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Core−Shell Polymers with Improved Mechanical Properties Prepared by Microemulsion Polymerization

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ABSTRACT: The synthesis of core−shell polymers of styrene and butyl acrylate by a two-stage microemulsion polymerization process is reported. The microemulsion polymerization was optimized by adding more monomer in a semicontinuous fashion to the latex resulting from the polymerization of the parent microemulsion to produce a high-solid-content polystyrene latex (ca. 40% solids) with small particle size ($<$30 nm) and high molar mass ($>2 \times 10^6$ g/mol). Core−shell polymers were characterized by transmission electron microscopy, quasielastic light scattering, IR spectroscopy, differential scanning calorimetry, and dynamic mechanical thermal analysis. The effect of adding a functional monomer (itaconic acid) on the mechanical properties (Young modulus, ultimate elongation, and hardness) of the microemulsion-made structured polymers is also reported. The core−shell polymers synthesized by microemulsion polymerization are more rigid and harder than core−shell polymers of similar composition made by emulsion polymerization. The presence of the functional monomer improves even more the mechanical properties of these materials.

Introduction

There is a great interest for improved acrylic polymers made by emulsion polymerization, capable of forming nonporous homogeneous films. These polymers have applications in paints, adhesives, the manufacturing of wax, paper, and textiles, and in other materials of daily use.[1−3] To improve the mechanical properties of acrylic polymers and to increase their compatibility with other materials and their adhesion to substrates, especially to those that are prone to corrosion, these polymers are being modified with small amounts of functional monomers such as *N*-methylolacrylamide or acrylic, methacrylic, or itaconic acids.[4,5]

An alternative process to emulsion polymerization for producing latexes with polymer particles of small particle size ($<$50 nm) and high molar mass ($>10^6$ g/mol) with fast reaction rates is microemulsion polymerization.[6−10] The potential for medical, biological, and industrial applications of microemulsion-made colloidal polymers is enormous.[11,12] However, the low solid content of microemulsion-made latexes and the large amounts of surfactant that are usually required in microemulsion polymerization have hindered its scale-up to industrial level.

In this work, the synthesis by a two-stage microemulsion polymerization process of core−shell polymers of styrene and butyl acrylate (and itaconic acid) with improved mechanical properties is reported. The microemulsion polymerization was optimized by adding more monomer in a semicontinuous fashion to the latex resulting from the polymerization of the parent microemulsion to produce a high-solid-content polystyrene latex (ca. 40% solids) with small particle size ($<$30 nm) and high molar mass ($>2 \times 10^6$ g/mol).[13]

Latexes were examined by quasielastic light scattering (QLS) and transmission electron microscopy (TEM) to determine particle size, particle size distribution, and morphology. Polymers were characterized by dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), and IR spectroscopy. The core−shell polymers were also modified with small amounts of itaconic acid, and their mechanical properties were compared with those of microemulsion-made nonfunctionalized core−shell polymers and functionalized core−shell polymers of similar composition made by conventional emulsion polymerization.

Experimental Section

Styrene (St) and butyl acrylate (BA) were 99% pure from Scientific Polymer Products. The inhibitor was removed from these monomers by passing them through a DHR-7 or DHR-4 silica gel column (SPP). Itaconic acid (IA, Aldrich) was 99% pure. Industrial grade allyl methacrylate (ALMA), used as cross-linked agent, was used as received. Sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB) were 99% pure from Aldrich and Tokyo Kasei, respectively. 2,2′-Azobis(2-amidinopropane) hydrochloride (V-50) from Wako Chemicals was recrystallized from methanol. Potassium persulfate (KPS) was 99%+ pure from Aldrich. Water was doubly distilled and deionized.

Core−shell polymers were made by a two-stage microemulsion or emulsion polymerization process. First, styrene was polymerized at 60 °C in the presence of small amounts of ALMA to produce slightly cross-linked particles that were used

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Table 1. Typical Recipe for the Synthesis of Functionalized Core−Shell Polymers by a Two-Stage Emulsion Polymerization Process

reagents	first stage (g)	second stage (g)
H_2O	60	
SDS	0.172	
ST	3.4	
ALMA	0.034	
KPS	0.034	0.045
BA		5.1
IA		0.51

Table 2. Typical Recipes for the Synthesis of Unfunctionalized and Functionalized Core−Shell Polymers by a Two-Stage Microemulsion Polymerization Process

reagents	first stage (g)	second stage unfunctionalized (g)	second stage functionalized (g)
H_2O	6.67	53	53
DTAB	1.17		
ST	0.326 → 3.4[a]		
ALMA	0.034		
V-50	0.0033	0.051	0.051
BA		5.1	5.1
IA			0.51

[a] The styrene content was increased from 0.326 g at the end of the typical microemulsion polymerization to 3.4 g by semicontinuous addition.

as seeds for the second stage. Emulsion-made polystyrene latexes (10% solid content) were made by polymerization with KPS (1 wt % with respect to monomer) using 0.2 wt % SDS as emulsifier. Microemulsion-made latexes were prepared by initiating a microemulsion containing 14.1 wt % DTAB, 79.9 wt % H_2O, and 6 wt % St with V-50 (1 wt % with respect to monomer) at 60 °C. To increase the solid content of the latex, more monomer was added to the latex in a semicontinuous fashion over more than 6 h, immediately after completion of the polymerization of the parent microemulsion. With this technique, the polystyrene content can be increased from 6 to ca. 40% at the end of the addition process while maintaining small particle size and high molar mass.[13] Then, this latex is diluted to 5−10% solid content before adding the butyl acrylate. In the second stage, butyl acrylate (and itaconic acid, in some cases) was added to form the shell around the seeded polystyrene particles made by emulsion or microemulsion polymerization. The weight ratio of PSt/PBA was 40/60. When IA was added, the weight ratio of IA/BA was 1/10. To maximize the incorporation of IA in the shell, the pH of the medium during the second stage was maintained at a value lower than the first pK_a (3.85) of this functional monomer.[14,15] The recipes for the two-stage emulsion and microemulsion polymerization processes are reported in Tables 1 and 2, respectively.

Core−shell polymers were recovered from the latexes by freezing and filtration. The product was washed to eliminate adsorbed surfactant and non reacted monomer, and dried in a vacuum oven. Glass transition temperatures were measured in a Mettler TC15 differential scanning calorimeter at a scanning rate of 20 °C/min and with a Polymer Laboratories DMTA MK II torsion rheometer at a frequency of 0.3 Hz. IR spectroscopy was performed in a Nicolet 5ZDX FTIR spectrometer.

Particle size was measured with a Malvern 4700C QLS apparatus at 25 °C. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle\Gamma\rangle$, ($\equiv 2q^2D$), where D is the diffusion coefficient and q is the scattering vector. The measured diffusion coefficients were represented in terms of the apparent radii using Stokes law and the assumption that the solvent has the viscosity of water. Latexes were diluted up to 1000 times before QLS measurements to minimize particle−particle interactions.

Particle size distribution (PSD) of the polystyrene latexes was measured directly with a JEOL 100CX transmission electron microscope. To improve the contrast, a drop of the latex was added to an aqueous solution of the negative stain, phosphotungstic acid (PTA). Then, a drop of this diluted latex was put in a carbon-coated copper grid and allowed to dry overnight. At least 400 particles were counted to estimate PSD.

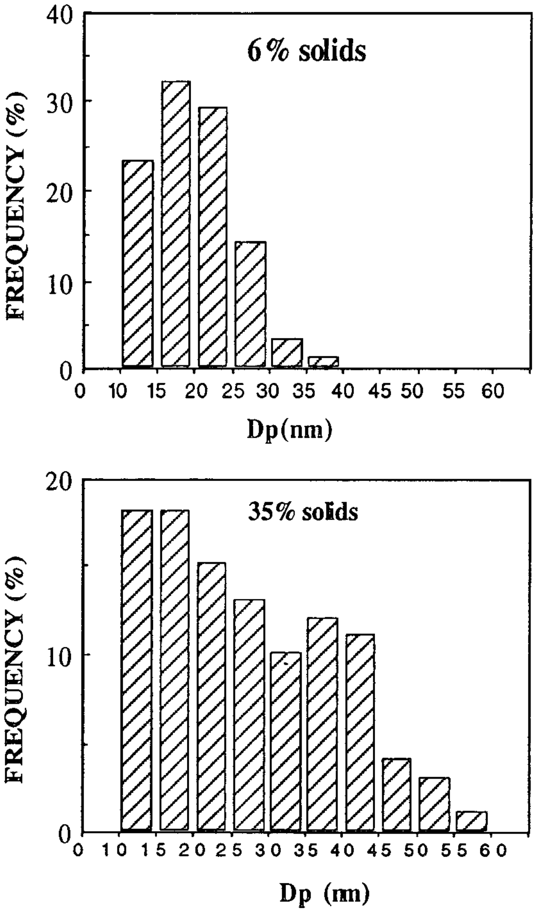

Figure 1. Particle size distribution histogram of (A) latex prepared by polymerization of parent microemulsion made with 6% St, 14.1% DTAB, and 79.9% H_2O and (B) latex containing 35% solids made by semicontinuous addition of more styrene to the parent microemulsion latex.

Polymer bars (11 × 12 × 0.3 cm) for tensile and hardness tests were made by heating at 120 °C and pressing at 125 bar the samples in a hydraulic press. Tensile tests were done at room-temperature according to the ASTM D-638 method at an elongation velocity of 3 in./s in a United EEC 3.5−60 universal testing machine. Hardness was measured according to the ASTM D2240 method in a PTC 307 L Shore hardness type D instrument.

Results and Discussion

To increase the ratio of polymer produced-to-surfactant employed in microemulsion polymerization and optimize the synthesis of core−shell polymers, a semicontinuous addition of monomer to a microemulsion-made latex with low solid content (6% solids) was used to yield a latex with near 40% solid content. Details are reported elsewhere.[13] PSD histograms, obtained by TEM, of the polystyrene particles at the end of the polymerization of the parent microemulsion and at the end of the semicontinuous addition of monomer are shown in Figure 1. Here, it is clear that the PSD of the latex produced after the semicontinuous addition of styrene to the parent latex (Figure 1B) remains within the range of microemulsion-made latexes, although the distribution becomes skewed toward larger sizes. The low-solid-content microemulsion-made latex (6% solids) has a number-average particle diameter (D_{p_n}) of 20.2

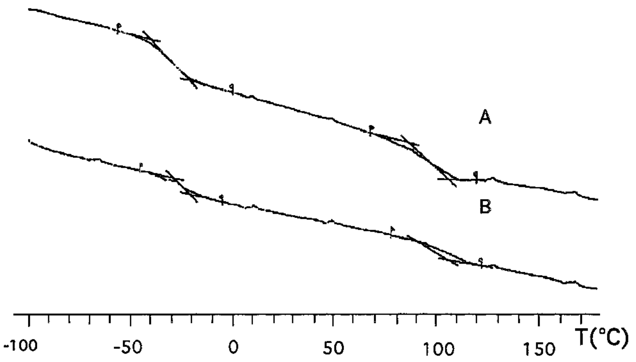

Figure 2. DSC thermograms of core−shell polymers of polystyrene and poly(butyl acrylate) made (A) without itaconic acid and (B) with itaconic acid. The ratio of itaconic acid to butyl acrylate was 1/10 (w/w).

nm with a size polydispersity (D_{p_w}/D_{p_n}) of 1.15 (Figure 1A), where D_{p_w} is the weight-average particle diameter. The latex containing 35% solids has a D_{p_n} of 27.0 nm with a size polydispersity of 1.27 (Figure 1B). These results demonstrate that, upon addition of monomer, there is almost no swelling of the existing particles but mainly generation and growth of new particles. The number-average molar mass ($\bar{M}_n$) is (2−3) × 10^6 g/mol and remains fairly constant during the addition process because chain transfer to monomer is the controlling mechanism for chain termination in microemulsion polymerization.[16−22]

After adding the butyl acrylate to the polystyrene particles in the second stage, the *z*-average particle diameter (D_{p_z}), measured by QLS, increases from 40 to about 60 nm. This increment suggests that the poly(butyl acrylate) grows around the seed particles, forming a core−shell structure. A simple calculation, assuming that the polymer has the density of bulk poly(butyl acrylate), shows that such a growth corresponds to the incorporation of most of the butyl acrylate added in the second stage. In the case of the emulsion-made material, the polystyrene particles used as seeds have a D_{p_z} of ca. 80 nm and grow to ca. 100 nm after the addition of the butyl acrylate.[14]

Figure 2 shows DSC thermograms of the core−shell polymers made by microemulsion polymerization without and with IA in the second stage. In both thermograms, two glass-transition temperatures (T_g's) are clearly observed, which demonstrates the existence of two separated polymeric microdomains within the same sample. The higher-temperature transition appears at the same temperature (ca. 100 °C) in both samples and corresponds to the T_g of the polystyrene forming the core. The low-temperature transition, on the other hand, appears at −45 °C in the sample made without IA (Figure 2A), which is quite close to the T_g of poly(butyl acrylate).[23] In the sample made with IA (Figure 2B), on the other hand, this transition is detected at higher temperatures (−29 °C). Although the T_g of poly(itaconic acid) has not been reported and we could not measure it because this polymer suffers degradation first, its value has to be higher than that of poly(butyl acrylate). Hence, the transition at −29 °C should correspond to the T_g of a copolymer of butyl acrylate and itaconic acid forming the shell. With the emulsion-made core−shell polymer containing IA, DSC (not shown) depicts a transition at −33 °C and another at 103 °C, which correspond to poly(butyl acrylate)-*co*-(itaconic acid) in the shell and to polystyrene in the core, respectively.

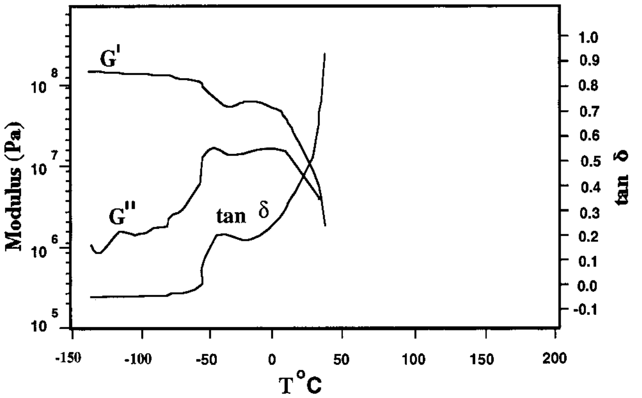

Figure 3. Elastic (*G*′) and viscous (*G*″) moduli and tan *δ* measured at 10 rad/s as a function of temperature for a core−shell polymer made by microemulsion polymerization without itaconic acid.

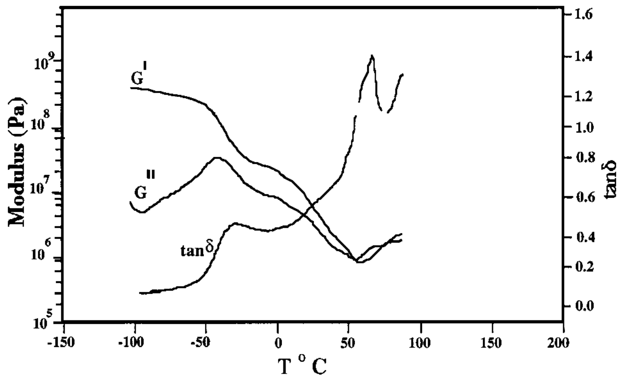

Figure 4. Elastic (*G*′) and viscous (*G*″) moduli and tan *δ* measured at 10 rad/s as a function of temperature for a core−shell polymer made by microemulsion polymerization with itaconic acid.

Figures 3 and 4 depict the dynamic moduli (*G*′ and *G*″) and tan *δ* (≡*G*″/*G*′) of core−shell polymers prepared by microemulsion polymerization without and with IA, respectively. In both cases, the elastic modulus (*G*′) is high (>10^8 Pa) at the lowest temperature examined (−100 °C) because this temperature is lower than the glass-transition temperatures of both polymers forming the core and the shell. The large value of *G*′ is typical of vitreous polymers.[24] However, the structured polymer prepared with IA has a larger vitreous modulus than the nonfunctionalized polymer (cf. Figures 3 and 4) probably because of the presence of the more rigid copolymer of itaconic acid and butyl acrylate in the shell. In addition, the incorporation of itaconic acid in the shell increases the glass-transition temperature (signaled by the peak in tan *δ* and the rapid decrease in *G*′ with increasing temperature) from −48 °C in the nonfunctionalized core−shell polymer (Figure 3) to −35 °C in the functionalized polymer (Figure 4) because, as discussed above, the T_g of poly(itaconic acid) must be higher than that of poly(butyl acrylate). The shift of this glass transition to higher temperatures upon addition of IA demonstrates that the shell is a random copolymer of butyl acrylate and itaconic acid. Because of the high content of butyl acrylate in the shell, the specimen becomes soft before the glass-transition temperature of the polystyrene core (ca. 100 °C) can be reached, and so, it cannot be detected by DMTA. Notice that the incorporation of IA in the outer layer of the structured polymer raises the softening temperature (signaled by

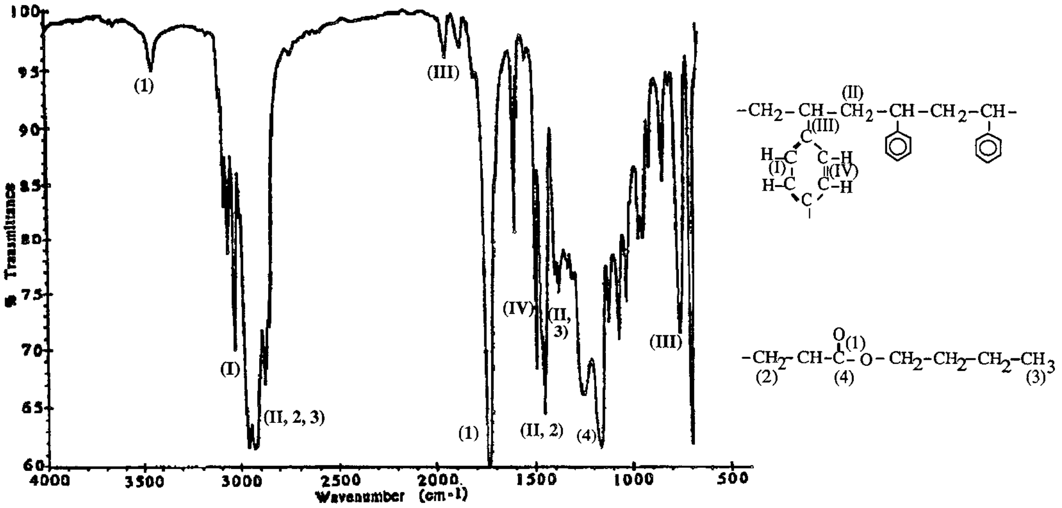

Figure 5. IR spectrum of a core–shell polymer made by microemulsion polymerization without itaconic acid. Characteristic absorption bands due to polystyrene are indicated with roman numbers and those of poly(butyl acrylate) with arabic numbers.

the crossover of the elastic and viscous moduli) from 40 to about 55 °C.

The incorporation of IA in the structured polymer is also confirmed by IR spectroscopy. Figure 5 shows an IR spectrum of a core–shell polymer made by microemulsion polymerization without IA. In this spectrum, the characteristic bands of polystyrene are indicated with roman numbers and those of poly(butyl acrylate) with arabic numbers in the chemical structures shown in the figure. Clearly, the characteristic spectra of poly(butyl acrylate) and polystyrene appear superimposed in Figure 5. For poly(butyl acrylate), the carbonyl group exhibits a vibration band at 1750–1735 cm^{-1} (1) with an overtone at 3480 cm^{-1} (1); the methylene group shows stretching bands at 2949–2915 and 2870–2845 cm^{-1} (2) and a flexion band at 1480–1440 cm^{-1} (2); the methyl group depicts vibration bands at 2979 and 2880 cm^{-1} (3) and flexion bands at 1450 and 1380 cm^{-1} (3); the C–O bond shows two broad bands at 1280 and 1180 cm^{-1} (4). For polystyrene, the aromatic C–H bond depicts a vibration band at 3080–3030 cm^{-1} (I); the methylene group shows stretching bands at 2949–2915 and 2870–2845 cm^{-1} (II) and a flexion band at 1480–1440 cm^{-1} (II); the out-of-plane aromatic C–H bond exhibits vibration bands between 900 and 650 cm^{-1} (III). In addition, the typical overtones of monosubstituted aromatic compounds are seen at the 2000–1600 cm^{-1} region (III) and the vibration bands of the aromatic C=C bond are detected at 1600–1500 cm^{-1}.

The spectrum of the core–shell polymer made in the presence of IA (Figure 6) depicts, in addition to the characteristic bands of polystyrene and poly(butyl acrylate) described above, a very broad vibration band at 3400 cm^{-1} (A), which hides the characteristic bands of the aromatic C–H bonds of styrene, and another less intense band between 950 and 900 cm^{-1} (A) due to the hydroxyl group of the itaconic acid. The carbonyl band of IA appears superimposed with that of the butyl acrylate at around 1750 cm^{-1}. Inasmuch as the core–shell polymers were washed with hot water and methanol to extract nonpolymerized IA and its homopolymer, the spectrum shown in Figure 6 must belong to a material containing polystyrene and a copolymer of BA and IA.

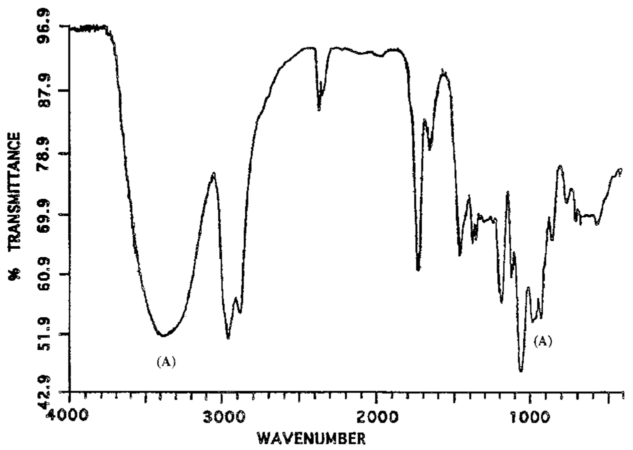

Figure 6. IR spectrum of core–shell polymers made by microemulsion polymerization with itaconic acid. Letter "A" in spectrum depicts the characteristic absorption bands of the hydroxyl group of the itaconic acid.

Figure 7 shows stress–strain tests performed on nonfunctionalized and functionalized microemulsion-made polymers. In addition, for comparison, an emulsion-made core–shell polymer made with IA is included in this figure. The composition of this material must be similar to that of the microemulsion-made functionalized material as evident from the similar glass-transition temperatures of these two materials (Figure 1). However, the average particle size of the emulsion-made polymers is larger (100 nm) than that made by microemulsion polymerization (60 nm). The emulsion-made polymer shows the typical rubbery behavior of core–shell polymers, i.e., an elastic response at small strains followed by flow up to a yield point where necking begins and then rupture. Microemulsion-made polymers, in contrast, behave like tough materials:[24] they are more rigid and have a much higher yield stress than the conventional core–shell polymers. Moreover, the Young modulus is larger and the ultimate strength of microemulsion-made polymers is higher than those of the emulsion-made material (Table 3). Notice that the rigidity, the Young modulus, and ultimate strength of the microemulsion-made polymers increase even more upon the incorporation of the functional monomer.

Table 4 reports the Shore "D" hardness of emulsion-made and microemulsion-made core–shell polymers. The core–shell polymers prepared by microemulsion polymerization are harder than the conventional emul-

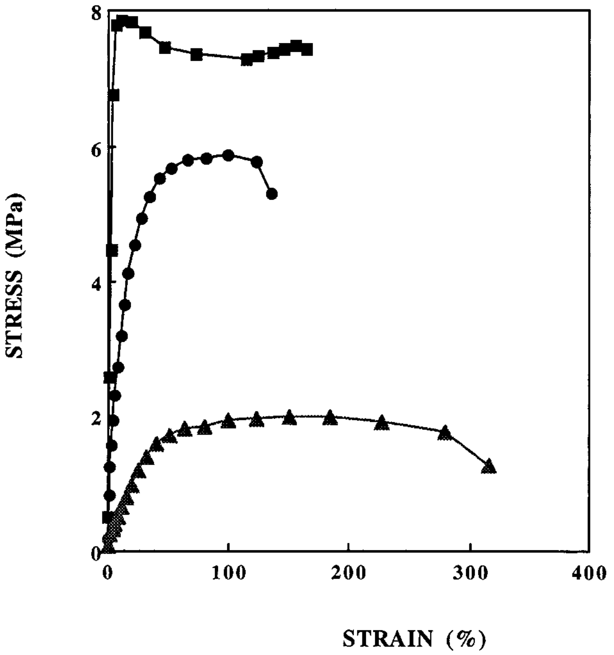

Figure 7. Stress-strain tests performed on core−shell polymers: (▲) emulsion-made with itaconic acid, (●) microemulsion-made without itaconic acid, and (■) microemulsion-made with itaconic acid.

Table 3. Young Modulus (*E*) and Ultimate Strength of the Emulsion and Microemulsion-Made Core Shell Polymers

sample	*E* (MPa)	ultimate strength (MPa)
functionalized emulsion-made	10.4	1.25
unfunctionalized microemulsion-made	53.6	5.3
functionalized microemulsion-made	170	7.4

Table 4. Hardness of Core−Shell Polymers of Styrene and Butyl Acrylate

sample	hardness Shore "D"
unfunctionalized microemulsion-made	91
functionalized microemulsion-made	94
functionalized emulsion-made	70

sion-made polymers. In addition, the presence of itaconic acid increases even more the hardness of the material.

Conclusions

Core−shell polystyrene/poly(butyl acrylate) were prepared by a two-stage microemulsion polymerization. The process was optimized by adding more styrene in a semicontinuous fashion immediately after completion of the polymerization of the parent microemulsion to increase substantially the number density of polystyrene particles in the latex without losing the characteristics of microemulsion-made latex, i.e., small particle size and high molar mass. The polystyrene particles of this latex were then used as seeds to form the core−shell polymer particles by adding butyl acrylate and, sometimes, small amounts of itaconic acid.

The smaller particle size of the core−shell polymers prepared by microemulsion polymerization leads to harder and more rigid materials with larger Young moduli and ultimate strength compared with conventional core−shell polymers made by emulsion polymerization. This improved behavior is probably the result of the higher specific surface area of the microemulsion-made polymers due to the smaller core−shell particles that form the polymeric films. The addition of small amounts of the functional monomer, itaconic acid, modifies substantially the mechanical properties of the microemulsion-made core−shell polymers; i.e., they become tougher. With emulsion-made polymers, the incorporation of functional monomers also changes substantially the mechanical properties of core−shell materials.[4,5,14] Tests of adhesion and gas permeability of microemulsion-made core−shell polymers are underway.

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References and Notes

(1) Kendall, K.; Padget, J. C. *Int. J. Adhes. Adhes.* **1982**, *1*, 149.
(2) Henry, F.; Cansell, F.; Guillaume, J. L.; Pichot, C. *Colloid Polym. Sci.* **1989**, *267*, 167.
(3) Trejo-O'Reilly, J. A.; Flores, R.; Cruz, A.; Vázquez-Polo, G.; Castaño, V. *Mater. Lett.* **1992**, *15*, 248.
(4) Rios, L.; Hidalgo, M.; Cavaille, J. Y.; Guillot, J.; Guyot, A.; Pichot, C. *Colloid Polym. Sci.* **1991**, *269*, 812.
(5) Hidalgo, M.; Cavaille, J. Y.; Guillot, J.; Guyot, A.; Pichot, C.; Rios, L.; Vassoille, R. *Colloid Polym. Sci.* **1992**, *270*, 1208.
(6) Candau, F. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 9, 215−219.
(7) Dunn, A. S. In *Comprehensive Polymer Science*; Eastwood, G. C., Ledwith, A., Sigwalt, P., Eds.; Pergamon Press: New York, 1988; Vol. 4, pp 219−224.
(8) Candau, F. In *Polymerization in Organized Media*; Paleos, C. M., Ed.; Gordon Breach Sci. Pub.: New York, 1992; pp. 215−282.
(9) Puig, J. E. In *Encyclopedia of Polymeric Materials*; Salamone, J. P., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 4, pp 4333−4341.
(10) Katime, I.; Mendizábal, E.; Puig, J. E. *Recent Dev. Phys. Chem.* **1997**, *1*, 271.
(11) Antonietti, M. *Macromol. Chem. Phys.* **1995**, *196*, 441.
(12) Puig, J. E. *Rev. Mex. Fis.* **1999**, *45* S1, 18.
(13) Rabelero, M.; Zacarías, M.; Mendizábal, E.; Puig, J. E.; Domínguez, J. M.; Katime, I. *Polym. Bull.* **1997**, *38*, 695.
(14) Hernández-Patiño, J.; Mendizábal, E.; Puig, J. E.; Castaño V.; Katime, I. *J. Appl. Polym. Sci.*, accepted for publication.
(15) Soto, V. M. M. Sc. Thesis, Universidad de Guadalajara, México, 1997. The pK_a's of itaconic acid (3.85 and 5.45) were measured potentiometrically at 25 °C.
(16) Guo, J. S.; Sudol, E. D.; Vanderhoff, J. W.; El-Aasser, M. S. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 691.
(17) Rodríguez-Guadarrama, L. A.; Mendizábal, E.; Puig J. E.; Kaler, E. W. *J. Appl. Polym. Sci.* **1993**, *48*, 775.
(18) Full, A. P.; Kaler, E. W.; Arellano, J.; Puig, J. E. *Macromolecules* **1996**, *29*, 2764.
(19) Escalante-Vázquez, J. I.; Rodríguez-Guadarrama, L. A.; Mendizábal, E.; Puig, J. E.; López R. G.; Katime, I. *J. Appl. Polym. Sci.* **1996**, *62*, 1313.
(20) Morgan, J. D.; Lusvardi, K. M.; Kaler, E. W. *Macromolecules* **1997**, *30*, 1897.
(21) Morgan, J. D.; Kaler, E. W. *Macromolecules* **1998**, *31*, 3197.
(22) Co, C. C.; Kaler, E. W. *Macromolecules* **1998**, *31*, 3203.
(23) Brandrup, J., Immergut, H., Eds.; *Polymer Handbook*; Wiley: New York, 1989.
(24) Lenk, R. S. *Polymer Rheology*; Applied Sci. Pub.: London, 1978.

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