

Synthesis and Characterization of Styrene-Butyl Acrylate Polymers, Varying Feed Composition in a Semicontinuous Emulsion Process

Carlos F. Jasso-Gastinel,¹ Luz C. López-Ureta,¹ Luis J. González-Ortiz,² Ignacio Reyes-González,¹ Fernando A. López-Dellamary T.,² Octavio Manero-Brito³

¹Chemical Engineering Department, Universidad de Guadalajara, Guadalajara, Jalisco CP 44430, Mexico

²Chemistry Department, Universidad de Guadalajara, Guadalajara, Jalisco CP 44430, Mexico

³Materials Research Institute, Universidad Nacional Autónoma de México, Circuito del Área de la Investigación Científica S/N, Ciudad Universitaria, Coyoacán CP 04510, México DF, Mexico

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ABSTRACT: Two-stage polymerization has been used to improve properties of two-component polymers. In this work, a semicontinuous emulsion process varying feed composition along the reaction is used to produce copolymer chains of different composition as conversion proceeds. Polymer composition and evidence of branching were determined by ¹H-NMR. Polymer molecular weight values determined by GPC are beyond the range where mechanical properties depend on molecular weight. Mechano-dynamic properties show a copolymer type behavior with

a synergistic effect around the 50/50 styrene/butyl acrylate composition ratio. For such composition, mechanical performance superiority of variable composition copolymer with respect to two-stage polymer was confirmed with stress-strain tests carried out at several temperatures. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3964–3971, 2007

Key words: emulsion polymerization; core-shell polymers; mechanical properties; NMR; copolymerization

INTRODUCTION

To synthesize engineering materials combining the properties of two or more components, polymer researchers have prepared different types of copolymers and blends since decades ago.^{1,2} However, usually as a new type of polymeric material has been obtained, the research field opens in different directions depending on the type of reaction, polymerization method, and number of stages used.^{3–5} Moreover, if a variation in composition is pursued throughout the bulk of a polymer, an additional parameter of study is included.⁶

In 1970s, with blends of homogeneous composition obtained by sequential bulk polymerization, better mechanical properties than those of equivalent random copolymers were obtained,⁷ but they were inferior than the ones of equivalent blends with gradient composition.^{7,8} Superior properties of described blends

may be obtained maintaining phase separation at microscopic level, increasing in that way the interaction between components;⁹ that applies for both homogeneous and gradient composition blends (in the latter ones, homopolymers contribution can be optimized designing the gradient in a specific way).^{10–12} In bulk polymerization, one way to reach a desired composition gradient is by controlling the diffusion of a second monomer in a host polymer, followed by an “*in situ*” reaction.¹³ Pursuing mechanical modification, the second monomer diffusion approach, has been used in amorphous^{7,8,10,11,13} and crystalline polymers.¹⁴ During polymer processing, gradients in morphology have been formed by annealing compression-molded sheets¹⁵ or by slow crystallization in injection molding.¹⁶

The gradient composition concept has been also applied in small beads prepared by suspension polymerization, to release, in a controlled way, a pharmaceutical drug over a prolonged time, due to the drug-distribution gradient.¹⁷ Looking at particle level, in seeded emulsion polymerizations (SEPs), seed latices have been used to prepare two-component materials in two-stage processes, pursuing properties combination. In such processes, as a consequence of the incompatibility between polymer components, two-phase particles are usually obtained. Unfortunately, because of the many variables involved in such polymeriza-

Correspondence to: C. F. Jasso-Gastinel (carlos.jasso@cucei.udg.mx).

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TABLE I
Polymerization Recipes Used to Synthesize PS Seed, T-S, and VCC latices

Substance	Load added (g)			
PS seed latex				
Styrene (S)		750		
Tween 20		7.5		
Potassium persulfate (KPS)		7.5		
Water		6735		
T-S latices				
S/BA ratio	85/15	70/30	50/50	30/70
Reaction code	T-S 85	T-S 70	T-S 50	T-S 30
PS in seed latex	1360	1120	800	480
Butyl acrylate (BA)	240	480	800	1120
KPS	1.60	3.20	5.33	7.47
Sodium bisulfite	0.80	1.60	2.67	3.73
Water (from seed latex)	5850	5850	5850	5850
VCC latices				
Reaction code	VCC85	VCC70	VCC50	VCC30
PS in seed latex	375	375	375	375
Styrene	2175	1725	1125	525
Butyl acrylate	450	900	1500	2100
KPS	16	16	16	16
Sodium bisulfite	8	8	8	8
Sodium bicarbonate	10	10	10	10
Water (total)	4000	4000	4000	4000

tion process, different particle morphologies may be obtained at the end of the reaction.^{18–20} 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,^{19,21–23} which is in fact, the result of the balance between several kinetic and thermodynamic factors.^{24,25} Besides, for a given chemical system, the mechanical behavior of the polymer bulk obtained through of a two-component SEP depends,^{25–28} 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.

Semicontinuous SEPs have been focused on the production of copolymers with constant composition.^{29,30} However, on the basis of the favorable mechanical behavior shown on systems of variable composition synthesized through sequential bulk polymerizations^{7,8,10,11} it can be expected *a priori* that a synergistic effect could also be obtained when a copolymer is synthesized by means of seeded emulsion copolymerizations, provided that the particles contain copolymer chains with a wide range of compositions. One way to favor that scheme, is to use a semicontinuous process promoting that, in the polymerization locus (e.g., polymer particle), the mono-

mers ratio change throughout the reaction, covering a wide range of ratios.

Therefore, in this work, a two-component monomer system is added to a polystyrene seed latex and polymerized in a semicontinuous process, varying feed composition throughout the reaction. In that way, copolymer chains of different composition can be obtained throughout the polymerization. Cumulative copolymer composition and evidence of polymer branches formation are determined by ¹H-NMR. Mechanical and rheological properties of such materials are measured and compared with those of materials with equivalent composition, prepared by means of two-stage SEPs (T-S).

EXPERIMENTAL

Materials

Styrene (from Pemex, Mexico) and butyl acrylate acquired from BASF (for both, purity > 99.5%) were treated with ion-exchange resin (from Sigma-Aldrich, Mexico) to remove inhibitor. Polyoxyethylene-20-sorbitan monolaurate (Tween 20) from ICI de México was used as emulsifier. Potassium persulfate and sodium bisulfite from Sigma-Aldrich (Mexico) were used as the redox initiation system.

Preparation

A polystyrene seed latex was prepared at 75°C by emulsion polymerization in a 10-L steel reactor,

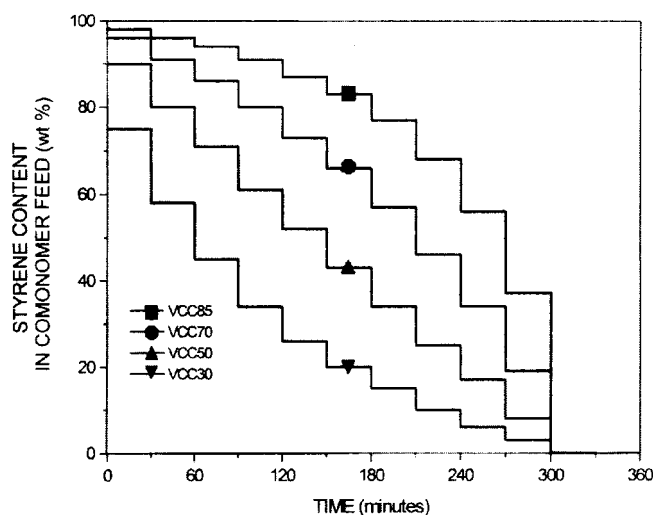


Figure 1 Instantaneous feed composition as a function of reaction time, for styrene-butyl acrylate VCC synthesis. For codes see Table I.

using the recipe shown in Table I. Such latex was used to prepare all polymeric materials. The T-S latices were synthesized at 75°C in the above-mentioned reactor. For that purpose, the required amount of polystyrene seed particles was charged to the reactor and the second monomer (butyl acrylate) was added to such latex at a rate of 0.7 mL/min while stirring continuously at 350 rpm, keeping temperature at 25°C. Monomer addition continued until the desired amount of butyl acrylate was achieved. After an extra stirring period of ~ 2 h, initiators were added, beginning afterwards the second polymerization at 75°C.

Variable composition copolymers (VCC) were prepared in the above-mentioned reactor at 75°C, using a multistep procedure, varying the feed composition in each step. First, the polystyrene seed latex was charged to the reactor, representing 12.5 wt % of final polymer content. To such latex, comonomers were simultaneously added using two Masterflex L/S peristaltic pumps in a semicontinuous process, while stirring at 350 rpm. To obtain copolymer chains with a certain composition pattern, feed composition was changed in a step-wise manner, as it is shown in Figure 1, varying the amount of each monomer fed on every step, following a linear pattern (increasing for butyl acrylate and decreasing for styrene). At the start of each step, 18 g of Tween 20 (to prevent coagulation), and 20 mL of an aqueous solution of redox initiation system containing 1.6 g of potassium persulfate and 0.8 g of sodium bisulfite were added to the reactor. Polymerization recipes to prepare the different types of polymeric materials are shown in Table I.

Characterization

Global composition of T-S polymers was obtained by gravimetry. For VCC materials, during each reaction,

several samples were taken to analyze their composition by $^1\text{H-NMR}$ (Varian Gemini 2000). Number-average molecular weight of final polymeric materials was measured by GPC (Perkin-Elmer Series 410, equipped with an LC-30 refractive index detector and coupled with a light scattering unit from Wyatt Technologies). For mechanical tests of the coagulated polymeric materials, polymer plates were prepared by compression molding (Schwabenthan polystat 200T), using a $20 \times 20 \times 0.3 \text{ cm}^3$ mold. Mechanodynamic measurements with a Dynamomechanical Analyzer (DMA, TA model Q800) were carried out using the three-point bending deformation mode at 1 Hz. Storage and loss moduli were measured as a function of temperature. Stress-strain tests were carried out on a Universal Testing Machine (United FM), equipped with a controlled temperature chamber, following ASTM D638, using a 0.083 cm/s crosshead speed. Measurements were performed at 25, 50, and 70°C.

RESULTS

For each reaction, cumulative composition of VCC materials was determined by $^1\text{H-NMR}$ analysis of samples extracted from the reactor at several time periods (30–270 min). For styrene mer quantification, the broad signal area between 6.1 and 7.2 ppm was calculated (aromatic hydrogens), while the methyl triplet signal appearing at ~ 0.9 ppm was used to evaluate the butyl acrylate mer. The average curves for cumulative composition of VCC materials are shown in Figure 2; mean square deviation between measured values and average curves, falls within experimental error (< 3 wt %).

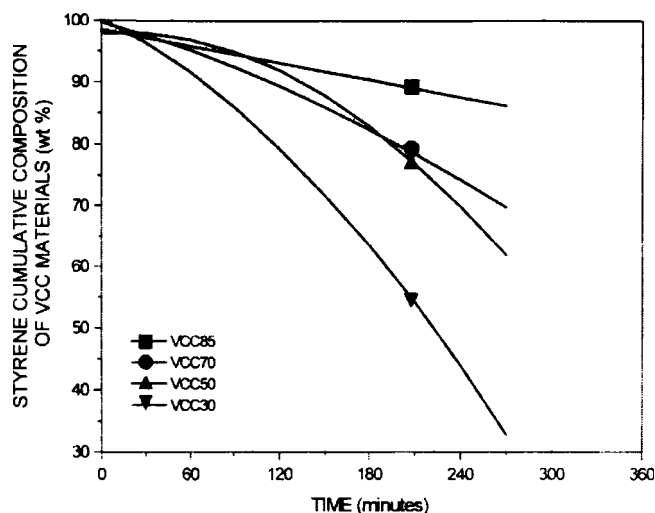


Figure 2 Cumulative polymer composition as a function of reaction time, for styrene-butyl acrylate VCC synthesis. For codes see Table I.

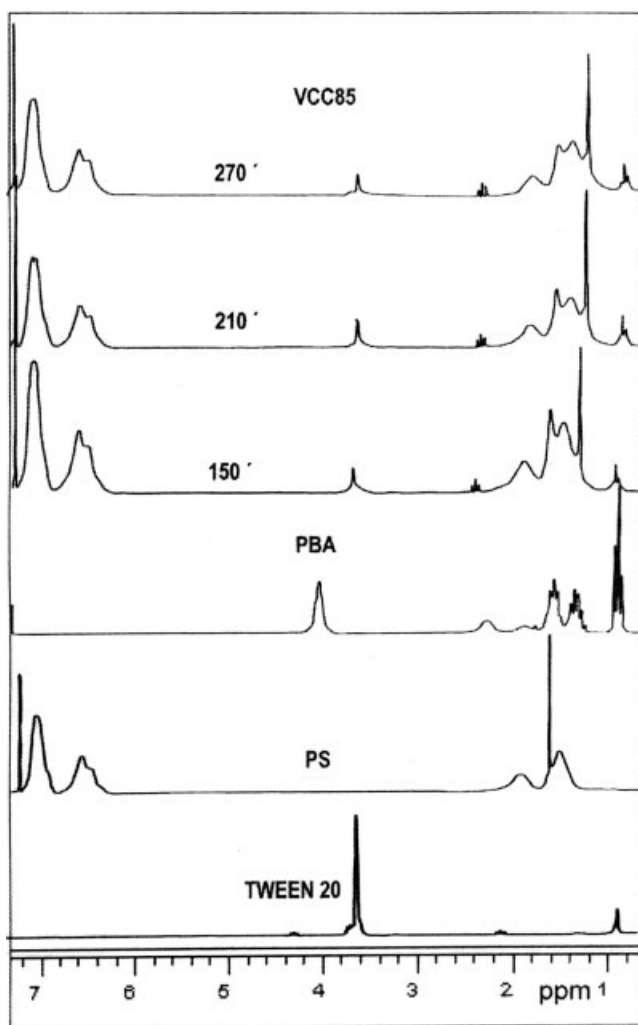


Figure 3 $^1\text{H-NMR}$ spectra of Tween 20, PS, PBA, and VCC85 materials at reaction times indicated in figure. For code see Table I.

Considering the used comonomer feed pattern and monomer relative reactivities ($r_{\text{BA}} = 0.21$ and $r_{\text{S}} = 0.82$ ^{31,32}), curves in Figure 2 are in accordance with expected results; that is, copolymer chains very rich in styrene mer are obtained at low conversions, and butyl acrylate mer fraction in copolymer chains increases as reaction proceeds.

In Figure 3, $^1\text{H-NMR}$ spectra of Tween 20, PS, PBA (polymerized in bulk at 60°C), and representative samples of VCC85 reaction, extracted at advanced degrees of conversion (150, 210, and 270 min) are presented. In the Tween 20 spectrum, a clear signal can be observed at 3.6 ppm (corresponding to protons of the ethylene oxide units; 80 protons/molecule). For the copolymers, signals corresponding to characteristic groups of styrene and butyl acrylate mers, used to construct Figure 2 can be observed in VCC85 spectra. However, it can be noticed that the PBA signal at 4 ppm (assigned to $-\text{OCH}_2-$) does

not appear in such spectra. That peak did not appear in any spectrum of the other VCC materials, up to a certain conversion (such conversion value depends on the predefined feed S/BA ratio), as it can be seen in Figure 4. Of all the samples extracted from the reactor, spectra of each one of the VCC materials that did not show an $-\text{OCH}_2-$ signal, and were collected at the longest corresponding reaction time, are presented in Figure 4. In addition, for such VCC materials, one or two spectra presenting the $-\text{OCH}_2-$ signal are included, showing that the higher the BA final content, the earlier the signal appearance. In those spectra, the OCH_2/CH_3 peak area ratio is smaller than the expected value (2/3). Areas of characteristic peaks for VCC materials spectra shown in Figures 3 and 4 are presented in Table II. The low OCH_2/CH_3 area ratio obtained, compared with the theoretical value for a linear polymer, is an evidence that polymer branching is occurring at the

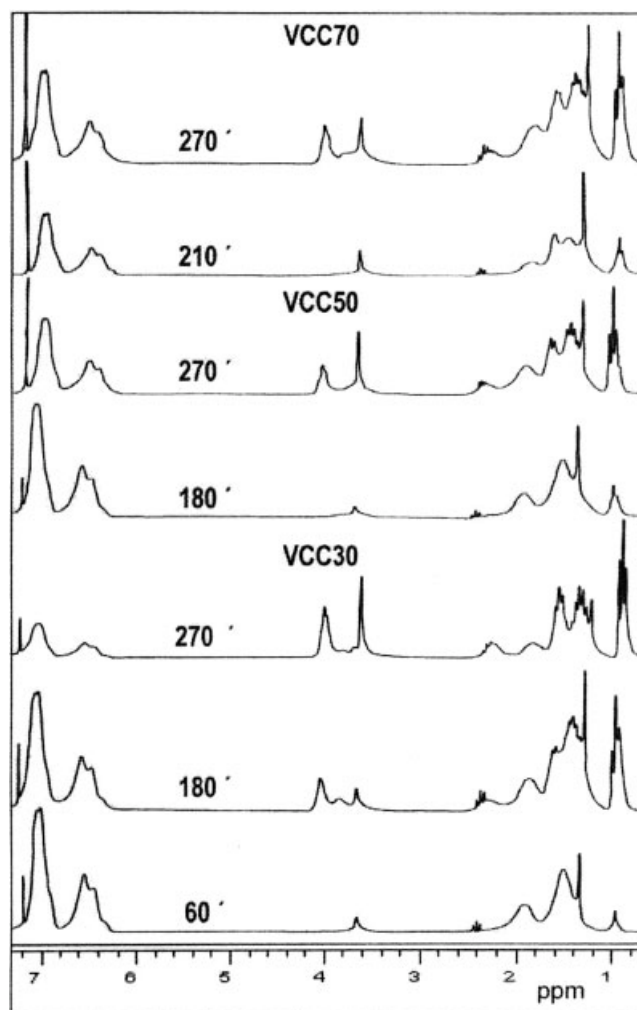


Figure 4 $^1\text{H-NMR}$ spectra of VCC30, VCC50, and VCC70 materials at reaction times indicated in figure. For codes see Table I.

TABLE II
Normalized Peak Areas of $-\text{C}_6\text{H}_5$, $-\text{OCH}_2-$, and $-\text{CH}_3$ signals, for VCC Materials
Spectra Shown in Figures 3 and 4 (for Codes See Table I)

Code-reaction time in minutes	$-\text{C}_6\text{H}_5$ (6.2–7.2 ppm) ^a	$-\text{OCH}_2-$ (~ 4.0 ppm) ^a	$-\text{CH}_3$ (0.9–1.0 ppm) ^a
VCC85–150	96.1	0	3.9
VCC85–210	93.9	0	6.1
VCC85–270	93.5	0	6.5
VCC70–210	87.1	0	12.9
VCC70–270	80.8	3.0	16.2
VCC50–180	91.1	0	8.9
VCC50–270	69.3	8.9	21.8
VCC30–60	96.0	0	4.0
VCC30–180	73.1	5.8	21.0
VCC30–270	41.2	18.5	40.3

^a Integral values were normalized to 100.

$-\text{OCH}_2-$ group. For butyl acrylate, branching has been reported in two-component seeded emulsion reactions³³ and solution polymerizations.^{34,35} Besides, in spectra of copolymers shown in Figures 3 and 4, the characteristic surfactant signal can also be noticed (3.6 ppm).

Since the relation between molecular weight and mechanical properties of polymers is a complex function up to a critical value of molecular weight, above which maximum property values are obtained,²⁷ the number-average molecular weight values of synthesized polymers are presented in Table III. Such values clearly exceed the critical number average degree of polymerization that is required to form enough number of entanglements and assure that mechanical properties are not affected by molecular size.²⁶ For such reason, polymer molecular weight is not a factor of influence for mechanical properties measured in this work.

Rheological behavior for synthesized polymers can be observed in Figures 5 and 6. In Figures 5(a) and 5(b), storage modulus (G') as a function of temperature is presented for T-S and VCC polymers. It can be seen that the curves for the "two component" materials are positioned between those of the pure polymers (modulus falls are between -40°C and

100°C). T-S 30 and T-S 50 materials [Fig. 5(a)] behave closer to the PBA curve, until styrene contribution allows the formation of a plateau that starts in the

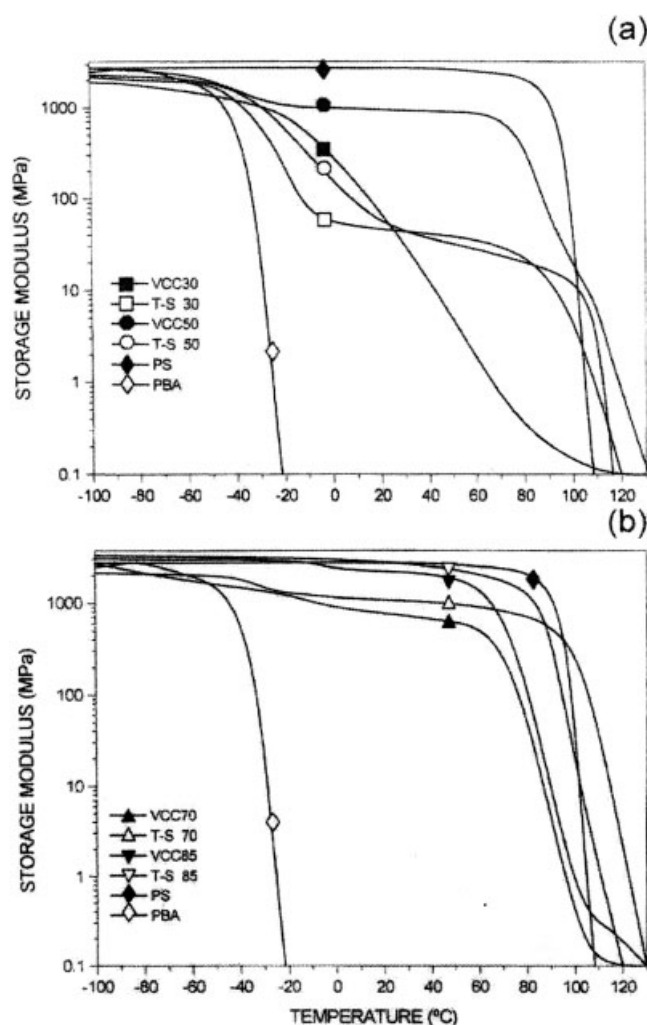


Figure 5 Storage modulus of homopolymers, T-S, and VCC materials as a function of temperature. For codes see Table I.

TABLE III
Number-Average Molecular Weight (\bar{M}_n) of T-S and VCC Materials (for Codes See Table I)

Reaction code	\bar{M}_n (10^{-5}) (g/mol)
T-S 85	5.1
T-S 70	6.4
T-S 50	6.4
T-S 30	5.4
VCC85	4.8
VCC70	3.4
VCC50	3.8
VCC30	3.6

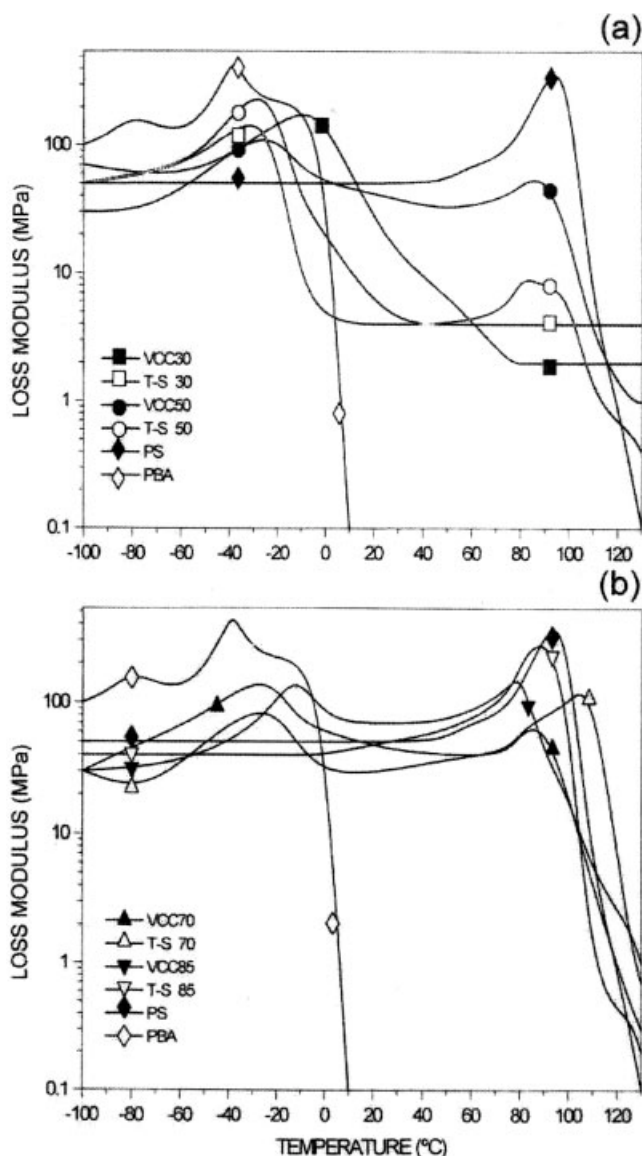


Figure 6 Loss modulus of homopolymers, T-S, and VCC materials as a function of temperature. For codes see Table I.

vicinity of 0°C. However, curves for T-S 70 and T-S 85 materials [Fig. 5(b)] allocate closer to the PS line, maintaining a high modulus up to 85°C. In fact, because of their high polystyrene content, curve for T-S 85 material follow the PS curve very closely.

Looking at G' for VCC materials, curve for VCC30 material does not present plateau [Fig. 5(a)], showing instead a progressive decrease that starts close to -20°C (copolymer type modulus decrease), but clearly separating from the PBA curve. VCC50 sample [Fig. 5(a)], presents for the 0–70°C temperature range, a modulus substantially higher than VCC30 sample, denoting a synergistic effect in this VCC material. Such type of behavior is in agreement with results presented with materials synthesized in

bulk.^{10,11} In fact, VCC50 sample resembles behavior of the VCC70 and VCC85 samples [Fig. 5(b)], which are lines that allocate closer to the PS curve.

The behavior comparison of materials with 30 wt % styrene [Fig. 5(a)] shows that the VCC30 line is above the T-S 30 line only in the -25°C to 25°C temperature range. In addition, in the above-mentioned temperature range, VCC30 line is even slightly above the T-S 50 line. There, it is also noticeable that both T-S polymers clearly show a typical two-phase material behavior, presenting a long plateau before the final modulus decrease. The synergistic contribution of styrene-rich polymer chains integrated in the whole particle, to increase modulus of VCC materials, can be clearly observed comparing lines with 50 wt % styrene. Beyond -20°C, the T-S 50 line is clearly below the one of the VCC50 sample. In the 0°C to 80°C temperature range, the VCC50 sample is able to maintain a high modulus, showing for that range, a value that is more than one order of magnitude higher than the one of the T-S 50 material, although both contain the same global amount of rubbery component. For styrene-rich polymeric materials [70 and 85 wt % in Fig. 5(b)], the polystyrene matrix of T-S materials imparts considerable rigidity, overcoming the G' value of equivalent VCC materials, and maintaining a high modulus up to 90°C. Looking at the whole composition range, the major performance difference between the two kinds of polymeric materials corresponded to the 50/50 S/BA composition, denoting that at intermediate compositions, the mechanical performance of the obtained polymeric materials is greatly influenced by the synthesis process.

In Figure 6, loss modulus (G'') of homopolymers, T-S, and VCC materials is shown as a function of temperature. For homopolymers, the maximum energy dissipation value appears at the corresponding glass-transition temperature (T_g). However, for the "two component" materials, the temperature value of each peak is a few degrees apart from the one of the corresponding homopolymer (in most cases, between homopolymers T_g). In general, because of copolymer chains formation in VCC materials, their G'' curves present wider peaks than those of equivalent T-S materials. Although materials of equivalent composition follow similar behavior as temperature increases, in the low temperature region, VCC30 and VCC50 materials show greater peak displacement and higher energy dissipation capacity beyond -10°C, than the equivalent T-S materials [specially in the 50 wt % materials; Fig. 6(a)]. For the high temperature region in Figure 6(b), VCC70 and VCC85 materials show lower T_g values than the equivalent T-S materials. However, in the 0°C to 75°C range, VCC materials present higher energy dissipation capacity.

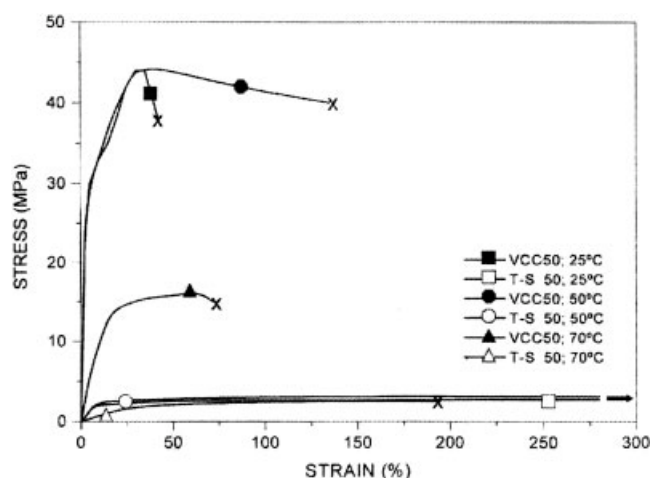


Figure 7 Stress–strain behavior of T-S 50 and VCC50 materials at different temperatures. For codes see Table I.

As the main difference in rheological behavior for T-S and VCC materials was obtained for the 50/50 (BA/S) composition ratio, complementary mechanical performance for such materials was evaluated. In Figure 7, stress–strain behavior for those polymeric materials is presented at 25, 50, and 70°C. There, the T-S material shows a rubbery behavior for the three temperatures, while the VCC material shows a hard and strong behavior at 25°C and a hard and tough performance at 50°C (following ASTM nomenclature). Moreover, at 70°C the VCC50 material still retains certain rigidity and tenacity. Superiority of VCC materials in Young's modulus (E) is clear, maintaining deformation capacity.

The dynamic and static mechanical properties panorama for VCC materials synthesized with the approach used in this work indicates that, the performance increment (with respect to T-S materials) is remarkable for the material where global comonomers content is similar. Such effect can be possible because styrene-rich copolymer chains contribute to increase material rigidity (that is, G' and E values increase beyond the ones that correspond to the T-S materials), while butyl acrylate mer in copolymer chains contributes to obtain high deformation capacity. Here, polymer particles with a continuous composition change pattern along the polymerization reaction were obtained, improving mechanical performance of VCC materials.

CONCLUSIONS

By varying composition feed in a semicontinuous process, "tailor made" emulsion copolymers can be produced, overcoming limitations of other feeding methods traditionally used. A synergistic effect can

be reached in copolymer material properties, by the contribution of chains rich in each one of both components, provided that an adequate composition variation pattern has been obtained. For polymeric materials synthesized in this work, the VCC materials mechanical properties enhancement is remarkable for middle compositions.

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