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 cmonomer properties when using the emulsion process (which is a process that is used in many industrial applications) [6-8], is to feed both cmonomers 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 cmonomer A, as well as chains rich in cmonomer 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 Tg, 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 stress-strain 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 deinhibited 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...
Comonomer flow as a function of reaction time, for styrene-butyl acrylate VCC synthesis: a) LS, b) NLS, c) NLBA and d) LSLBA.

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.

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 NLS 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°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 0-60, 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.

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 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 60-65 (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
compare copolymers behavior. The high dissipation capacity of the VCC polymers makes them suitable for damping applications or toughened plastics.

References


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.