11º CONGRESSO BRASILEIRO DE POLÍMEROS
16 a 20 de Outubro de 2011
Campos do Jordão - SP

SBS elastomeric electrospun nanofibers from a solvent/cosolvent binary blend

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Abstract. Elastomeric is a common dispersing system in agricultural use but it is not easy to make nanofibers from an elastomer, whose polymer chain is flexible in its amorphous state. The styrene–butadiene–styrene triblock copolymer (SBS) Kraton D1101 was dissolved in different mixtures of tetrahydrofuran and dimethylformamide in a 14-20% polymer solution to produce electrospinning nanofibers. In terms of the Flory Huggins χ interaction parameter and Hansen solubility parameters, THF is a good solvent for SBS, while DMF is not. Both methods can be used as a guide to predict the miscibility of a solution. The addition of dimethylformamide as a cosolvent to the solution improved the stability of the electrospinning jet. When the THF/DMF ratio was higher than 60:40 the miscibility started to improve(χ_{smp}<0,6), and then after, 90:10 it diminished again. The preparation of SBS nanofiber was made by electrospinning. Almost beadless nanofibers were produced from a 14 % SBS with 75:25% (THF/DMF). The Flory Huggins χ interaction parameter could predict qualitatively the trend of the SBS solubility in the solvent mix.
Keywords *SBS, electrospinning, binary solvent mix.*

Introduction

According to Sé and Aznar [1] copolymers are gaining an increased amount of commercial interest because of their unique and desirable physical properties. Elastomeric in the form of rubber septa is a common volatile organic compound (VOC) dispersing system in agricultural use because of its similar solubility parameter compared to rubber. Nowadays, synthetic rubbers are being more and more used in many fields. Among these materials [2], maybe styrene–butadiene rubbers are the most important ones because of their low manufacturing cost and good properties. They can also be a good replacement for natural rubber in almost all applications. These rubbers are copolymers of both butadiene and styrene with a styrene weight fraction ranging between 0.2 and 0.3. An example of a commercial elastomeric product is the styrene–butadiene–styrene triblock copolymer (SBS). Different from electrospinning the crystalline polymer, it is not easy to make nanofibers from an elastomer whose polymer chain is flexible in the amorphous state and only a few studies had been reported on elastomers according to Yamashita and colleagues [3]. Fong and Reneker [4] were pioneers in using electrospinning to make SBS elastomeric nanofibers with a mixture of tetrahydrofuran (THF) and dimethylformamide (DMF) to form a 14 % polymer solution.

This present study aims to obtain nanofibers of an SBS triblock copolymer prepared from a binary solvent mix using the χ interaction parameter as a guide for solvent selection.

Experimental

SBS Solution preparation

The styrene–butadiene–styrene triblock copolymer (SBS) was supplied from Shell Chemical Co. (Kraton D1101), in the form of rubbery pellets which contain 30% polystyrene in weight. Analytical grade THF and DMF were purchased from Vetec Química Fina Ltda. SBS was dissolved with a magnetic stirrer in different mixtures, by weight, of tetrahydrofuran and dimethylformamide to form a solution that contained 14-20 %. polymer. A 20% polymer solution, as suggested by Yamashita and colleagues [3] could not be used for electrospinning because the viscosity was too high, so a 14% wt. solution was chosen, using the same concentration of Fong and Reneker in their original paper [4].

To test the different solvent/cosolvent ratios, a range from 0 to 100% of THF:DMF was selected, with 15% increments up to 75%. Later, a 10% increment was adopted to establish the best binary solvent ratio for the SBS electrospinning nanofiber.

Nanofibers produced by electrospinning

A custom made electrospinning machine was used. A 60 kV HV supply powered the machine. The syringe pump consisted of 3 ml syringes and a rotary aluminum collector adjusted to about 60 rpm. An Advantive™ 3 ml 22 g 1 Luer Lock™ syringe with a blunted end needle was used. A 1.81 kV/cm voltage was applied between the needle and collector with a 6 ml/h solution running out of each syringe. The nanofiber film was collected on the collector, to cover glass slides or directly to the metal stubs. The experiments ran at a temperature of 23^{o}C and 63% humidity. Each sample consisted of 2 ml were performed in the same day, in sequence.

Scanning electron microscopy (SEM) analysis:

Fiber diameters were measured using a scanning electron microscope (XL-30, Philips). The diameter of the fiber part in 30 places, within 3 different regions, of each sample was measured by using the ImageJ™ picture processing software.

The diameter of the electrospun SBS nanofibers produced with a 14 % SBS from a 75:25 THF:DMF binary solvent mix had a mean diameter of 111.88 nm $\pm$ 41.03 nm SD (standard

deviation) and a median of 113.93 nm, and with a diameter range between 50.99 and 167.58 nm. Smooth and bead-in-string nanofibers were obtained (Fig. 1).

Droplet formation and scattering of the nanofiber outside of the collector were defects observed in the film forming. Spinning was not possible with a SBS percentage over 20% because of the solutions high viscosity.

Results and discussion

SBS elastomeric nanofiber consisted of plane films collected on the rotary collector. Up to 60:40 of THF:DMF ratio could not make films because of the high viscosity. Starting at 60% of THF it is possible to form nanofibers which are smooth and regular. The film formed had a good yield in the macroscopic and microscope inspection. On the other hand, with the increase in the ratio of THF to more than about 85%, the fibers start to be more irregular, according to Fig. 1-B. The decrease in the DMF content, nanofibers also became sparse and irregular (Fig. 1).

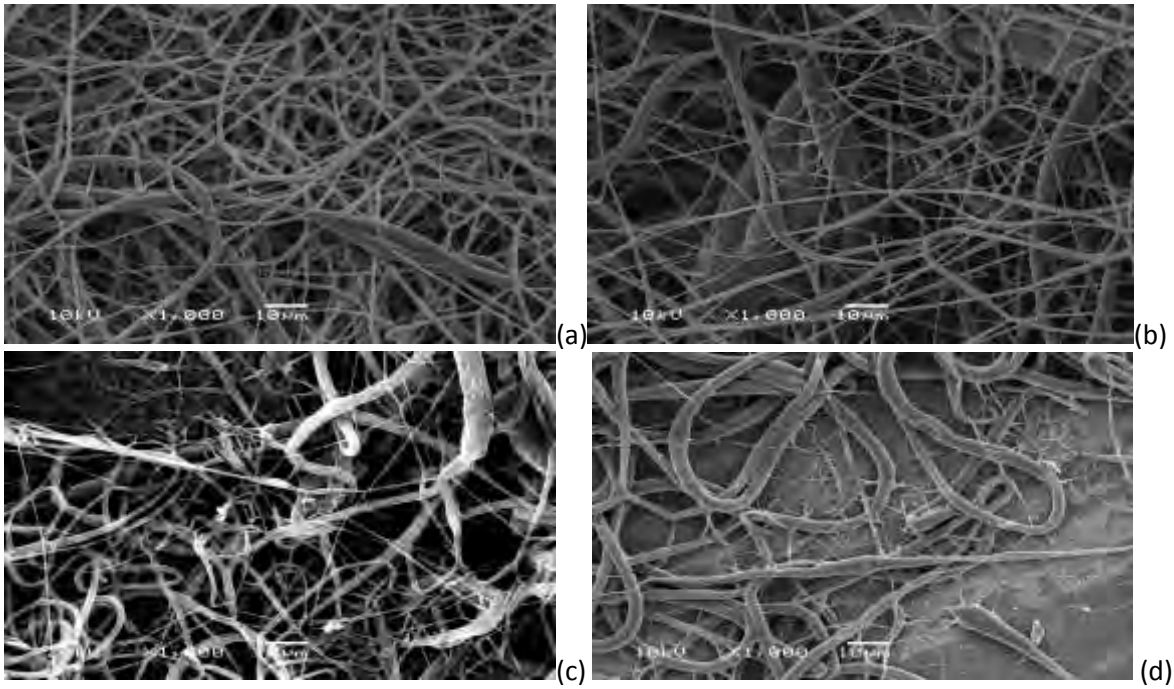

Figure 1. Photographs of electrospun 14% SBS elastomer fiber with different concentration of solvents. THF:DMF 75:25% (a); 85:15% (b), 95:5% (c) and 100:0% (d). SEM images with 1,000x of magnification.

According to the THF:DMF ratio, the nanofiber formed can be more regular or irregular; with a smooth or rough surface and with the presence of fuse-like or bead-in-strings shapes. A close view of a bead is shown in Fig. 2.

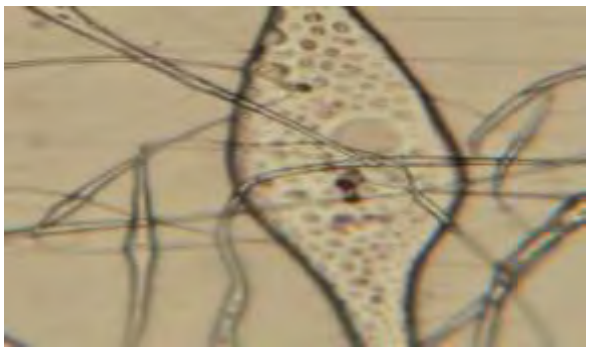

Figure 2. SBS 14%. THF: DMF 95:5. 400 x optical zoom. Close of a bead image.

Fong and Reneker [4], after staining the nanofibers with osmium tetroxide, examined them using transmission electron microscopy (TEM). Separated phases of styrene and butadiene blocks were observed and showed a typical microphase-separated thermoelastomer. Their findings are showed below.

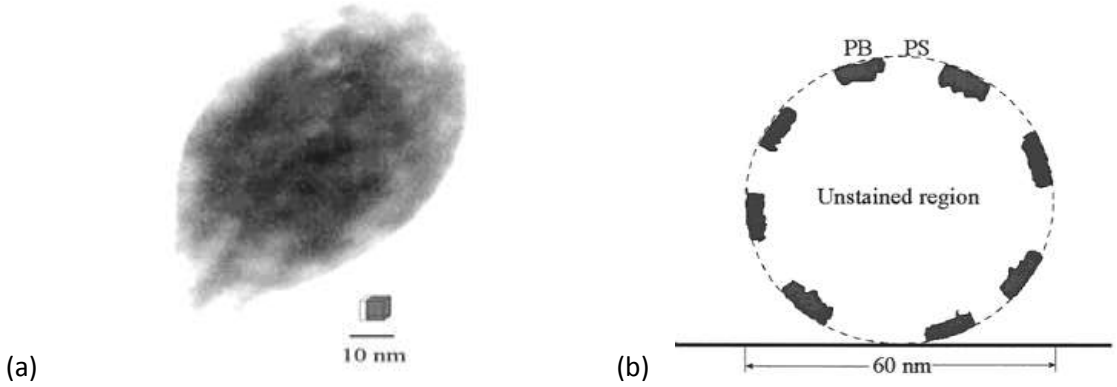

Figure 3. (a) Phase separation in a bead, with a cube showing the volume of an SBS molecule on the same scale; (b) schematic diagram of a representative cross section of a bead (Fong and Reneker) [4]

The Fig. 3 indicates that phase separation occurs on a scale of two or three typical SBS molecules. The osmium stain penetrates only about 3 nm from the surface, so only the parts of the polybutadiene phase near the surface are stained [4].

The results of SEM analyses showed that the THF:DMF at 75:25% in a binary solvent mix resulted in a better film forming, because the addition of 25% dimethylformamide which improved the stability of the electrospinning jet [4]. In terms of the Flory Huggins χ interaction parameter and Hansen solubility parameters these results are analyzed in the following discussion.

Jeong and Lee [5] studied the solubility parameters of a 30% polystyrene block SBS triblock copolymer. They found the solubility parameter as presented in the table below:

Table 1: solubility parameters of polymer and solvents. [5]					
Polymer/ solvent	V_m	δ_d	δ_p	δ_{hb}	δ_t
THF	81.7	16.8	5.7	8	19.46
DMF	77	17.4	13.7	11.3	24.86
SBS		17.55	3.36	2.7	18.07

As can be seen in the table above, THF is a good solvent for SBS, while DMF is not. From the solubility parameter of both polymer and solvent, the Flory Huggins χ interaction parameter can be determined by applying the following equations: [2]

$$\chi_{sp}=\chi_S+\chi_H \qquad (1)$$

, where χ_S= 0.34 (using Hildebrand solubility's).

$$\chi_H= (V_{sm}/RT)\, A_{smp} \qquad (2)$$

, where V_{sm} is the solvent binary mixture calculated according to Guetari et al [6] ,

$$A_{smp}= (\delta_{smd}-\delta_{pd})^2+ 0.25*(\delta_{smp}-\delta p_p)^2 + 0.25*(\delta_{smp}-\delta_{pp})^2$$

A_{smp} is a measure of the difference between the Hansen solubility parameter of the polymer and the mixed solvents.

According to the same authors [6], the χ_S empirical factor of Eqs. (1) which is employed with the Hildebrand solubility parameters as an average correction, should not be required if the Hansen solubility parameters are used instead of the Hildebrand solubility parameters. The χ_c was considered to be about 0.5, because of the large polymer average molecular weight. The Flory-Huggins χ interaction parameter is shown in Fig. 4, related to the volume fraction of the THF solvent:

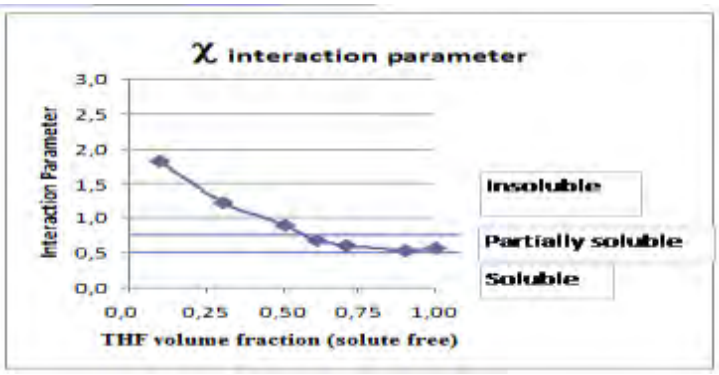

Figure 4: Predicted solubility of SBS in THF: DMF binary mixed solvents.

The results of the χ interaction parameters shows that the miscibility is higher ($\chi_{smp} < \chi_c$) when the THF:DMF ratio approaches to 75:25. When the ratio is higher than 60:40 the miscibility starts to improve (χ_{smp}<0,6), but over 90% of THF the spinnability of the solution worsens.

All the thermodynamics calculus were made using the data of Jeong and Lee [5], which creates a potential bias in the case of the polymer used in this study, although the polymer has almost the same styrene content.

Conclusion

The preparation of nanofiber films from an elastomer was successfully performed using the electrospinning process from a SBS solution. Beadless nanofibers were produced from a 14 wt% SBS with 75:25% THF:DMF, using a 1.8 kV/cm voltage applied. The mean diameter of the fiber was 111.88 nm ± 41.03 nm. The Flory Huggins χ interaction parameter could predict qualitatively the trend of the SBS spinnability in the solvent mix.

Acknowledgments

Acknowledgments to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FINEP (Financiadora de Estudo e Projetos) for financial support. Thanks also to Shell Chemical Co. for supplying the SBS.

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