mainly of ethylene-propylene copolymers. Furthermore, the weak resonance at 2.2 ppm in the spectra suggests the presence of carbonyl groups in the rubber samples. These studies did not provide conclusive information in regard to the nature of this carbonyl group; however, information gleaned from the literature [2,6] leads us to believe that the carbonyl group is due to the presence of succinic anhydride moieties (and/or its hydrolyzed form) attached to the rubber molecules.

The weak resonance at ∿ 5.2 ppm in the ^{1}H-NMR spectrum of the DuPont sample indicates the presence of protons attached to carbons in C=C double bonds. A comparison of this chemical shift with those in the literature [7] leads us to assign this resonance to R-C-CH=CH-C in DuPont's product. In agreement with the IR findings, unsaturation was absent in the I.C.I. sample.

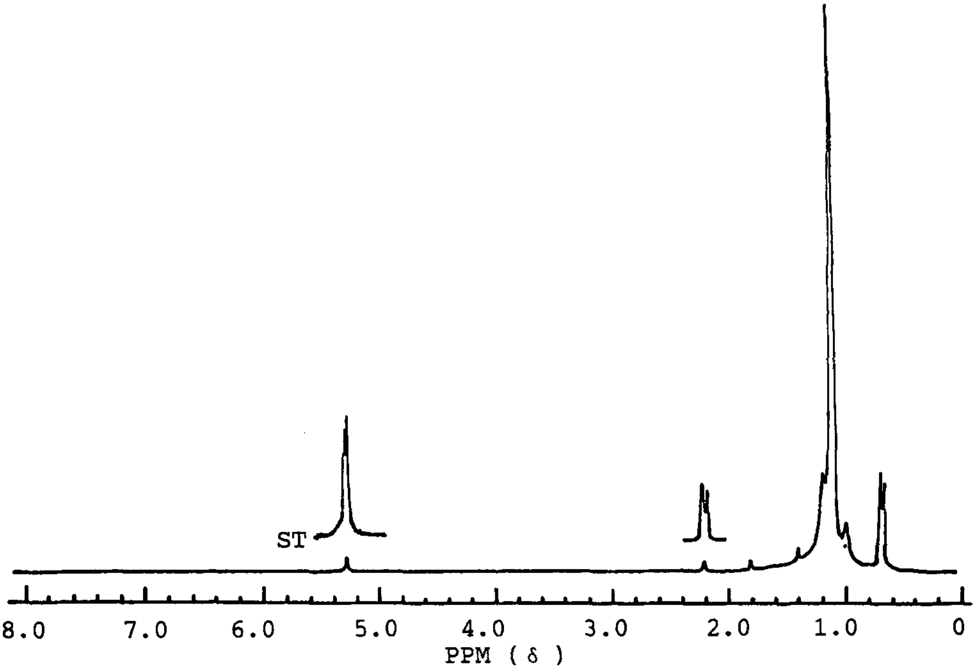


Figure 2. ^{1}H-NMR Spectra of $HCCl_3$-Sol. Rubber in ST-801

According to IR and ^{1}H-NMR spectroscopy the rubber in DuPont's product is maleinated EPDM with 1,4-hexadiene as the termonomer; and the rubber in I.C.I.'s product is maleinated EPR.

The ethylene/propylene ratio, unsaturation content, and maleic anhydride residue content in the rubbers were quantitated by integrating the salient ^{1}H-NMR resonances. Molecular weight and molecular weight distribution data were obtained by GPC analysis. Table II shows the results.

The effect of hydrolysis on the molecular weight and molecular weight distribution of the rubber in the rubber-toughened nylons has been investigated. Thus a representative EPDM Sample (Nordel 2522) was treated under hydrolysis conditions and the molecular weights were determined before and after contact with HCl. Table III shows the results.

Evidently hydrolysis conditions do not affect the molecular weight and distribution of EPDM.

Analysis of the $CHCl_3$-Insoluble Rubber Fraction

Although it is very difficult to characterize quantitatively the insoluble rubber, attempts have been made to determine its swelling-index. The latter is a measure of the crosslink-density of the rubbery phase which strongly affects the ultimate property of rubber-toughened nylons. The swelling index is defined as follows:

Table II. Quantitative Characterization of the $CHCl_3$-Soluble Rubber Fractions

	Method	DuPont	I.C.I.
E/P (wt.)	NMR	69/31	66/34
$\overline{M}_n$	GPC	62,800	43,978
$\overline{M}_w$	GPC	157,400	102,480
$\overline{M}_z$	GPC	264,300	174,180
$\overline{M}_n/\overline{M}_w$	GPC	2.5	2.33
Type of Termonomer	NMR	HD[a]	-
Termonomer Content (mole/100g polymer)	NMR	0.6	-
Carbonyl Content (mole/1000g polymer)	NMR	0.59	0.94

a) 1,4-hexadiene

Table III. The Effect of Hydrolysis on EPDM

	Before Treatment	After Treatment
$\overline{M}_n$	236,870	207,500
$\overline{M}_w$	359,340	347,250
$\overline{M}_z$	555,190	575,950
$\overline{M}_w/\overline{M}_n$	1.52	1.67

$$\rho = \frac{\text{Weight of Solvent Imbibed by the Rubbery Network (g)}}{\text{Weight of Rubber (g)}}$$

To measure the weight of the solvent imbibed by the rubbery network, solid bubble-free samples are required. The samples obtained by exhaustive hydrolysis were porous foams which could not be used for swelling index determinations. While reliable absolute swelling indexes could not be obtained, a series of relative values have been generated for comparison purposes. Thus the chloroform-insoluble fractions were placed in chloroform (5 hrs at ambient) and the swollen samples were centrifuged (15 sec at 3,000 rpm) to remove the supernatant solvent. The weight of the chloroform-swollen rubber samples were then determined. Subsequently the samples were dried in a vacuum oven at 60°C for 5 hrs and after the solvent was removed, the samples were weighed again. The relative swelling index was obtained by the following expression

$$\rho' = \frac{W_1-W_2}{W_2}$$

where W_1 and W_2 are the weight of the $CHCl_3$-swollen network and dry network, respectively. Table IV shows the results (triplicates).

According to these results the reproducibility of the method is acceptble. Evidently, the crosslink-density of the I.C.I. product is much higher than that of the DuPont rubber.

Figure 3 shows representative DSC traces of the chloroform-insoluble rubber samples. The chloroform-soluble fractions exhibit essentially identical patterns. Evidently all the samples exhibit a Tg at about -50°C which is characteristic of ethylene-propylene copolymer rubbers. Significantly, however, the products show in addition to the expected Tg two sharp melting peaks at about 10 and 50°C respectively which are most likely due to short blocks of polyethylene (or perhaps polypropylene) in these rubbers.

Table IV. Swelling Index Determination

Sample	Rubber(g)	Solvent(g)	ρ'	$\bar{\rho}'$
DuPont	0.6578	7.2374	11.0024	
(St-801)	0.8372	7.7383	9.2431	9.7771
	0.5540	5.0336	9.0859	
I.C.I.	0.6452	3.0231	4.6855	
(TA-510)	0.9118	4.6241	5.0714	5.0852
	0.5042	2.7724	5.4986	

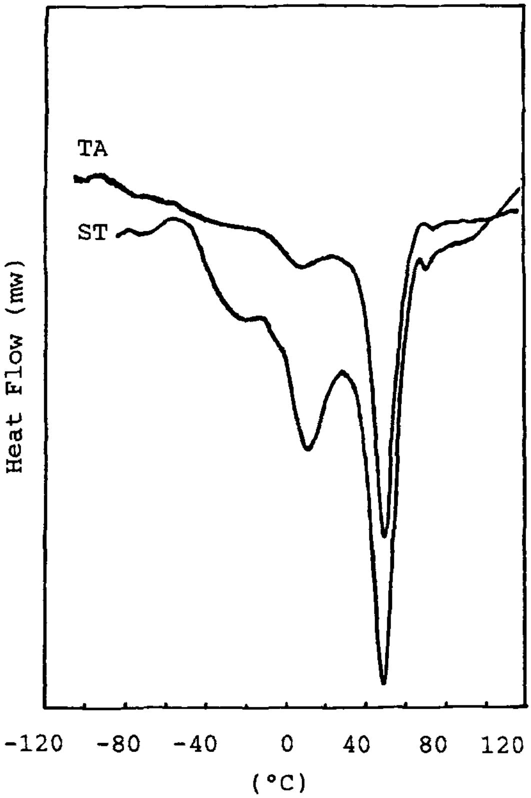


Figure 3. DSC Diagram of CH_3Cl-Insol. Rubber in ST-801 and TA-510
Sample Sie = 3.5 mg
Heting Rate = 20°C/min

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