

Research Article

The Effect of Feeding Profile in The Distribution of Chains Composition and Mechanical Performance of Styrene/Butyl Acrylate Emulsion Copolymers

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Abstract

A semicontinuous process was used to prepare copolymers varying the feed composition profile, to vary in a gradual manner the composition of the copolymer chains being formed through an emulsion reaction, for the (50/50, w/w) styrene/butyl acrylate system. With the cumulative composition of the copolymers (¹H-NMR), the weight distribution of chains composition (WCD) was estimated, constructing a histogram that is used to elucidate the mechanical behavior (DMA, stress-strain and, impact strength) of the synthesized copolymers.

Introduction

Searching for properties optimization, two component polymers have been prepared through several decades, using different types of polymerization reactions and processes. In bulk, the mechanical superiority of polymer blends containing a gradual change in composition over materials with uniform composition is attributed to the optimization of the contribution of each component [1]. In suspension, the non-uniform composition concept has been used to control transport properties [2], or to optimize ionic exchange capabilities [3]. In emulsion, core-shell type polymers have been prepared in two stages trying to combine homopolymers properties within a particle; however, generally two-phase systems form due to kinetic and thermodynamic factors [4,5]. One way to combine comonomer properties when using the emulsion process (which is a process that is used in many industrial applications) [6-8], is to feed both comonomers using a semicontinuous process, trying to optimize component interaction; as in bulk polymer blends, it would be expected that certain synergism in properties could also be obtained in copolymer materials, provided that they contain important amounts of copolymer chains covering a wide composition interval, including chains rich in comonomer A, as well as chains rich in comonomer B. With that approach, in a first attempt, a certain mechanical improvement was found using a simple composition feed variation [9]. Here, four different feeding profiles for the styrene/butyl acrylate system are used (50/50, w/w), to study how the copolymer chains composition is affected, and what would be its effect in the mechanical properties of the copolymers. As a reference, a core-shell type material was also prepared in two stages (T-S).

As the differences in mechanical behavior among the different copolymers may be slight, to understand such differences, it is necessary to determine the relative amount of chains within a certain copolymer composition interval. To solve that problem, we present here a new tool in polymer science that can be applied to understand copolymer behavior. With the cumulative composition evolution followed through the reaction, histograms showing the weight fraction distribution of the copolymer chains for the different compositions (weight composition distribution, WCD) are estimated. With those histograms, the amount of copolymer chains distributed within a given composition interval of the WCD, are used to explain

and compare the mechanical performance of the VCCs and their results are confronted with the T-S material.

Here, a polystyrene seed for the S/BA system is used; this system possesses a wide difference in homopolymers T_g, which is useful to separate clearly the contribution of each component for mechanical properties. With the same purpose, a 50/50 wt% S/BA composition is used.

Therefore, the aim of this work, is to see how the feeding profile in a semicontinuous emulsion process, affects the profile of the WCD, and as a consequence, the mechanical performance of the synthesized VCC materials. For the mechanical performance evaluation, DMA characterization is used to observe how storage and loss moduli (G' and G''), respectively) vary as a function of temperature, evaluating the area under the loss modulus curve to evaluate damping capacity (LA) [10]. To complement the moduli and damping capability information, Izod testing (for impact strength) and stressstrain at 25 and 50 °C, are performed. The VCCs are compared with the T-S polymer and among themselves, to establish the differences in performance, and their potential applications.

Experimental

Styrene (S) and butyl acrylate (BA) monomers (both from Sigma Aldrich, purity > 99%), were deionized with ionic exchange resins; methyl ester hydroquinone resin was used for BA, and 4-tert-butylcatechol for S. As surfactant, sodium dodecylsulfate (SDS; Aldrich, purity > 98%) was used as acquired. Potassium persulfate was used as initiator (KPS; Aldrich, purity > 98%). Sodium bicarbonate was used to buffer pH changes induced by initiator decomposition

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(NaHCO₃; Arm and Hammer). Distilled water was used for every polymerization reaction. In all polymerizations, nitrogen gas was used to purge the reaction system. PS seed was obtained by batch emulsion polymerization. The reactions were carried out at 70°C in a 4 L glass reactor, stirring the system at 400 rpm; to assure high conversion (followed by gravimetry), reaction times > 12 h were used. The formed latex contained 20 wt% of polystyrene. The two-stage polymer was obtained adding to a 4 L glass reactor the required amount of PS seed. Then, the second stage monomer (BA) was quickly added to such reactor at room temperature, while stirring at 400 rpm; the BA/PS weight ratio was 50/50. Before the addition of the required amount of the other components, the whole system was heated up to 70°C. The reaction time was > 12 h. Four different VCC materials were obtained by means of seeded semicontinuous emulsion processes; the type of variation (linear (L) or non-linear (NL)) in the feeded comonomer composition (along the 2 h predefined feeding time), is shown in Figure 1(a-d), where the comonomer flows comply with the following schemes: a) linear variation, following a decreasing profile for S and an increasing one for BA with different slopes (LS and LSLBA materials; for codes see Figure 1), b) non-linear variation of S, following a parabolic decrease for S and a linear increase for BA (NLS) and, c) non-linear variation of BA, with a linear decrease for S and a parabolic increase for BA (NLBA) and, d) non-linear variation of BA, with a linear decrease for S and a parabolic increase for BA (NLBA). The polymer content at the end of each reaction was 20 wt%. As in T-S material, for the VCC materials, the S/BA global weight ratio was 50/50. For the synthesis of such copolymers, the reactor and reaction conditions used for T-S polymer synthesis were also used. At the start of each copolymerization reaction, the reactor was charged with the seed latex containing 50 g of PS and the amount of distilled water required to complete 1600 g of total load. Then, 10 sequential “comonomer feeding stages” of 12 minutes each one were implemented. At the beginning of each stage, an aqueous solution containing 45 g of distilled water, and the required amounts of KPS, SDS and, NaHCO₃ were added as a batch to the reaction system. In each stage, the amount added of each salt was the one corresponding to 2% of the total mass of comonomers to be added in the correspondent stage. The feeding flow was modified at the start of each stage, and pumped to the reactor at constant flow rate during the stage. For the characterization of each VCC material, 7 samples were extracted at predetermined reaction times, and its respective global styrene content was measured by ¹HNMR (Varian Gemini 2000); such contents were fitted considering a third-order polynomial curve. Then, the composition of the copolymer chains formed in the course of the reaction was numerically estimated, considering a numerical differentiation methodology, the above-mentioned fitting curve, the conversion curve and, the corresponding mass balance. Such information was used to build a histogram for each reaction (Figure 2(a-b)), which shows the distribution of the composition profile for the copolymer chains contained in the respective VCC material at the

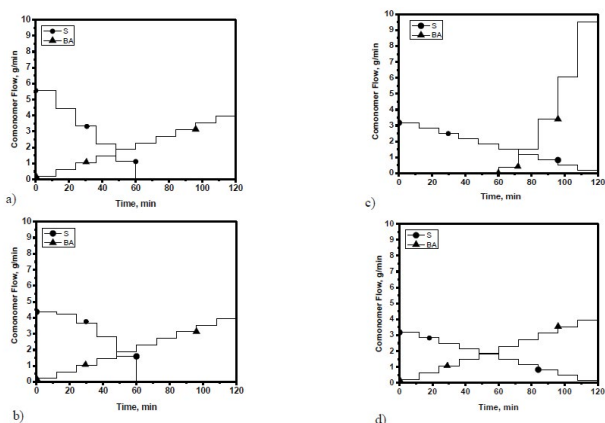


Figure 1: Comonomer flow as a function of reaction time, for styrene-butyl acrylate VCC synthesis: a) LS, b) NLS, c) NLBA and d) LSLBA.

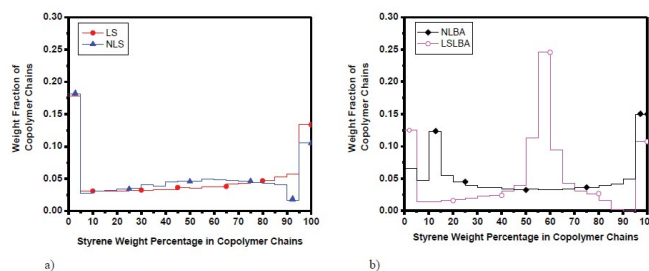


Figure 2: Weight fraction of chains for the copolymer composition spectrum, estimated for: (a) LS and NLS materials and (b) NLBA and LSLBA materials. For codes, see Figure 1.

end of the reaction. All latexes were dried by evaporation at room temperature; the collected polymers were used to prepare samples by compression molding (Schwabenthan polystat 200T) to carry out all mechanical tests. Stress-strain measurements were performed at 25 and 50°C (ASTM D638, samples Type IV, crosshead speed: 0.0083 cm/s; Universal testing machine SFM10, equipped with temperature chamber). Mechanodynamical tests were carried out as a function of temperature (DMA, ASTM D-5023, three point bending clamp, 1 Hz, heating rate: 1°C/min; TA Instruments Q800). Izod impact tests were performed following ASTM D-256 (Ceast 6545).

Results and Discussions

In Figure 1(a-d), the four different feeding profiles using linear trajectories (a and d), and linear-parabolic (b and c), are presented. Their different trajectories cause the changes in histograms shape (Figure 2 (a-b)), which in turn modify mechanical properties. For stress-strain measurements, observing Figure 3a, the LS material shows a hard and brittle behavior with very low ultimate strain at 25°C. The NLS copolymer follows LS material in modulus, showing yielding and certain deformation capacity before failure, while the NLBA copolymer shows a lower yield stress and lower deformation capacity. LSLBA follows closely in modulus position (with respect to the NLBA material), but shows the highest deformation capacity of the VCC materials. The T-S polymer, shows the lowest modulus and similar to NLS ultimate strain. Such behavior confirms that the two homopolymers obtained in the T-S synthesis, do not promote properties combination of the components.

At 50°C (Figure 3b), all materials maintain their relative modulus position, although they decrease in ultimate stress. LS material still presents a rigid behavior, but showing yielding before failure. NLS and NLBA copolymers increase 81 and 370% respectively in deformation capacity (with respect to their respective values at 25 °C), while LSLBA material shows a rubbery behavior with low modulus and high deformation (230%) capacity. Again, the T-S material shows a very low modulus, and due to the high PBA content, it also presents high ultimate strain (210%).

Looking at the histograms in Figure 2(a-b), the stress strain behavior of the VCCs can be disclosed. In Figure 2a, the main

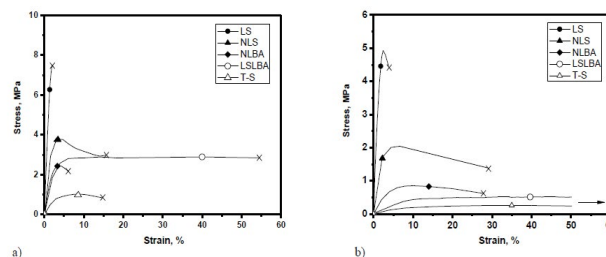


Figure 3: Stress-strain behavior of T-S and VCC materials at: (a) 25°C and (b) 50°C (crosshead speed: 0.0083 cm/s). For codes, see Figure 1.

difference between LS and NLS materials is in the 80 to 100 styrene wt% (CI 80-100). The higher weight fraction for LS material (0.34 versus 0.25 for NLS copolymer) in that composition interval acquaints for the higher modulus of the LS copolymer. The deformation capacity of the NLS material is mainly attributed to excess of copolymer chains accumulated in the CI 20-60 present in the NLS material (NLS:0.4%; LS:0.3%) weight fraction of those copolymer chains). It is noteworthy to mention that in both cases, there are significant weight fractions of chains very rich in BA (CI 0-5), and S (CI 95-100); however, the copolymer chains content in the CI 5-95, allows for component interaction, which is not the case for the T-S material, who presented the poorest behavior. In Figure 2b, the NLBA material presents an accumulation of 0.58 weight fraction in the CI 0-60, and 0.32 in the CI 80-100, while for LSLBA copolymer, the weight fractions are 0.68 and 0.15 for the same CI. Those values indicate that the LSLBA material contains a higher amount of elastic chains and will have lower temperature resistance than the NLBA copolymer. The LSLBA material in addition to the presence of chains rich in BA and S, presents a considerable weight fraction in the CI 45-70, which is close to the middle region; that contributes to an intermediate behavior in modulus, and a considerable deformation capacity supported by the whole weight fraction value on the left side of the composition scale (CI 0-50).

In Figure 4a, the storage modulus (G') of the two component materials is presented. There, LS and NLS materials follow very similar trajectories up to 0°C; then they separate slightly, staying above the LS copolymer all the way up to the terminal zone. Both of them present a G' decay at -40°C, due to an important BA contribution, continuing with an inclined decay (which is typical of copolymers; $T > 50^\circ\text{C}$), until they start and almost vertical G' fall at approximately 80°C. The NLBA material does not show the step like behavior at -40°C as the former two copolymers; it rather shows an inclined decay from -30°C to 0°C, continuing then the decay with smaller slope, until it approaches the terminal zone at approximately 50 °C. The LSLBA copolymer follows a copolymer type trajectory, maintaining a slightly higher G' value than the NLBA material between -30 and 39°C, where a crossover point appears, denoting a slightly higher temperature resistance of the NLBA material, when both approach the terminal zone. The G' of the T-S polymer, is lower than the value of all VCC materials, up to 50°C. Such low value is attributed to the lack of interaction between components. For the curve, the G' value shows a sharp decay at the PBA glass transition temperature (approximately at -40°C), and a plateau stays until the temperature approaches the PS glass transition. The differences or similarities in behavior among copolymers can be explained looking at the histograms in Figure 2(a-b). The statements established on Figure 2(a-b) that were applied for the stress-strain behavior of VCC materials (Figure 3(a-b)), apply also in Figure 4a. Additionally, the G' step like decay at -40°C for LS and NLS materials, can be assigned to the considerable weight fraction shown in the CI 0-5 (Figure 2a), and the temperature resistance, to the weight fraction that they show in the CI 80-100. The higher modulus of LSLBA material (compared to NLBA copolymer) from -30 to 39 °C (Figure 4a), is due to the higher weight fraction accumulated in the CI 40-70 (0.59, Figure 2b), while the higher temperature resistance of the NLBA, is due to its higher weight fraction in the CI 80/100. Figure 4b

For loss modulus (G''), LS and NLS copolymers in Figure 4b, follow very similar trajectories (as in G'), in the whole test temperature range. The peak at -40 is assigned to a glass transition response, due to the chains accumulated in the CI 0-5 (Figure 2a); then, G'' maintains a certain value with a copolymer type behavior, until it falls at 80°C, in accordance with G' decay (Figure 4a). NLBA material, shows a wide peak around -25 °C, because there is a considerable amount of chains in the CI 0-20 (not just in the CI 0-5); then, it shows a smooth decay in accordance with the G' curve (Figure 4a). It does not present

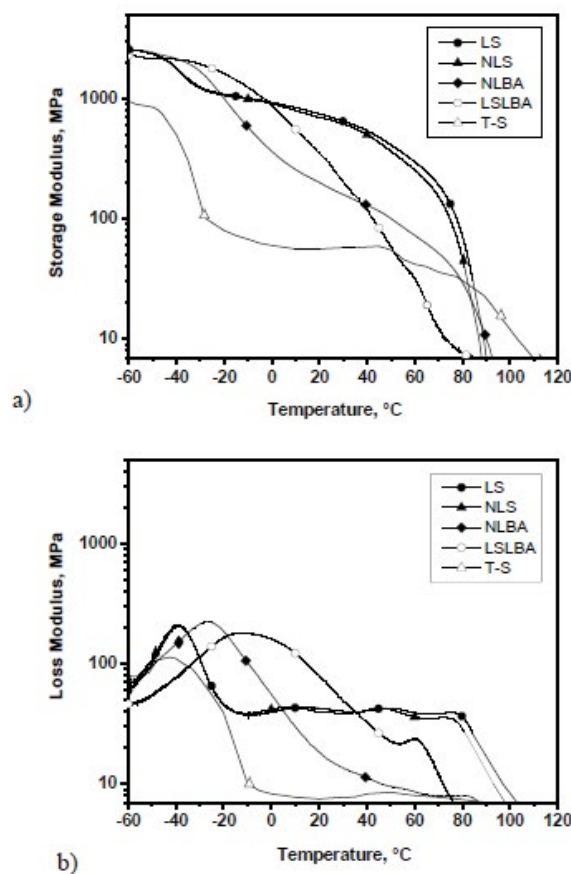


Figure 4: Storage modulus (a) and loss modulus (b) as a function of temperature for: T-S and VCC materials (frequency: 1Hz). For codes, see Figure 1.

a peak that can be assigned to the styrene presence in the CI 95-100, probably because it has considerable accumulation of chains in the CI 60-95 (0.3 weight fraction), that contributed greatly to a copolymer type behavior. LSLBA material shows the widest G'' curve, with a peak at -10 °C. That value is influenced by the chains accumulated in the CI 40-70. The G'' value decreases slowly, until it presents a shoulder formation tendency at 60°C, which is a signal influenced by the accumulation of chains in CI 60-85 and CI 95-100. As the area under the loss modulus curve (LA) indicates energy dissipation capacity, and a linear relation between impact resistance and dynamic energy loss has been reported [11], the Izod impact strength is plotted versus LA in Figure 5. There, the linear correlation between both variables can be observed for the two component materials. The T-S polymer presents the lowest coordinate values, while the LSLBA copolymer shows the highest LA and impact strength. The other VCC materials are grouped presenting values that are between 22 and 38% less than the LSLBA copolymer. Overall, the LSLBA presented the best energy dissipation capacity, while the LS and NLS, presented the higher modulus and temperature resistance. The NLS also presented considerable impact resistance (30 kJ/m²).

Conclusions

It has been shown that even small variations in feeding profile originate significant changes in the composition of copolymer chains that are formed through the reaction. Those changes in the WCD generate marked changes in mechanical and thermal behavior for a particular copolymer system. All the VCC materials presented better mechanical performance than the T-S polymer. The WCD histogram is a new tool in polymer science that is very useful to understand and

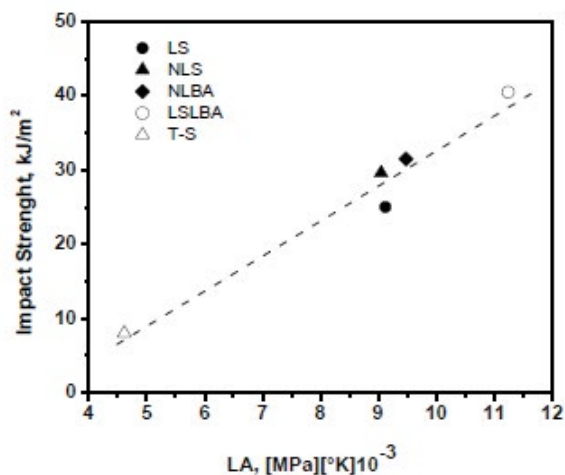


Figure 5: Impact strength as a function of the area under the loss modulus curve (LA) for: T-S and VCC materials. For codes, see Figure 1.

compare copolymers behavior. The high dissipation capacity of the VCC polymers makes them suitable for damping applications or toughened plastics.

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