

Synthesis and Characterization of Epoxidized Styrene–Butadiene Rubber/Silicon Dioxide Hybrid Materials

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ABSTRACT: Hybrid materials were synthesized from epoxidized (68, 43, or 14%) styrene–butadiene rubber (SBR) and the hydrolysis product of tetraethoxysilane (TEOS) *in situ* under ultrasonic irradiation. The products were characterized with thermal analysis (differential scanning calorimetry and thermogravimetric analysis), stress–strain tests, scanning electron microscopy (including energy-dispersive spectrometry), and swelling in tetrahydrofuran and water.

The most transparent were those prepared from SBR with the highest degree of epoxidation, whereas those obtained from less epoxidized SBR and with larger amounts of TEOS showed distinct phases that could be considered two hybrid phases (one rich in TEOS and another rich in SBR). © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 798–803, 2004

Key words: nanocomposites; silicas; rubber; networks

INTRODUCTION

Until recently, processing differences in ceramic and polymeric materials did not allow hybrid materials to be produced. The sol–gel process¹ is a relatively new method for ceramic preparation, making use of lower temperatures and opening the possibility of hybridization between ceramic and polymeric materials. Hybrid materials synthesized from organic polymers and inorganic materials, presenting nanosized phase dispersions, have been intensively studied in the last decade.^{2–8} Most of the work has been carried out with sol–gel reactions involving metallic alkoxides, in which the reaction conditions determine the final microstructure of the ceramic material. According to the literature,² hybrid organic–inorganic materials can be classified into two main groups: materials with great component interaction occurring through covalent bonds and materials presenting weaker interactions, such as hydrogen bonds. Early examples of ormosils (organically modified silicates) are those obtained from thermoplastic materials⁹ based on diphenylsilanes and photocurable ligands, such as methacrylates, vinyl, or allyl, combined with a variety of polymerizable monomers used in coatings, adhesive films, and so forth; a classic example of *ceramers* (a word created from *ceramic* and *polymers*) via the sol–gel process involves the incorporation of poly(dimethyl

siloxane) with tetraethoxysilane (TEOS), which produces transparent materials with good flexibility.¹⁰

The addition of silica to a polymer structure can sometimes promote system porosity. In such cases, synthesized ceramic materials are calcinated to render a porous ceramic structure¹¹ through polymer removal.

The incorporation of organic molecules can also yield materials with applications in optics, catalysis, and sensors.² For example, transition-metal-modified alkoxides of Si and Sn present optical properties, such as photochromism, luminescence, and nonlinear optics.¹²

In a recent work,¹³ the synthesis of hybrid materials prepared from polystyrene and silica gel, resulting in a transparent material in which the siloxane bonds promote the crosslinking of the polymer structure with a final product showing nanometric phases, has been described. Works describing the production of coatings have shown the development of organic–inorganic hybrids from sunflower seed oil, linseed, and TEOS.¹⁴ The results suggest that an acid catalyst promotes organic phase dispersion in a rigid system. Recently, the synthesis of a new class of composites¹⁵ obtained from the reaction between polyimides and silica nets, with the components chemically bound, has been described. Bonding has a significant effect on the properties of the formed films, mainly in the mechanical properties. Many other works concerning the synthesis and characterization of hybrid systems containing silica have been published,^{16–20} reporting a new class of materials with particular properties.

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The hydrolysis of the alkoxides precursors usually requires the addition of a solvent because these compounds are water-insoluble. The use of a common solvent can be avoided if the mixture is subjected to intense ultrasonic irradiation.²¹ This modification favors the synthesis of materials with smaller pores and requires shorter gelation times; it has been used in the preparation of hybrid materials.²²

So far, works involving styrene–butadiene rubber (SBR) and TEOS have been related only to the reinforcement of the rubber with silica, such as the sol–gel method of TEOS in latex,²³ the reinforcement of epoxidized natural rubber,²⁴ and SBR and butadiene rubber vulcanized with silica generated *in situ*.²⁵

In this work, hybrid materials from SBR with three different epoxidation intensities (68, 43, and 14%) and the hydrolysis product of TEOS subjected to ultrasound irradiation were prepared and characterized.

EXPERIMENTAL

Materials

SBR (with 68, 43, or 14 mol % epoxidized butadiene units), TEOS (Aldrich), deionized water, formic acid (98%), and tetrahydrofuran (THF) were used. SBR (Bayer AG, Leverkusen, Germany), a random copolymer of styrene and butadiene (with 25 mass % styrene and 32 mol % butadiene units in vinylic positions), was epoxidized in the laboratory by the *in situ* performic acid method.^{26,27}

Film preparation

The epoxidized SBR was dissolved in THF, and the solutions were acidified to pH 1.5 with formic acid. TEOS was added in mass proportions of 95/05, 85/15, 75/25, 50/50, and 25/75 SBR/TEOS. Water was added to the systems in the molar proportions of 2/1 water/TEOS. The hydrolysis of TEOS was carried out *in situ* by ultrasonic irradiation (T7 ultrasonic bath, Thornton, Indaiatuba, Brazil). The resulting sols were cast into Teflon plates. After gelling, the films were dried in a vacuum dryer at 40°C to a constant weight.

Film characterization

The films were characterized by macroscopic observation, swelling in THF and water, thermal analysis [differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)], tensile stress tests, and scanning electron microscopy [SEM; including energy-dispersive spectrometry (EDS)].

Determination of the degree of swelling

The degree of swelling was determined by the soaking of the film samples in THF and water in a thermostatic

bath at 23°C for 48 h. The initial mass (m_0) and final mass (m) were determined, and the swelling degree (Q) was calculated as follows:¹⁶

$$Q = \frac{m - m_0}{m_0 \rho} \quad (1)$$

where ρ is the solvent density ($\rho_{\text{THF}} = 0.889 \text{ g/cm}^3$ and $\rho_{\text{water}} = 1.0 \text{ g/cm}^3$)

Measurement of the mechanical properties

Stress–strain measurements were performed in a Wolpert TZZ 0.5 testing machine (Ludwigshafen, Germany) with samples with approximate dimensions of 30 mm × 10 mm × 0.4 mm at a speed of 10 mm/min.

Thermal analysis

TGA was performed in a Universal V2.6D TA instrument from 0 to 800°C, under nitrogen, at a heating rate of 20°C/min. DSC was performed with Polymer Laboratory thermal equipment from –50 to 220°C at a heating rate of 10°C/min.

SEM analysis

The morphology of the cryogenically fractured samples was examined with SEM (JSM 5800, JEOL, Peabody, MA) on gold-coated surfaces. EDS analysis were also performed for a few selected samples.

RESULTS AND DISCUSSION

Physical characteristics of the films

The films prepared from SBR with a higher state of epoxidation were macroscopically homogeneous over

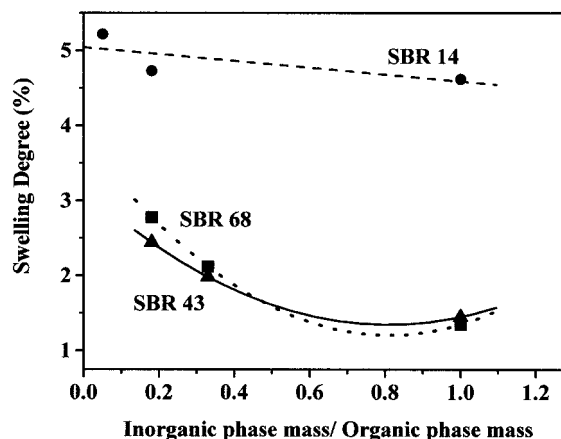


Figure 1 Swelling coefficient (in THF) of hybrids as a function of the proportion of phases (weight ratio of the inorganic phase to the polymeric phase).

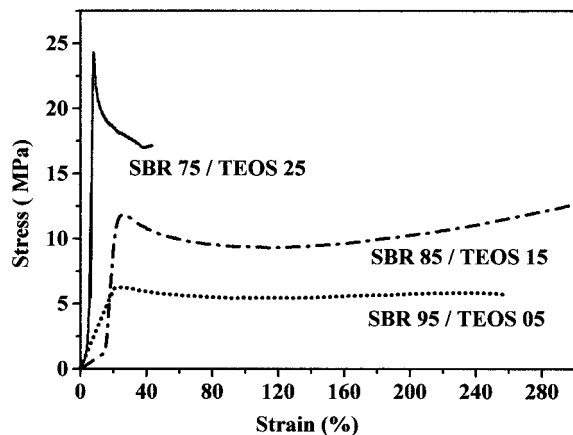


Figure 2 Stress-strain curves of hybrids obtained from SBR (68% epoxidized) with the following proportions: 95/5, 85/15, and 75/25 SBR/TEOS.

a relatively large range of compositions and were also transparent in those compositions in which epoxidized SBR predominates. Unlike pure SBR, the new materials did not dissolve in an HF solvent but only swelled. With normal rubber, films could not be obtained; instead, the result was a rubbery mass, soluble in THF, that generated two phases when soaked in THF: the dissolved rubber and the powdered silica. However, the films prepared from rubbers with smaller degrees of epoxidation were more whitish, whereas the films containing a smaller proportion of silica were the most transparent.

Determination of the degree of swelling

The tested materials did not swell in water, but significant swelling occurred in THF, varying with the proportion of the inorganic phase, as shown in Figure 1. Materials obtained from SBR of higher degrees of epoxidation presented similar swelling behavior,

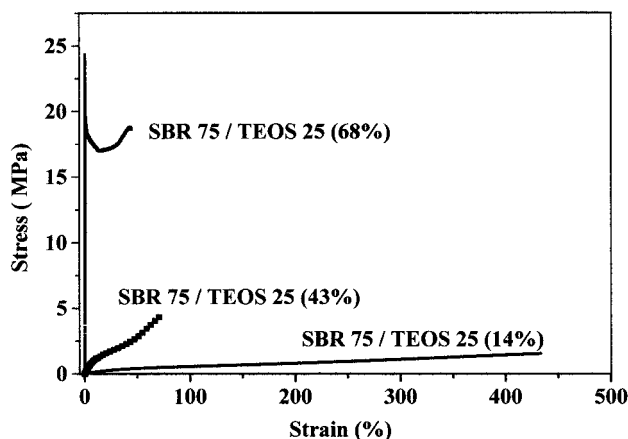


Figure 3 Stress-strain curves of SBR75/TEOS25 hybrids with epoxidation degrees of 68, 43, and 14%.

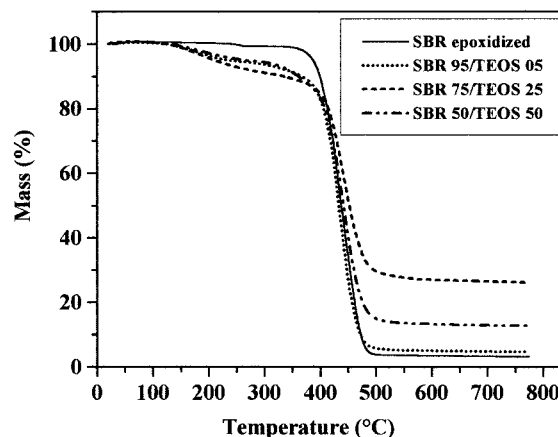


Figure 4 TGA curves of a series prepared with SBR (68% epoxidized).

whereas those obtained from SBR with a low extension of epoxidation presented a much higher degree of swelling with a small linear variation.

Mechanical analysis

Figure 2 shows the results of a mechanical analysis of the hybrid films with higher SBR contents with a degree of epoxidation of 68%. The SBR50/TEOS50 films were very breakable, resisting only small deformations and presenting some practical problems, such as sample fixing and rapid rupture. Qualitatively, it was possible to observe that there was a great increase in the stress and a reduction of the elasticity as the proportion of the inorganic phase increased. Films prepared with up to 15% TEOS withstood up to 200% deformation, whereas 25% TEOS films withstood deformations of 20–40%. The hybrid formed from 68% epoxidized SBR, from a mechanical point of view, was more similar to a plastic than to a rubbery material.

Figure 3 presents a comparative study of films prepared with identical amounts of SBR/silica (SBR75/TEOS25) with rubber with different degrees of epoxidation. The material prepared with SBR of a higher epoxidation degree (68%) presented plastic behavior, whereas those prepared with smaller degrees of ep-

TABLE I
Experimental and Theoretical Silica Residues at 800°C from TGA

Sample	Silica residue			
	Calculated (%)	Residual mass (%)		
		SBR 68%	SBR 43%	SBR 14%
Epoxidized SBR	—	3.136	3.94	2.36
SBR85/TEOS15	4.33	3.516	6.24	8.562
SBR75/TEOS25	7.212	12.72	10.72	13.79
SBR50/TEOS50	14.423	26.12	23.39	27.44

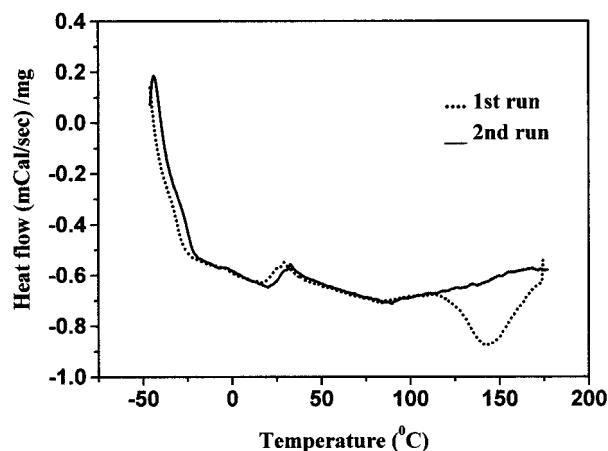


Figure 5 First and second runs of DSC for an SBR (68% epoxidized)/TEOS hybrid.

oxidation (43 and 14%) presented elastomeric behavior.

Thermal analysis

A thermal analysis was carried out to estimate the hybrid stability and incorporated silicate fraction. Figure 4 shows typical TGA curves for a hybrid series prepared with 68% epoxidized SBR.

The epoxidized rubbers presented a small weight loss around 200°C (ca. 1%) and a greater weight loss beginning at about 350°C. They also showed small residues that may have come from the epoxidation. All the hybrid films showed two distinct mass-loss regions: one was at about 110°C and came from the remaining water (despite vacuum drying), and the second loss was the rubber itself. In all cases, the hybrid stability was similar to that observed for pure SBR. There was also a small residue that increased with the proportion of TEOS. The residue was a little bit larger than the theoretical value, especially in the SBR50/TEOS50 sample. Table I shows the residues, as mass percentages, at 800°C. The calculated mass was estimated from the amount of TEOS used in the film preparation and from a consideration of the total conversion to silica. The calculated values were always larger than the experimental ones, and the difference

TABLE II
 T_g Values for Pure Epoxidized SBR and SBR/TEOS Hybrids with Different Compositions

SBR/TEOS	T_g (°C)	
	SBR 68%	SBR 43%
100/0	1.8	-10.2
95/5	58.7	18.7
85/15	54.9	26.1
75/25	56.7	17.1

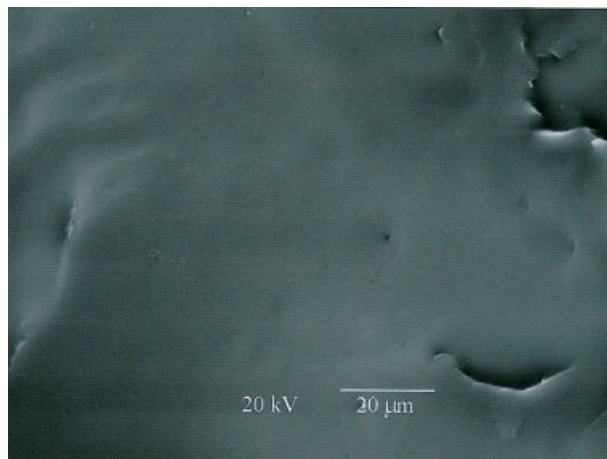


Figure 6 SEM image of SBR (68% epoxidized).

increased as the proportion of TEOS increased. Similar results can be found in the literature⁷ for poly(vinyl acetate)/TEOS hybrids, and the effect has been attributed to the presence of the remaining silanol groups in the network.

Figure 5 shows DSC curves for the first and second runs. In the first run, a large peak can always be observed, with a maximum in the 100–150°C region, that is not present in the second run. This behavior is also reported in the literature²⁸ for poly(ethylene oxide-*b*-amide-6) (PEBAX)/ZrO₂ hybrids, and it has been attributed either to water and alcohol still present in the film or to the fusion of some crystalline phase that can be present in the system when the films are prepared from solutions but that is not formed when the system is crystallized by fusion.

For the SBR/TEOS system, it should be attributed only to water or alcohol, because the SBR does not crystallize.

Table II shows the glass-transition temperatures (T_g 's) of pure epoxidized (68% and 43%) SBR and

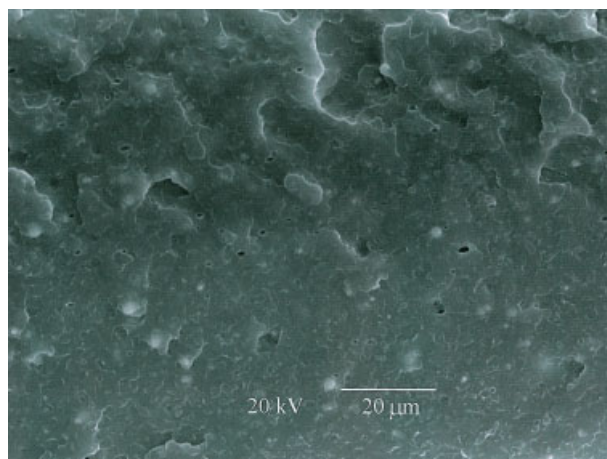


Figure 7 SEM image of SBR (68% epoxidized)75/TEOS25.

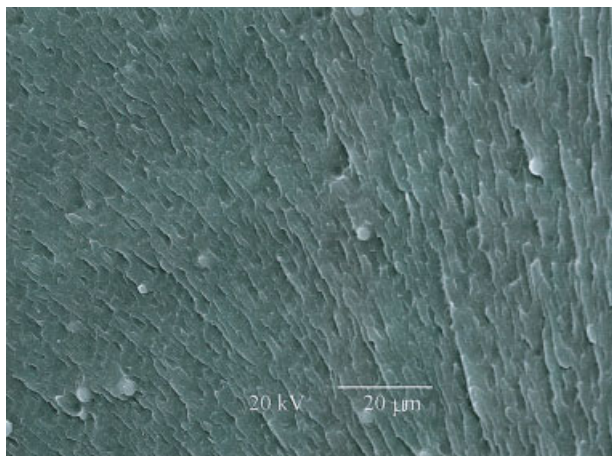


Figure 8 SEM image of SBR (68% epoxidized)50/TEOS50.

SBR/TEOS hybrids. The 14% epoxidation rubber series showed approximately the same T_g values as the rubber, indicating that a new compound was probably not formed at this degree of epoxidation; instead, a material made of 14% epoxidized SBR reinforced with silica was created. For the 68 and 43% series, the results indicated the presence of a characteristic phase, with T_g close to 56°C for the 68% epoxidation series and close to 20°C for the 43% series. In both cases, T_g occurred at higher temperatures than T_g of the rubber and at lower temperatures than T_g of the silica. In each series, there were small differences among T_g 's, which could be attributed to the sensitivity of the method instead of system characteristics.

SEM

The morphological characterization of the films was carried out through SEM analysis. Films containing an excess of rubber and a higher degree of epoxidation were as homogeneous as pure epoxidized rubber. Fig-

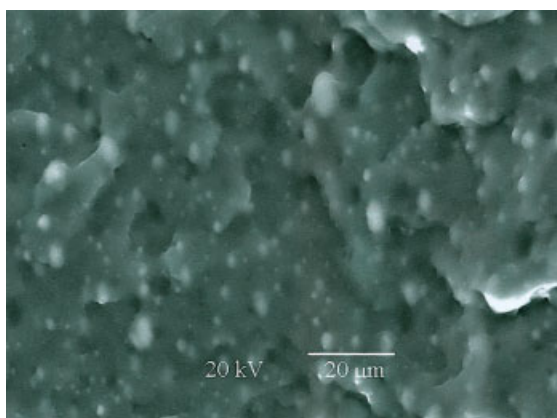


Figure 9 SEM image of material SBR (43% epoxidized)50/TEOS50.

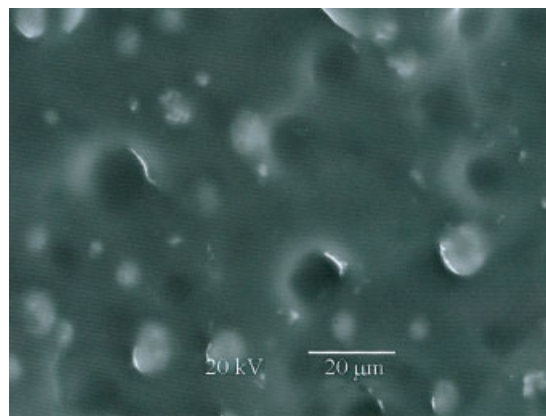


Figure 10 SEM image of material SBR (14% epoxidized)50/TEOS50.

ure 6 shows a fracture micrograph of pure SBR (68% epoxidized), and Figure 7 presents an SEM image of a hybrid prepared from the same rubber and TEOS [SBR (68%)75/TEOS25]. With larger amounts of TEOS (up to 50%), the films were no longer transparent, and this indicated phase separation; this effect was more pronounced for larger amounts of TEOS and lower epoxidation values. Figures 8–10 show SEM images of films prepared from 50% SBR and 50% TEOS from SBR with 68, 43, and 14% epoxidation, respectively.

With the addition of a larger amount of TEOS, changes in the morphology occurred, including the presence of spherical particles over the continuous phase of the structure. EDS analyses of the spherical particles (Fig. 10) for an extreme situation such as SBR (14% epoxidized)50/TEOS50 (a very low degree of epoxidation and a very high concentration of TEOS) resulted in an approximate mass percentage composition: 44% Si, 47% C, and 9% O (Fig. 11). However, the continuous phase was richer in carbon, even though it also contained silicon (5% Si, 93% C, and 23% O). The

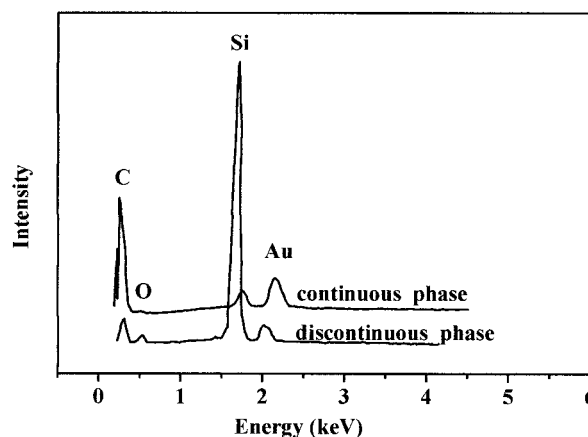


Figure 11 Continuous and discontinuous phases of EDS spectra of SBR (14% epoxidized)50/TEOS50.

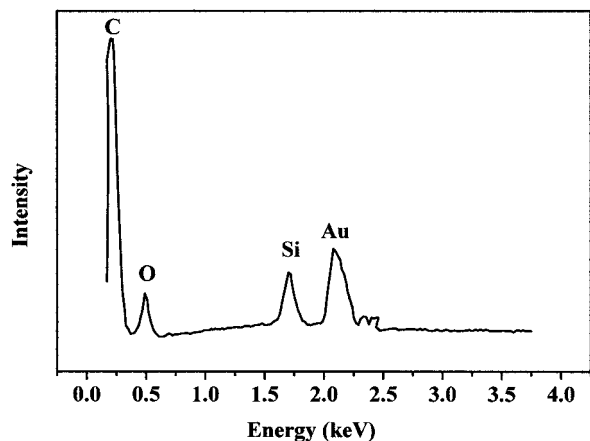


Figure 12 EDS spectra of SBR (68% epoxidized)85/TEOS15.

epoxidized rubber contained oxygen in its composition. The material prepared from SBR (14% epoxidized)50/TEOS50 could be considered a composite containing two phases, one of which was a hybrid material rich in silicon and the other of which was a hybrid material rich in carbon. For a more homogeneous material, such as the one prepared with SBR (68% epoxidized)85/TEOS15, the approximated mass percentage composition of which 26% Si, 72% C, and 2% O, the EDS analysis at several points showed approximately the same mass percentage values, according to the spectrum shown in Figure 12.

CONCLUSIONS

It is possible to obtain hybrid films from epoxidized SBR and TEOS. A network is generated, the microstructure of which depends on the degree of epoxidation of the rubber. The obtained films present thermal stability similar to that of rubber, and the mechanical strain increases considerably with the incorporation of silica. SEM analyses indicate higher phase separation as the degree of epoxidation decreases.

References

1. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic: New York, 1990.
2. Schmidt, H. *Ultrastructure Processing of Advanced Materials*; Wiley: New York, 1992; Chapter 38, p 409.
3. Sforça, M. L.; Yoshida, Y. V. P.; Nunes, S. P. *J Membr Sci* 1999, 159, 197.
4. Honma, I.; Nomura, S.; Nakajama, H. *J Membr Sci* 2001, 185, 83.
5. Wei, Y.; Wang, W.; Jin, D.; Yang, D.; Tartakovskaya, L. *J Appl Polym Sci* 1997, 64, 1893.
6. Lee, J. H.; Choi, S. Y.; Kim, C. E.; Kim, G. D. *J Mater Sci* 1997, 32, 3577.
7. Zoppi, R. A.; de Castro, C. R.; Yoshida, I. V. P.; Nunes, S. P. *Polymer* 1997, 38, 5705.
8. Matějka, L.; Dukh, O.; Kolarík, J. *Polymer* 2000, 41, 1449.
9. Schmidt, H.; Seiferling, B. In *Better Ceramics Through Chemistry II*; Brinker, C. J., Clark, D. E., Uhlrich, D. R., Eds.; Materials Research Society; Pittsburgh, PA, 1986; p 739.
10. Huang, H.; Orlor, B.; Wilkes, G. L. *Polym Bull* 1985, 14, 557.
11. De Luca, M. A. Ph.D. Thesis (in Portuguese), Universidade Federal do Rio Grande do Sul, 1998.
12. Sanchez, C.; Ribot, F.; Lebeau, B. *J Mater Chem* 1999, 9, 35.
13. Tamaki, R.; Chujo, Y. *Chem Mater* 1999, 11, 1719.
14. Ballard, R. L.; Tuman, S. J.; Fouquette, D. J.; Stegmiller, W.; Soucek, M. D. *Chem Mater* 1999, 11, 726.
15. Chen, Y.; Iroh, J. *Chem Mater* 1999, 11, 1218.
16. Pereira, A. P. V.; Vanconcelos, W. L.; Oréfice, R. *Polím Ciênc Tecnol* 1999, 9, 104.
17. Chan, C.; Chu, I. *Polymer* 2001, 42, 6089.
18. Jordens, K.; Wilkes, G. *J Macromol Sci* 2000, 37, 177.
19. Kim, G. D.; Inakura, T.; Chujo, Y. *Polym Bull* 2001, 46, 351.
20. Chaker, J. A.; Damouche, K.; Craievich, A. F.; Santilli, C. V.; Pulcinelli, S. H. *J Appl Crystallogr* 2000, 33, 700.
21. Zarzycki, J. *Ultrastructure Processing of Advanced Materials*; Wiley: New York, 1992; Chapter 13.
22. Morita, K.; Hu, Y.; Mackenzie, J. D. *J Sol-Gel Sci Technol* 1994, 3, 109.
23. Yoshikai, K.; Ohsaki, T.; Furukawa, M. *J Appl Polym Sci* 2002, 85, 2053.
24. Kohjivya, S.; Ikeda, Y. *Rubber Chem Technol* 2000, 73, 534.
25. Ikeda, S.; Tanaka, A.; Kohjiya, S. *J Mater Chem* 1997, 7, 1497.
26. Pedrini, C.; Jacobi, M. M.; Schneider, C. Presented at the 22nd Annual Meeting of the Brazilian Society of Chemistry, Minas Gerais, Brazil, 1999 (in Portuguese).
27. Jacobi, M. M.; Pedrini Neto, C.; Schneider, C. G.; Rocha, T. L. A. C.; Schuster, R. H. *Kautsch Gummi Kunstst* 2002, 55, 590.
28. Zoppi, R. A.; Soares, C. G. A. *Polím Ciênc Tecnol* 2000, 10, 70.