

New Fluorescent Elastomeric Materials Based on Synthetic and Natural Epoxidized Rubbers

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ABSTRACT: New fluorescent elastomeric materials were successfully prepared by reaction of an excited state intramolecular proton transfer-exhibiting silyl-functionalized benzothiazole dye with synthetic and natural epoxidized rubbers. The fluorescence emission and excitation spectra were obtained from the dye and the elastomeric materials to characterize its photophysical behavior. The benzothiazole derivative is fluorescent in the yellow region and presents a Stokes shift of 188 nm (solution) and 198 nm (solid state). After purification, the obtained materials from epoxidized rubbers presented excitation and emission maxima located

at 358 nm and 550 nm, respectively, with a Stokes shift of 192 nm. The fluorescent dye could not be extracted from these films by solubilization-precipitation procedure, indicating the presence of covalent bonding between the dye and the matrix. On the other hand, the dye could be readily washed out of films that had been prepared using the corresponding nonepoxidized rubbers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 282–287, 2008

Key words: benzazoles; ESIPT; epoxidized rubber; fluorescence; elastomers

INTRODUCTION

Functionalized polymers continue to attract much research attention by virtue of the widespread applications that can be envisaged for these new materials.¹ Particular interest has recently been shown in a new class of hybrid polymers that involve a silyl-epoxy interaction.^{2–9} In this context, the application of epoxidized styrene-butadiene rubber (SBRepos) is particularly attractive, since SBR is the most commonly available and the cheapest synthetic rubber, and different degrees of epoxidation can be obtained on a laboratory scale.¹⁰ The reinforcement of elastomers has already been described¹¹ employing a system in which the silica is generated *in situ* through a sol-gel process.^{12–17} This procedure provides a product with a low initial viscosity, thus allowing the formation of transparent films by dip-coating, spraying, or spin coating.¹⁸

Although many studies have already been reported in respect of this particular silica-epoxy network,^{2–9} to the best of our knowledge no simple

method has been described for the production of highly fluorescent elastomers using a dye covalently bound to the hybrid matrix material. With this aim in view, we have employed the photoactive silyl dye 2-[5'-N-(3-triethoxysilyl)propylurea-2'-hydroxyphenyl] benzothiazole (HBTS; Scheme 1),^{19,20} which exhibits a large Stokes shift through an excited state intramolecular proton transfer (ESIPT) mechanism. The photophysical characteristics of the benzazole dyes are very valuable,^{21–23} giving rise to applications in many different fields of research including the formation of ultra violet (UV)-light stable²⁴ and novel polymeric materials,^{25–27} and as fluorescent probes for labeling proteins.^{28,29}

EXPERIMENTAL

Materials and methods

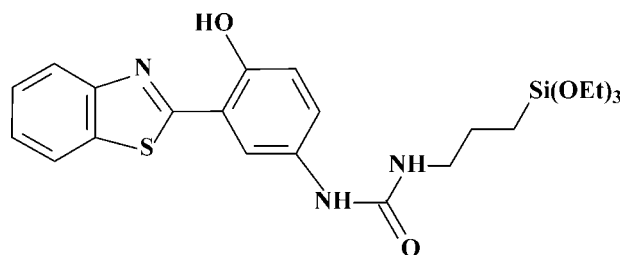
Commercial SBR-53 with 8 mol % of styrene and 53 mol % of 1,2 butadiene units (Bayer AG, Leverkusen, Germany), with a weight-average molar mass (M_w) of 236,750 g mol⁻¹ was used without any further purification and was epoxidized as already presented.¹⁰ The degree of epoxidation was determined by ¹H NMR and ¹³C NMR spectroscopy in an NMR Varian XL-20, where the polymer samples (16–20 mg) were dissolved in CCl₄ with a D₂O capillary. The epoxidation reaction of the SBR-53 was monitored by ¹H NMR spectroscopy through the disappearance of the

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Scheme 1 Structure of the ES IPT-exhibiting dye HBTS.

unsaturated double bond at around 5.4 ppm and the appearance of the epoxy ring at around 2.4–2.7 ppm.

The commercial epoxidized natural rubber (ENR) EpoxyrenTM, with two degree of epoxidation (25 and 50%), was used as received. The fluorescent dye HBTS was synthesized and purified as described in the literature.^{19,20} All other reagents were from Aldrich/Acros and were used as received or purified using standard procedures.³⁰ Infrared spectra were recorded on a FT-IT Mattson Galaxy Series FT-IR3000 model 3020. Fluorescence spectra were measured with a Hitachi spectrofluorometer model F-4500. Spectrum correction was performed to enable measuring a true spectrum by eliminating instrumental response, such as wavelength characteristics of the monochromator or detector using Rhodamine B as a standard (quantum counter). The SBR-53 glass transition temperature analysis was carried out using a DSC polymer laboratory thermal equipment at a heating rate of 10°C min⁻¹.

The SEM pictures were obtained with a JEOL JSM 6060 microscope, with 20 kV and a magnification of 1000X. The samples were fractured under liquid nitrogen, recovered with a thin gold layer (15 nm) and observed perpendicularly to the fracture.

Preparation of the fluorescent epoxidized/nonepoxidized rubbers

The fluorescent elastomers were prepared by dissolving either SBRepos or ENR in THF, and adding a $\sim 10^{-6}$ M solution of the fluorescent dye also dissolved in THF. No catalyst was required to facilitate opening of the epoxy moieties. The mixture was stirred at room temperature for 2 h, and the resulting sols were cast in Teflon plates. Following gelation and slow evaporation of the solvent, the films were dried at 60°C. Purification of the films was carried out by solubilization in THF for 1 week followed by precipitation with ethanol, a procedure that was repeated three times to extract all unbound fluorescent dye.

RESULTS AND DISCUSSION

Figure 1 shows the photophysical behavior of the benzothiazole dye in solution and in the solid-state. The fluorescence curves were obtained using the

absorption or excitation maxima as the excitation wavelengths. The solution experiments were performed in chloroform at room temperature in a concentration range of 10^{-6} M. An absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$) located at 353 nm, with molar extinction coefficient values (ϵ_{max}) in agreement with π - π^* transitions, could be observed. A dual fluorescence could be observed to the HBTS. A main band located at 541 nm, ascribed to the ES IPT band and a blue shifted one, located at 432 nm. This photophysical behavior confirms a conformational equilibrium in solution in the ground state, as already observed to similar heterocycles.³¹ The ES IPT band presents a Stokes shift of 188 nm. The obtained spectra in the solid-state presents an excitation maxima located 352 nm, as well as a main emission band located at 550 nm.

The epoxidized SBR presented a content of epoxidation of 48 mol % and a glass transition temperature of -38°C . An exactly similar preparative procedure was performed using nonepoxidized SBR for comparison purposes. To evaluate the homogeneity of the fluorescence of the polymers produced, pictures of the films were taken under UV radiation and then digitized. A fluorescence intensity profile, to provide a quantitative indication of the level of intensity variation in an image, was performed from the picture of each elastomeric material. This profile was obtained from points taken each 0.04 mm from a horizontal line of 10 mm. The intensities of these points were estimated using Adobe Photoshop (version 6.0), and it was assumed that a lower relative noise would indicate a more homogeneous sample. Figure 2 depicts the elastomeric films based on epoxidized

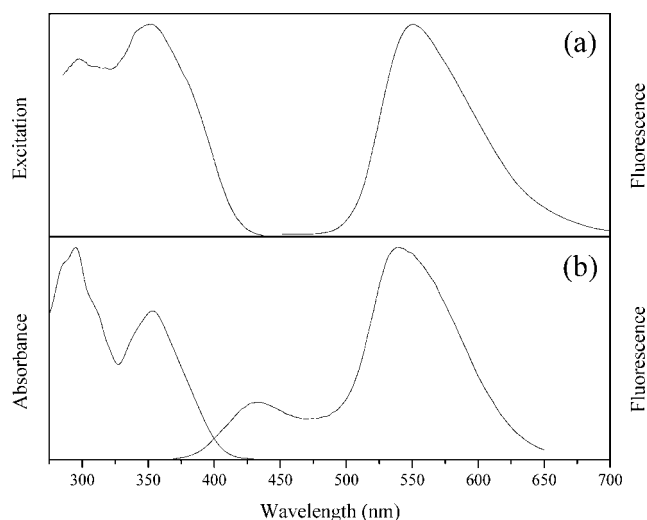


Figure 1 Photophysical study of the benzothiazole dye, where: (a) fluorescence emission and excitation spectra in the solid-state and (b) UV-Vis absorption and fluorescence emission spectra in solution (CHCl_3 [10^{-6} M]). The spectra are normalized.

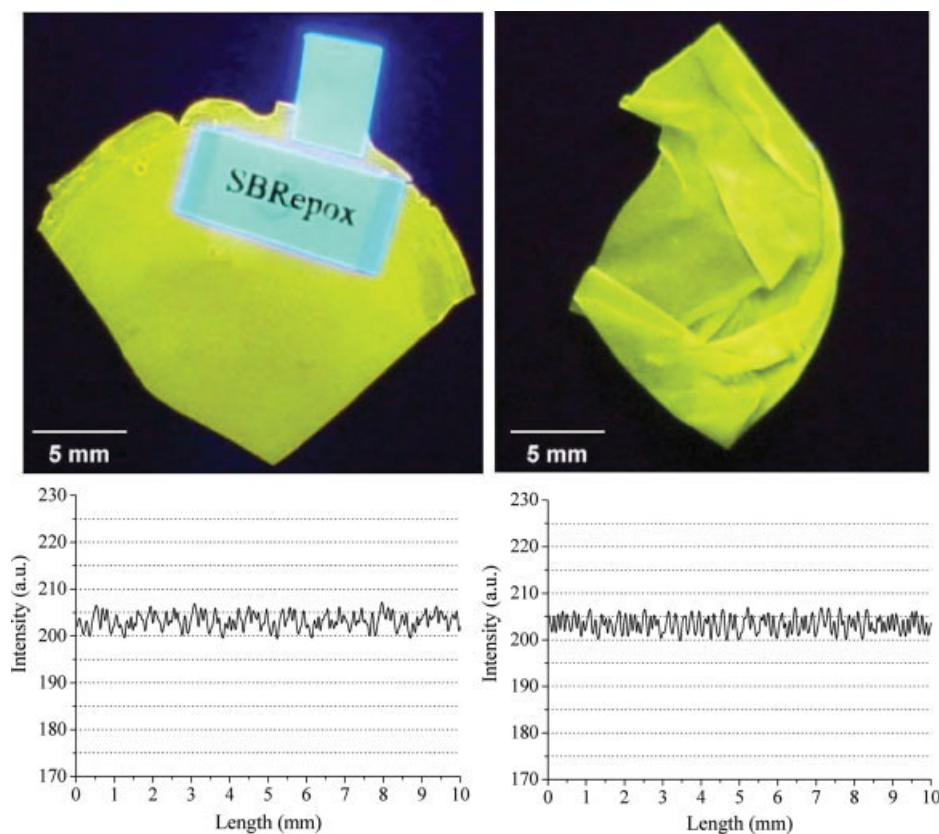


Figure 2 HBTS/Epoxidized styrene-butadiene films: before (left) and after (right) purification. A fluorescence intensity profile is shown below to the corresponding image. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SBR, where the fluorescence intensity profile indicates high homogeneity, even before purification.

Figure 3 presents the steady-state fluorescence emission and excitation spectra from the elastomeric material based on SBRepos, measured before and after purification. Before purification, the fluorescent material presents a main band located at 552 nm, corresponding to the ESIPT band. The same photophysical behavior could be detected after purification, where the emission band is located at 550 nm. Despite of the normalized curves, it could be observed that this material maintained its emission with practically the same intensity. The excitation spectra presented a maximum located at 340 and 358 nm, before and after purification, respectively, which probably indicates the matrix influence on the electronic transition of the dye.

The elastomeric material prepared using the non-epoxidized SBR presented fluorescence emission and excitation spectra only before purification. It could also be observed before purification, that the fluorescence intensity homogeneity was significantly less than that obtained for the films prepared with SBRepos. The purification step showed to be very efficient to remove all unbound dye, since it became colorless. The violet color depicted in Figure 4 was due to the UV lamp reflection.

Figure 5 presents the photophysical study of the elastomeric materials prepared using non-epoxidized SBR. As already observed to the material prepared with SBRepos before purification, a main band

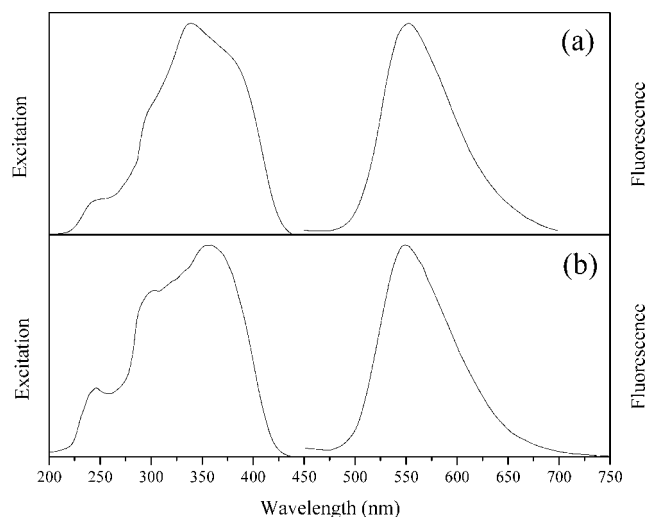


Figure 3 Solid-state fluorescence emission and excitation spectra of the elastomeric material based on SBRepos: (a) before and (b) after purification.

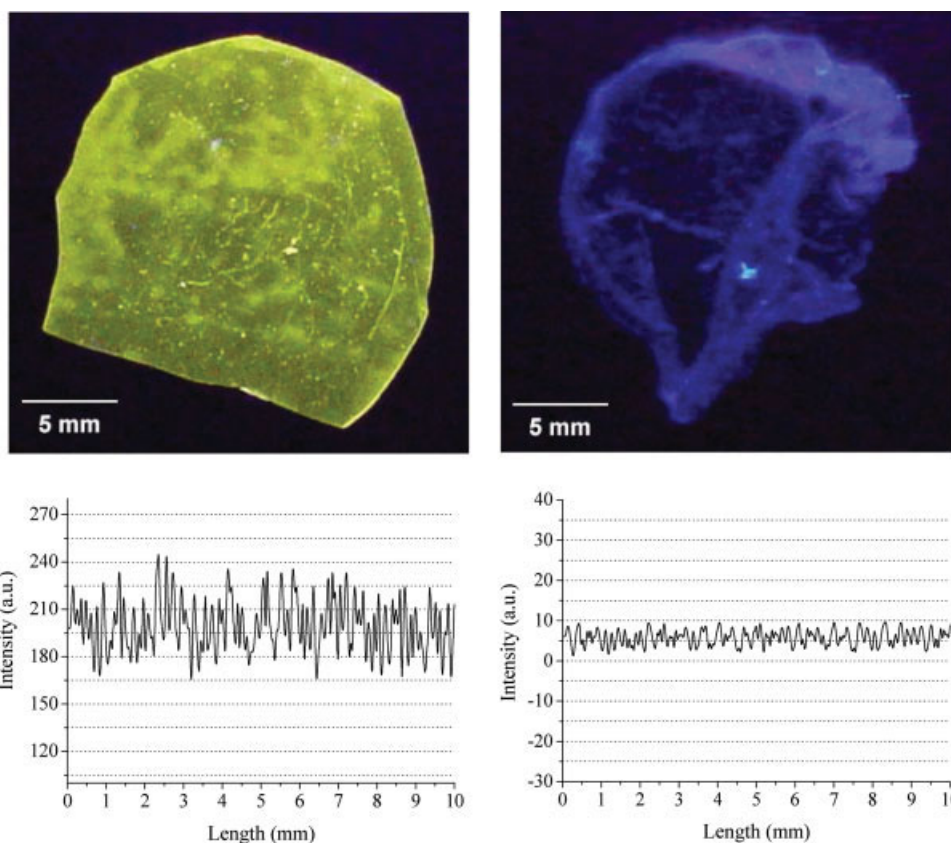


Figure 4 HBTS/nonexoxidized styrene-butadiene elastomeric materials: before (left) and after (right) purification. A fluorescence intensity profile is shown below to the corresponding image. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

located at 551 nm can be observed. However, following purification, a lack of fluorescence indicates that the dye was removed. This result indicates that the

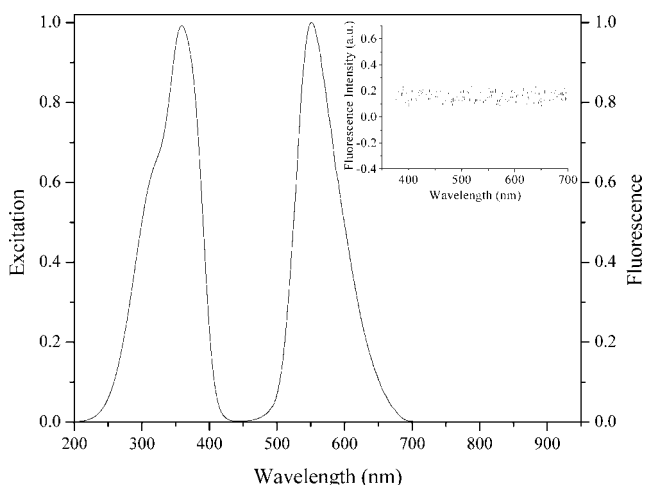


Figure 5 Solid-state fluorescence emission and excitation spectra of HBTS/nonexoxidized styrene-butadiene rubber. The inset presents its fluorescence emission spectra after purification.

epoxy moiety play a fundamental role on the covalent bond between the fluorescent dye/elastomeric matrix.

The same result was obtained using ENR and non-epoxidized natural rubber (NR). Even after purification, the material prepared with the epoxidized NR kept its fluorescence. On the other hand, the dye could be completely removed after purification when the elastomeric material was prepared with nonexoxidized NR. In this way, the epoxy moiety showed one more time, to be decisive in the covalent bond with the fluorescent dye. Figure 6 depicts the elastomeric material with or without epoxy groups after purification. Following purification, the film produced with nonexoxidized NR, which was opaque in contrast to the transparent films obtained with nonexoxidized SBR, exhibited a light blue color probably due to the UV lamp reflection, since this material is not fluorescent (Fig. 6).

Figure 7 presents the photophysical study of the elastomeric materials prepared using natural rubber. As already observed to the materials previously prepared with SBRepos, after purification, a main band of fluorescence emission, located at 550 nm can be

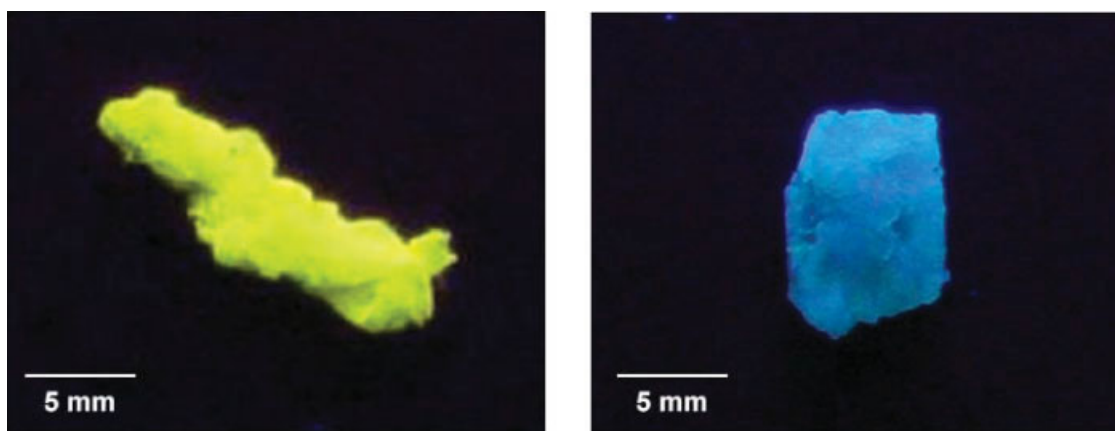


Figure 6 HBTS/epoxidized (left) and nonepoxidized (right) natural rubber films after purification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

observed. The excitation spectra presented a maximum located at 369 nm, with a Stokes shift at around 181 nm.

The purified SBR and SBRebox films were also studied under the scanning electron microscope (SEM; Fig. 8). The elastomeric material prepared with the nonepoxidized rubber presented a homogeneous texture corresponding to the styrene-butadiene matrix, while small spots could be observed on the SEM images of the epoxidized rubber film. Previous SEM studies have indicated that hybrid materials prepared from epoxidized rubbers and tetraethoxysilane exhibit phase separation on a micrometric scale,¹⁶ from which it was concluded that the small aggregates observed are probably due to the fluorescent dye.^{32,33}

The photophysical data obtained from the elastomeric materials indicates that the epoxy moieties

showed to be decisive in the covalent bond with the fluorescent dye HBTS. In this way, to better illustrate this interaction, in Figure 9 are presented the nonepoxidized and the epoxidized rubber with the HBTS before and after purification. Since the SBR or NR do not allow any chemical bond with the fluorescent dye, the HBTS was completely removed after the purification step. The same behavior could not be observed when SBRebox or ENR were used. After the purification step, the elastomeric materials keep its fluorescence, indicating a covalent bond between the epoxy moiety and the fluorescent dye.

Additional attempts, including IR and NMR spectroscopic studies, at characterizing the linkage between the polymer and the inorganic species were made. However, since the HBTS dye was employed as a fluorescent probe in the investigation of these films, it was present only in very small concentrations that were below the limits of detection of these spectroscopic techniques.

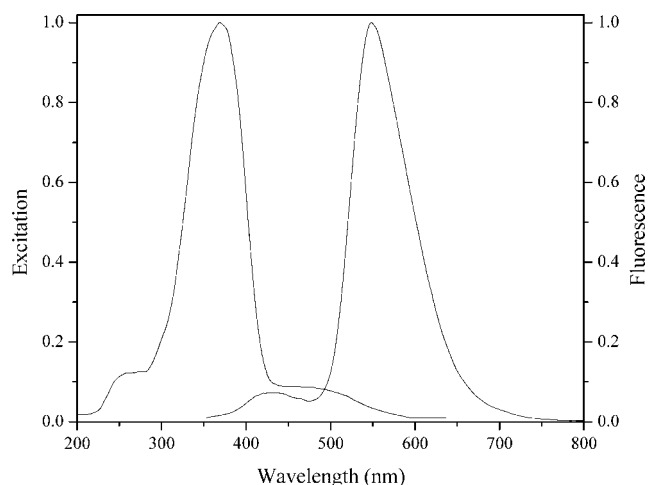


Figure 7 Solid-state fluorescence emission and excitation spectra of HBTS/Epoxidized natural rubber after purification.

CONCLUSIONS

In conclusion, novel, highly fluorescent, epoxidized synthetic and NR films were successfully prepared using an ESIPT-exhibiting silyl-functionalized benzothiazole dye. The dye could not be extracted from these films by solubilization in THF and precipitation in ethanol, indicating the presence of covalent bonding between the dye and the matrix. In contrast, the dye could be readily washed out of films that had been prepared using the corresponding nonepoxidized rubbers. The direct fluorescence emission detection of these hybrids provided a very sensitive and useful methodology by which to study the silica/epoxy bond. Additional studies about the chemical bonding in these hybrid materials are in progress and will be published elsewhere.

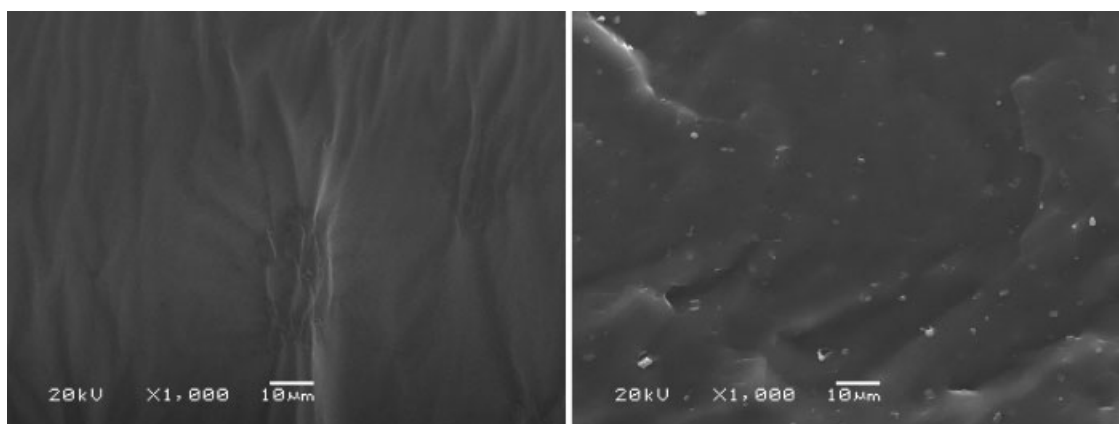


Figure 8 SEM images of the elastomeric materials prepared with nonepoxidized (left) and epoxidized (right) styrene-butadiene rubbers after purification.

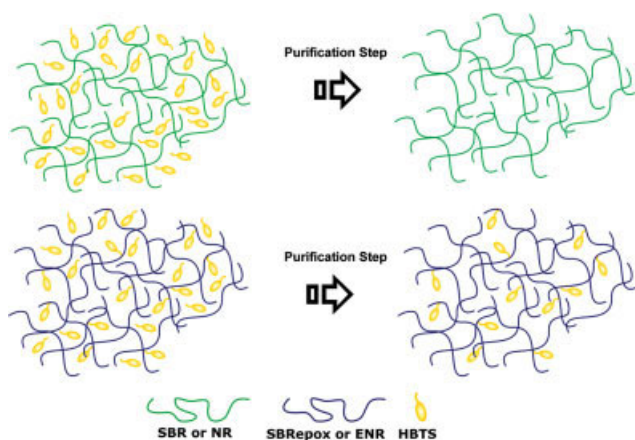


Figure 9 Obtention scheme of the elastomeric materials prepared with epoxidized and nonepoxidized rubber. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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