EFFECT OF CERTAIN EXPERIMENTAL CONDITIONS ON MECHANICAL PROPERTIES OF TWO-COMPONENT MATERIALS OBTAINED BY SEMICONTINUOUS SEEDED EMULSION COPOLYMERIZATION

Francisco J. Aranda-García, Carlos F. Jasso-Gastinel, Francisco A. Nuñez-Pérez, M. Judith Sánchez-Peña, Nebai Zavala-García, Luis J. González-Ortiz✉

Universidad de Guadalajara, Centro Universitario de Ciencias Exactas e Ingenierías, Blvd. Marcelino García Barragán 1451, CP. 44430, Guadalajara, Jalisco, Mexico.

✉ljglez@yahoo.com.mx

ABSTRACT. Trying to improve mechanical properties of two-component materials, in this work, a semicontinuous seeded emulsion process was used, varying feed composition throughout the copolymerization reaction. Polystyrene seed size (d_p ~50 or, ~300 nm), total feeding time (2 or, 8 h) and, global polymer composition (S/BA: 85/15, 70/30, 50/50 or, 30/70) were varied to examine mechanostatic properties performance (stress-strain and flexural properties). To support explanations related to the mechanical behavior of different samples, GPC, ^{1}H-NMR and TEM results were additionally considered.

INTRODUCTION. Pursuing properties combination, the seeded emulsion polymerizations (SEPs) have been used to prepare two-component materials, using two-stage processes. In such processes, as a consequence of the incompatibility between polymeric components, two-phase particles have been usually obtained. Unfortunately, due to the many variables involved in such polymerization process, materials with different particle morphologies and final mechanical properties may be obtained (1). It has been reported that, changes in the monomer/seed ratio, type and amount of emulsifier, and feed mode of emulsion components, are just some of the different process parameters controlling the development of particle morphology throughout a SEP (2), which is, in fact, the result of the balance between several kinetic and thermodynamic factors (3). Besides, for a given chemical system, the mechanical behavior of the polymer bulk obtained through of a two-component SEP depends (3-6), among other factors, on the morphology of particles used to prepare such bulk, the thermomechanical treatment suffered by the material to obtain the bulk (that could even modify its morphology), the system composition, the molecular weight distribution of linear polymer chains and, the amount and structural characteristics of branched polymer chains that could be produced throughout the polymerization reactions. Regarding to semicontinuous seeded emulsion copolymerization, it can be mentioned that, such experimental procedure has been focused on the production of copolymers with constant composition (7). However, based on the favourable mechanical behaviour shown on systems of variable composition synthesized through sequential bulk polymerizations (8), it can be expected a priori that, a synergistic effect could also be obtained when the polymeric material is synthesized by means of such semicontinuous processes, provided that the particles contain copolymer chains within a wide range of compositions. One way to favour that scheme, is to favour that, in the polymerization locus (e.g. polymer particle), the monomer 1/monomer 2 ratio changes throughout the reaction, covering a wide range of ratios. Recently (9), the above ideas have been considered, proposing a general procedure to add the reaction components to a seed latex, in a semicontinuous way, obtaining materials with improved properties, as compared with the obtained with traditional two-stage SEPs. At those circumstances, in this work a two-component monomer system (styrene and butyl acrylate) is added to polystyrene seed latex, and polymerized in a semicontinuous process, varying feed composition throughout the reaction. Besides, looking for the improvement of final mechanical properties of polymer, in this work, the seed particle diameter, the total feeding time and the monomer 1/monomer 2 ratio were used as variables, producing 16 different polymeric materials, which were mechanically characterized. Moreover, to obtain additional information supporting the proposed mechanistic explanations, measurements of MWD (by GPC), particle morphology (using

TEM) and cumulative composition (by ^{1}H-NMR) were carried out.

EXPERIMENTAL. *Seed latex.* By means of batch emulsion polymerizations, they were synthesized two PS seed latexes; the first (PSS1; d_p~50 nm) used as surfactant sodium dodecyl sulfate (SDS), and the other one (PSS2; d_p~300 nm) used Tween 20; additional details about polymerization recipes are shown in Table 1. Reaction was carried out in a 4 L reactor, thermostatized at 70^{o}C and stirred at 500 rpm; previous to start the reaction, a gas nitrogen flow was fed to reactor during 1 h. To promote a high final conversion, which was followed gravimetrically, reaction times > 12 h were used.

Two-component materials. For each one of the seed latexes, were prepared 8 two-component materials with some of the following S/BA ratios (w/w): 30/70, 50/50, 70/30 y, 85/15; for each S/BA ratio, two equivalent latexes were prepared, considering, respectively, two different total feeding times (2 h, or 8 h). Previous to start each reaction, a gas nitrogen flow was fed to reactor during 1 h and, during reaction, the reacting system was thermostatized at 70^{o}C, and stirred at 400 rpm. For each reaction, an initial batch of components (1300 g of distillated water and 250 g of seed latex) was added to reactor. After it, 10 sequential “addition stages” were carried out; the time elapsed in each stage was the same. To start each “addition stage”, an aqueous solution containing potassium persulfate (KPS), SDS and sodium bicarbonate was added to reactor; the amount used of each salt, was the one corresponding to the 2% of the total mass of comonomers to be added in the stage. In each stage, the comonomers were pumped to reactor, at a constant flow rate; the feeding flow was only changed to start each stage. The mass of each comonomer to be added to reactor in each stage, varied linearly with the number of stage; the S monomer follows a decreasing profile, and the BA monomer follows an increasing one. At the end of each reaction, the solid content was of 20%.

Mechanostatic Characterization. Each one of latexes was dried by evaporation, and the obtained solid material was processed by compression molding to obtain the sheets to be mechanically characterized; for it, a Universal Testing Machine (SFM10) was used, and the ASTM procedure was followed.

RESULTS. To explain the global composition effect on mechanical properties of the materials synthesized here, some of the results are shown in Figures 1 and 2. Figure 1 shows the results corresponding to the two-component materials prepared with the PSS1, while Figure 2 shows the mechanostatic characterization corresponding to the samples prepared with the other seed latex (PSS2). In such figures, it can be clearly seen the mechanical superiority of the samples prepared with an S/BA ratio of 70/30. On the other hand, the effect of the process conditions (seed particle diameter or total feeding time) on mechanical behavior of S/BA materials with a 70/30 ratio can be seen in the Figure 3. There, it can be clearly observed that the total feeding time is the most important variable among the ones considered here, obtaining the best mechanical properties when a feeding time of 2 h was used. Besides, it can be noticed that, at least for this S/BA ratio, the seed particle diameter did not produce important changes in the mechanical behavior of samples.

CONCLUSIONS. From this work results, it can be concluded that, to look for the mechanical behavior optimization, the total feeding time is a process parameter more important that the seed particle diameter. Besides, regarding to the composition effect, it can be affirmed that, a synergistic behavior could be obtained by using an S/BA ratio of 70/30.

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Table 1. Polymerization recipe used to synthesize the polystyrene seed latexes.

Component	Amount added, g
Distilled water	2000
Styrene	500
KPS	10
Surfactant	10

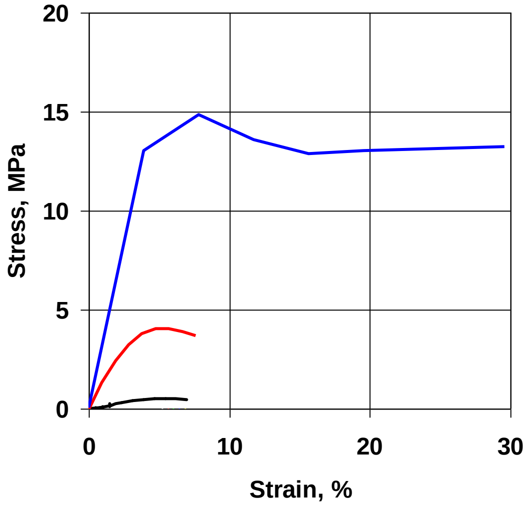

Figure 1. Stress-strain behavior of materials prepared with the PSS1, and that used a total feeding time of 2 h. S/BA ratios (w/w): 30/70 (__), 50/50 (__) and, 70/30 (__).

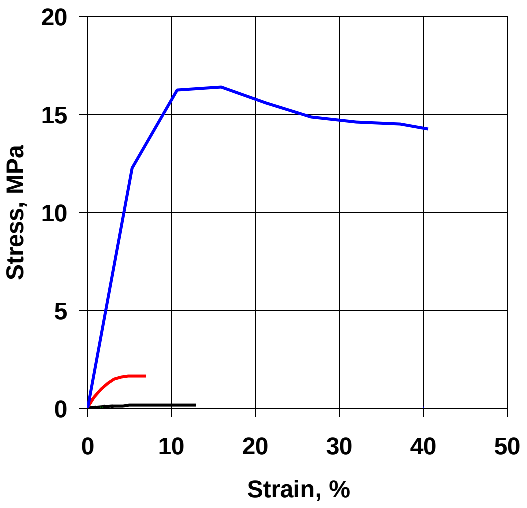

Figure 2. Stress-strain behavior of materials prepared with the PSS2, and that used a total feeding time of 2 h. S/BA ratios (w/w): 30/70 (__), 50/50 (__) and, 70/30 (__).

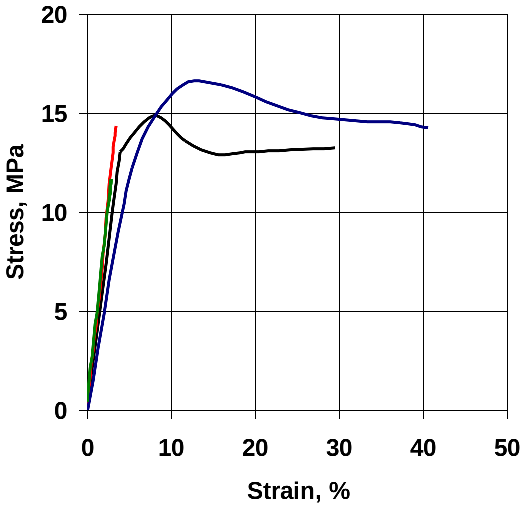

Figure 3. Stress-strain behavior of two-component materials (S/BA ratio -w/w-: 70/30). Seed latex/total feeding time: PSS1/2h (__), PSS1/8h (__), PSS2/2h (__) and, PSS2/8h (__).