

## Butyl Rubber Functionalization with Maleic Anhydride Using Nitroxide Chemistry and Their Use in Polymer Blends.

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### 1. Abstract

Butyl rubber (BR) functionalization with 4-hydroxy-TEMPO was carried out in solution at 135°C in the presence of 2,5-di(*t*-butylperoxy)-2,5-dimethylhexane as *t*-butoxy radical source (nitroxide/initiator, N/I=2.7). The functionalization was demonstrated by <sup>1</sup>H-NMR. Functionalized butyl rubber was grafted with singles units of maleic anhydride (MA) by interchange of nitroxide moieties by MA units (BR-g-MA) obtaining thus, a compatibilizer; which was used in blends with nylon 6. The amount of MA (1 wt.%) present in the compatibilizer was obtained by titration to the MA groups. Notice that: i) the functionalization of this kind of substrates is not trivial, because only have along their polymeric backbone, 1.5 mol.-% of potential functionalization sites (double bonds) provides by the isoprenic fraction; and ii) in the industry does not exists commercially BR with grafts of maleic anhydride. Finally, blends BR-g-MA/nylon 6 (not reported before) showed similar mechanics behaviors (Izod impact strength and ductile-brittle transition) in comparison with blends EPR-g-MA/Nylon 6. EPR (ethylene-propylene rubber).

### 2. Introduction

Grafted elastomers are very attractive polymeric materials from both the scientific and the industrial point of view due to their potential applications like: compatibilizers<sup>[1]</sup>, adhesives<sup>[2]</sup>, etc. Butyl rubber (BR) is the copolymer of isobutylene and a small amount of isoprene. First commercialized in 1943, the primary attributes of BR are excellent impermeability/air retention and good flex properties, resulting from low levels of unsaturation between long polyisobutylene segments<sup>[3]</sup>. On the other hand, BR grafted with reactive groups (e.g. MA) is not yet commercially available, and then compatibilization studies (blends) and their corresponding mechanical behaviors are not known yet. Thus, in this work synthesized BR with grafts of MA using the nitroxide chemistry reported by our group before <sup>[4]</sup>. This model compatibilizer was used in polymer blends with nylon6 in order to study their mechanical behavior.

### 3. Experimental

**3.1 Materials:** Butyl rubber (Exxon Butyl 268,  $M_n = 192,095$  Da, PD = 2.4, 1.5 mol-% of unsaturation), nylon6 high molecular weight (Capron B135WP,  $M_n = 29,300$  Da, MFI = 1.2 g/10 min, Honeywell), 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (DTBH), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (4-hydroxy-TEMPO), methanol, toluene, maleic anhydride (MA) and chloroform were used as received. All reactive were supplied by Aldrich.

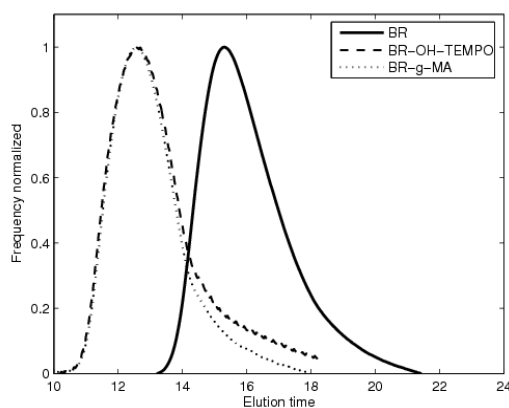
**3.2 Functionalization of BR with 4-hydroxy-TEMPO:** 20 g of BR (1.8 wt.-% isoprenic portion = 0.36 g = 0.0052 mol) and 0.901 g (0.0052 mol) of 4-hydroxy-TEMPO were dissolved in toluene in a 100 mL glass reactor heated by a jacket and equipped condenser and magnetic stirrer. After that, the temperature was increased until 137°C. In these moment 0.55 g (0.0019 mol) of initiator DTBH/toluene were added dropwise in order to prevent the cross-linking reaction. The functionalization reaction proceeded under argon feed during 7h. The functionalized polymer (HBR1) was purified by precipitation in methanol and dissolution in chloroform and was characterized by  $^1\text{H}$ -NMR and GPC

**3.2.2 Grafting of MA onto BR functionalized with 4-hydroxy-TEMPO:** 16 g of HBR1 were dissolved in toluene (80mL) in the presence of MA (0.5 g) at 125°C during 2 h. Grafted polymer was dissolved in chloroform and isolated in methanol. Finally was dried in a vacuum oven at room temperature for 24h and characterized by  $^1\text{H}$  NMR and GPC. The amount of MA (1 %.-wt) was determinate by titration.

**3.3 Polymer blends of nylon6/BR and nylon6/BR-g-MA:** Polymer blends were carried out in a micro-compounder (DSM, 5mL). The residence time, rpm's and temperature to the blend were fixed at 15 min, 80 rpm and 240 °C, respectively. The blends were transferred to the micro-injector (DSM bench-top) in order to obtain specimens to 7.3×1×0.32cm. The molding temperature and injection pressure were fixed at 130 °C and 275.7 kPa/1 min, respectively.

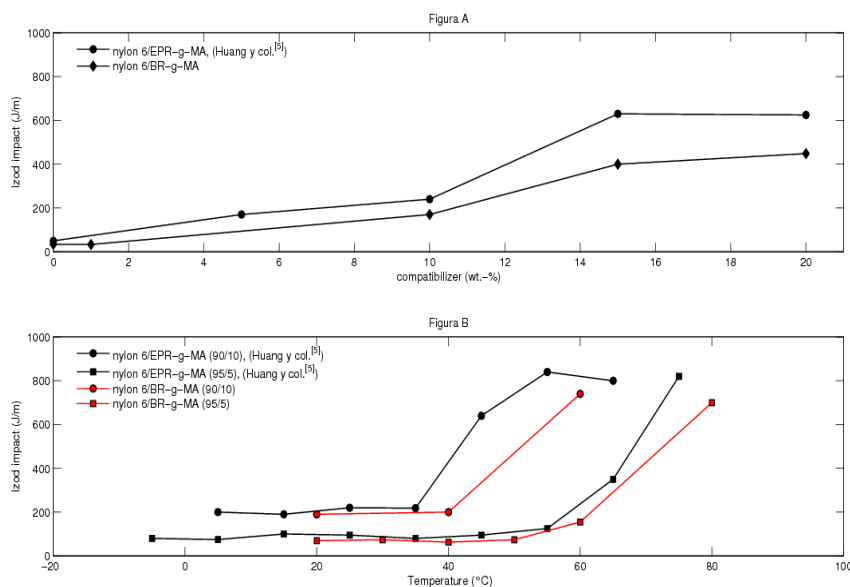
## 4. Results and discussion.

Figure 1 corresponding to GPC chromatograms of unmodified BR, BR-OH-TEMPO and BR-g-MA respectively, comparatively shows the shift of BR-OH-TEMPO (192,000 Da, PDI = 2.4) toward higher molecular weights, which is mainly attributed to the modification of the hydrodynamic volume of BR with nitroxide moieties, indicating that the functionalization took place. On the other hand, BR-g-MA (194,000 Da, PDI = 2.4) shows the same shift than BR-OH-TEMPO.



**Figure 1** Gel permeation chromatograms (GPC) to unmodified butyl rubber (BR), functionalized BR with nitroxide (BR-OH-TEMPO) and butyl rubber grafted with MA (BR-g-MA)

This is desirable in the synthesis of compatibilizers because the structure from original polymer is not modified. The invariability in the molecular weight distribution was attributed to the interchange to the nitroxide group by MA moieties. Each site occupied by a nitroxide radical (which is in dynamic equilibrium), was substituted by a single unit of MA.



**Figure 2.** A) Comparison of the Izod impact strength of binary blends BR-g-MA/nylon6 and EPR-g-MA/nylon6 as a function of total rubber content B) Izod impact strength as a function of temperature for binary blends BR-g-MA/nylon6 and EPR-g-MA/nylon6.

Figure 2A shows the Izod impact strength as a function of EPR-g-MA and BR-g-MA content of binary blends where the matrix is nylon6. Interestingly, the toughness of nylon6

as measured by Izod value increases gradually with BR-g-MA content up to about 15% and then appears to level off. This same effect was previously observed by Huang *et al.*<sup>[5]</sup> using EPR-g-MA (MA=1.2wt.-% ). Up to 15wt.-% of compatibilizer is not observable some improves in the mechanical properties to the blend. This behavior was attributed at that the blend reached a “saturation point”. On the other hand, Figure 2B shows Izod impact strength as a function of temperature for binary blends containing varying amounts of BR-g-MA. With addition of BR-g-MA, regardless of the matrix, the blend shows a ductile–brittle transition which shifts to lower temperatures the larger the amount of BR-g-MA added. Also, this same effect was previously observed by Huang *et al.*<sup>[5]</sup> using EPR-g-MA. In the blend 90/10 (nylon 6/BR-g-MA) the fracture brittle was observable at 40°C, after this value, the behavior to the fracture is ductile; increasing the Izod impact value suddenly due to an slightly increase of temperature. Finally, when is used less amount of rubber (compatibilizer) 95/5 (nylon 6/BR-g-MA) the Izod impact strength value decreases, and the brittle fracture cover a wide range of temperature (20-60)°C.

## 5. Conclusions

We demonstrate the synthesis of compatibilizer on basis to BR. First, BR was functionalized with 4-hydroxy-TEMPO using the “well know” bimolecular process of synthesis in solution in the presence of initiator ( $N/I = 2.7$ ). <sup>1</sup>H-NMR spectra (not showed here) and GPC analysis confirmed this fact. In a second pathway, the BR functionalized with nitroxide moieties in the presence of MA in solution leads BR grafted with single units of MA (model compatibilizer), which was tested in blends with nylon6. The blends exhibited analogous mechanical behaviors (Izod impact strength and ductile-brittle transitions) in comparison with commercial compatibilizers on basis to EPR.

## 6. References.

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