Effect of Morphology on Mechanical and Rheological Properties of Butyl Acrylate–Methyl Methacrylate Multiphase Polymers

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SYNOPSIS

Polymers of butyl acrylate–methyl methacrylate with different morphologies were synthesized by emulsion polymerization. Four types of polymers were obtained: copolymer, core–shell, three layer, and a core–shell with a copolymer layer of variable composition (gradient). The effect of the morphologies on the mechanical and rheological properties of these polymers was studied. It was found that when the same overall composition was used the properties of the polymer can be varied from those of rigid plastic to those of an elastomeric material. It was also found that increasing the content of butyl acrylate (BA) improves the mechanical properties and the presence of a copolymer zone improves the impact resistance of the material. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Modern technology demands new plastics with improved properties. In many applications, it is required that the polymers present good impact resistance combined with mechanical strength. To meet that demand, several routes may be used: synthesis of new monomers followed by their polymerization, copolymerization of available monomers, and blending of polymers or synthesis of structured polymers (core–shell, confettilike, multilayer).[1-3] Since structured polymers present a broad spectrum of properties depending on the monomers used and particle morphology (phase distribution),[4] their study is of increasing importance. This type of polymer can be produced by multistage emulsion polymerization,[5-8] where a previously formed seed is grown by the addition of monomer(s), avoiding the formation of new particles. Particles with different morphology may be obtained depending on the sequence and form of the addition of the monomers

(continuously, batch, etc.), as well as the type of monomers.[4,9-11] It has been reported that multiphase polymers (core–shell and multilayer) present different mechanical behavior in spite of having the same overall composition.[12,13] It has also been reported that preparation of these types of polymers usually is not straightforward, since phase incompatibility may cause the formation of heterogeneous structures such as confettilike and raspberrylike particles.[4,14-16] One way to reduce phase separation is by forming *in situ* a grafted copolymer which can be a compatibilizer of both phases.[6,17] Another method to overcome phase incompatibility consists of forming a copolymer layer of variable composition (gradient) between both homopolymers.[18-20] In this method, the polymer composition at the beginning of the gradient zone is richer in the polymer that forms the seed, and at the end of the gradient zone, the copolymer is richer in the second polymer. To produce the gradient zone between both homopolymers, the reaction is carried out in a semicontinuous mode under "starved conditions" where the rate of addition of the monomers is slower than is the rate of reaction, causing the instantaneous copolymer composition

Table I Polymerization Conditions Used to Obtain the Seed for the Multiphase Polymers

Type of Structure	Gradient	PBA/PMM	Core–Shell PMMA/PBA	Trilayer PBA/ PMMA/PBA
BA (mL)	25.0	75.0	—	45.0
MMA (mL)	—	—	75.0	—
EDGMA[a] (%)	0.6	0.6	—	0.6
ALMA[a] (%)	—	3.0	3.0	3.0
TDDM[b] (%)	—	—	0.45	—
PSP (g)	1.21	0.61	0.61	0.37
SDS (g)	1.55	1.55	1.55	1.55
Agua (mL)	300.0	300.0	300.0	300.0

[a] Volume percent based on BA.
[b] Volume percent based on MMA.

to be determined by the monomer feed composition.[17,20]

In this work, the effect of morphology and composition on the mechanical and rheological properties of structured polymers (hard core–soft shell, soft core–hard shell, gradient, and multilayer) and copolymers of methyl methacrylate (MMA) and butyl acrylate (BA) obtained by emulsion polymerization is presented.

EXPERIMENTAL

Materials

Butyl acrylate and methyl methacrylate monomers were purified by vacuum-distillation. Ethylene glycol

methacrylate (EGDM), allyl methacrylate (ALMA), and ter-dodecyl mercaptan (TDDM), used as crosslinking, bonding, and transfer agents, respectively, were industrial grade and used as received. The sodium dodecyl sulfate (emulsifier) and the potassium persulfate (initiator) were of analytical grade.

Polymerization

Polymerizations were carried out in a 1 L stirred glass reactor under nitrogen atmosphere. The reactor was provided with a monomer(s) delivering system. The seeds were prepared using the formulations presented in Table I. The poly(butyl acrylate) (PBA) seeds were slightly crosslinked to prevent
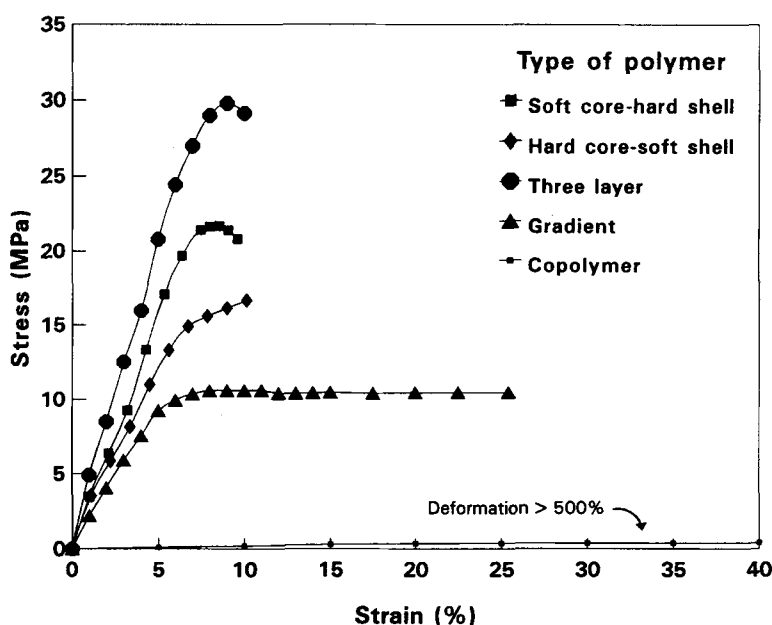

Figure 1 Stress–strain curves for multiphase polymers (PBA/PMMA) with overall weight composition 50 : 50.

Table II   Mechanical Properties of Multiphase Polymers PBA/PMMA with Overall Composition 50 : 50 by Weight

Type of Polymer	Ultimate Stress (MPa)	Ultimate Strain (MPa)	Young's Modulus (MPa)	Impact Energy (J/cm)
Gradient	10.46	25.43	178.30	16.12
Core–shell				
PBA/PMMA	27.11	9.00	444.20	0.36
Core–shell				
PMMA/PBA	16.67	10.12	244.22	0.19
Trilayer				
PBA/PMMA/PBA	29.15	10.00	416.00	0.20
Copolymer	1.63	563.83	2.98	No break

polymer migration toward the particle surface and also to increase their elastomeric properties.

The bonding agent (ALMA) used in the core–shell and three-layer polymers may form copolymers with PBA and PMMA in the interface by the reaction of its residual double bond and, in this way, can increase the compatibility of the PBA and PMMA phases. The seeds were formed carrying out the polymerizations at 70°C and the outer layers were formed at 85°C. To obtain core–shell polymers, the second stage was carried out by continuous addition of the shell-forming monomer to the corresponding seed particles.

The gradient-type polymer was obtained by adding a mixture of BA and MMA (of varying composition) to the PBA seed, at a rate of 2.5 mL/min. The feed composition was varied every 10 min by increasing the MMA content. At the end of the reaction, only MMA was added to form an external layer of PMMA.

The multilayer polymers (PBA/PMMA/PBA) were obtained by addition of the MMA to the PBA seed to form the second layer and then adding BA monomer to produce the exterior layer. The particle size of the latexes was determined by light scattering (Brookhaven Model BI90).

The polymers were recovered by freezing the latex and filtering and washing with distillate water to remove the emulsifier. The polymer was dried under vacuum at 60°C. The dried polymer was formed into
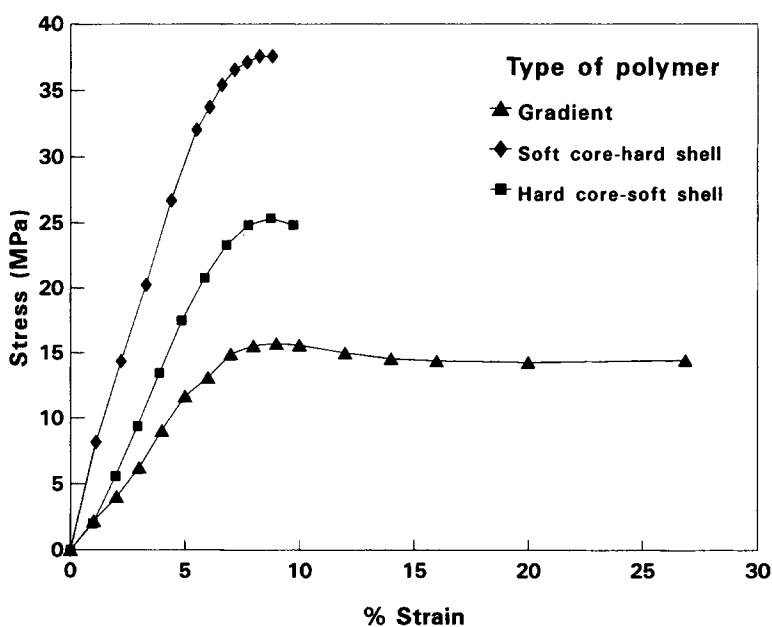

Figure 2   Stress–strain curves for multiphase polymers (PBA/PMMA) with overall weight composition of 40 : 60.

Table III   Particle Size for Core–Shell and Trilayer Polymers. Diameter in (nm).

Overall Composition (by Weight)	First Step	Second Step	Third Step
Core–shell			
PBA : PMMA			
40 : 60	72	107	
60 : 80	87	108	
Trilayer			
PBA : PMMA/PBA			
10 : 50 : 40	47	79	106
30 : 50 : 20	68	88	112

11×12 cm^2 plates by compression-molding. From these plates, samples for mechanical and rheological properties were obtained.

Equipment

Viscoelastic properties were obtained in a Rheometrics dynamic spectrometer (RDS II). A rectangular geometry was used and the experiments were carried out at a frequency of 10 rad/s and a strain of 3%. Glass transition temperatures were also obtained by differential scanning calorimetry using a DSC Mettler at a heating rate of 20°C/min.

Stress–strain measurements were done in an Universal Testing Machine (United) accordingly to ASTM D638-74. Impact properties were obtained by following the method of the falling weight (ASTM D3029).

RESULTS AND DISCUSSION

Figure 1 shows stress–strain curves for polymers of MMA/BA with the same overall composition (50% weight PMMA), but with different morphologies, as well the curve for a copolymer of the same composition. Depending on particle structure, polymers with different properties were obtained. These properties varied from those of a rigid plastic to those of an elastomeric material. Table II shows mechanical properties of the same polymers. From Figure 1 and Table II, it can be seen that the PBA–PMMA copolymer behaves as an elastomeric material; it presents a very low Young's modulus, very low tensile strength, and percent elongation at break greater than 500%. The gradient-type polymer presents a much higher Young's modulus, and its curve is similar to that of a rigid and tough material. Core and shell polymers behave more like a rigid plastic, being less tough than the gradient polymer. Because the continuous matrix has a greater effect on tensile properties[2] when processing the core–shell polymers by compression molding, if the shell is of PMMA, the rigid material will be the continuous phase, giving a higher Young's modulus and ultimate tensile
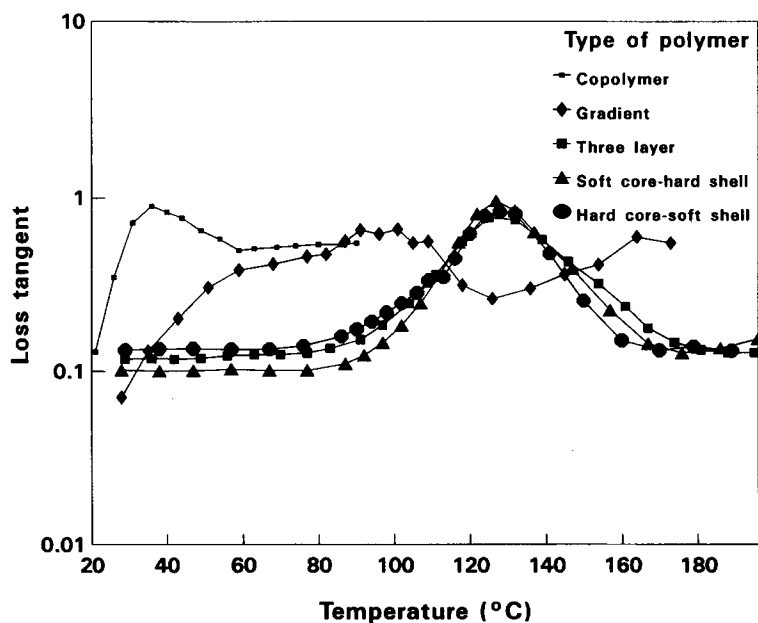

Figure 3   Loss tangent–temperature curves for multiphase polymers (PBA/PMMA) with overall weight composition of 50 : 50.
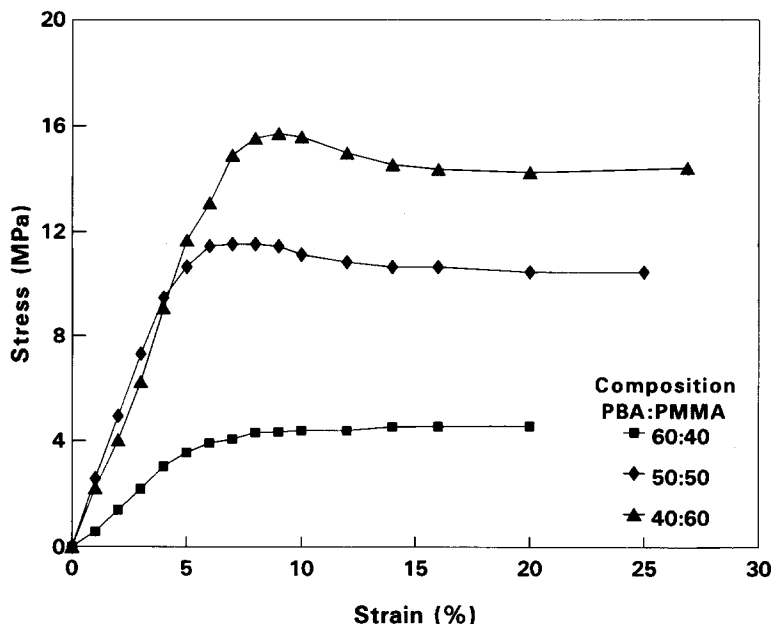
Figure 4   Stress–strain curves for gradient polymers with different overall composition.

strength than when the shell is of PBA. The polymer with three layers is the material that presents the higher modulus and ultimate strength.

In Figure 2, stress–strain curves for the same type of polymers but with a higher content of PMMA are presented. Their behavior is similar to the one described before, but the materials are more rigid because they have more PMMA content, which is a rigid plastic.

In Figure 3, loss tangent vs. temperature curves for polymers of MMA/BA with the same overall composition (50% weight of PMMA), but with different morphologies, as well as the curve for a copolymer of the same composition are presented. The shape of the curves can give some insight into the morphology of the polymers. The copolymer curve shows that the glass transition temperature (T_g) of the material is near 34°C (maximum of the peak); since this value is between the T_g of the PMMA (108°C) and the T_g of the PBA (−54°C), it can be concluded that a copolymer was obtained. This value is close to that calculated (33°C) using the equation proposed for random copolymers by Wood.[21] The curve for the gradient-type polymer shows a broad peak that goes from about 20 to 115°C; this indicates that the particles are formed by a mixture of copolymers of different composition, including a phase of PMMA. For core–shell polymers and three-layer polymers, only one narrow peak can be seen near the T_g of the PMMA. The peak denoting the presence of PBA was not obtained since the equipment

used was not able to work at the lower temperatures needed to detect the T_g of the PBA. However, using DSC, two T_g were detected, one near −49°C and another at around 114°C. These data show that there are at least two distinct regions (the homopolymers are segregated). Table III shows that the particle diameter increases upon the addition of the layers, indicating that the polymers are incorporated over the particles, probably giving the desired structure. In the case of the core–shell polymers, one of the regions is of PMMA and the other of PBA. For the three-layer polymers, one of the regions is PMMA and the other two are PBA. The slightly higher values for the T_g of the PMMA can be due to a higher molecular weight or to the presence of the bonding agent that can also act as a crosslinking agent, increasing the T_g of the PMMA. The material was easily processed, indicating that the amount of crosslinking was rather low. For the core–shell and three-layer polymers, it was necessary to include a bonding agent in the formulation; otherwise, the polymer presented poor mechanical properties and phase separation was evident.

Table II shows impact properties for the different polymers studied here. The impact resistance of the gradient polymers is much higher than those of the core–shell and three-layer polymers. This high-impact resistance of the gradient polymer is obtained without a great reduction of the Young's modulus. The copolymer does not break in this test but has a very low Young's modulus, making this material

Table IV   Mechanical Properties of Multiphase Polymers PBA/PMMA with Different Overall Composition

Type of Polymer	Young's Modulus (MPa)	Ultimate Stress (MPa)	Ultimate Strain (%)	Impact Energy (J/cm)	Shore Hardness Type "D"
Gradient					
PBA : PMMA					
40 : 60	269.5	15.94	23.6	34.16	—
50 : 50	178.3	10.46	25.4	28.68	—
60 : 40	70.3	4.47	23.4	22.39	—
Core–shell					
PBA : PMMA					
20 : 80	820.0	45.9	7.0	0.43	80.3
40 : 60	675.0	37.6	11.5	0.66	77.8
60 : 40	291.2	17.3	15.0	1.66	63.6
80 : 20	38.6	3.4	23.0	3.10	36.0
Core–shell					
PMMA : PBA					
20 : 80	5.6	0.9	21.1	7.75	13.8
40 : 60	96.1	5.5	18.3	3.55	47.0
60 : 40	359.9	24.9	9.7	0.27	70.3
80 : 20	662.7	35.4	5.8	0.21	80.6
Trilayer					
PBA : PMMA : PBA					
10 : 50 : 40	325.6	16.7	6.0	0.53	66.1
20 : 50 : 30	453.3	17.6	4.0	0.20	76.7
30 : 50 : 20	416.7	29.2	10.0	0.49	69.7
40 : 50 : 10	396.7	30.2	11.0	0.76	69.0
Trilayer					
PMMA : PBA : PMMA					
10 : 50 : 40	385.0	23.6	6.0	0.42	68.0
20 : 50 : 30	260.0	24.1	11.0	0.36	68.8
30 : 50 : 20	245.0	17.7	10.0	0.23	69.6
40 : 50 : 10	220.0	13.7	7.0	0.20	66.0

useless for applications where good rigidity and high impact resistance is desired.

The copolymer is an elastomeric like material because its T_g is near room temperature. The gradient polymer is a tough material (has very good impact resistance) because the gradient layer can act as a good shock absorber; as it goes from the shell to the core layer, the copolymer that forms the gradient layer continuously decreases its rigidity, acting as a spring of increasing flexibility as it goes toward the center of the particle. The core–shell and three-layer polymers present a lower impact resistance than do the gradient polymers, because the transition from the hard plastic to the soft core is abrupt. However, they have a higher Young's modulus and ultimate strength because they have more rigid material than the gradient polymers. The gradient polymer has only 16.6% of PMMA (the rest of the PMMA is in

form of copolymer) compared with 50% of PMMA in the other types of polymers.

The effect of varying composition on the properties of the different types of polymers was also studied. In Figure 4, stress–strain curves for three gradient polymers of different overall composition are shown. The Young's modulus, ultimate strength, and elongation at break values increase as the PMMA content in the polymer increases (Table IV). Polymers with the higher PBA content behave more as a soft material, whereas the polymer with the higher amount of PMMA resembles that of a rigid and tough material. In all cases, the gradient layer represented 66.6% by weight of the particle. In Figure 5, the storage modulus (G') as a function of temperature for the three gradient polymers is presented. The storage modulus decreases rather slowly with temperature during the interval of 25–120°C;
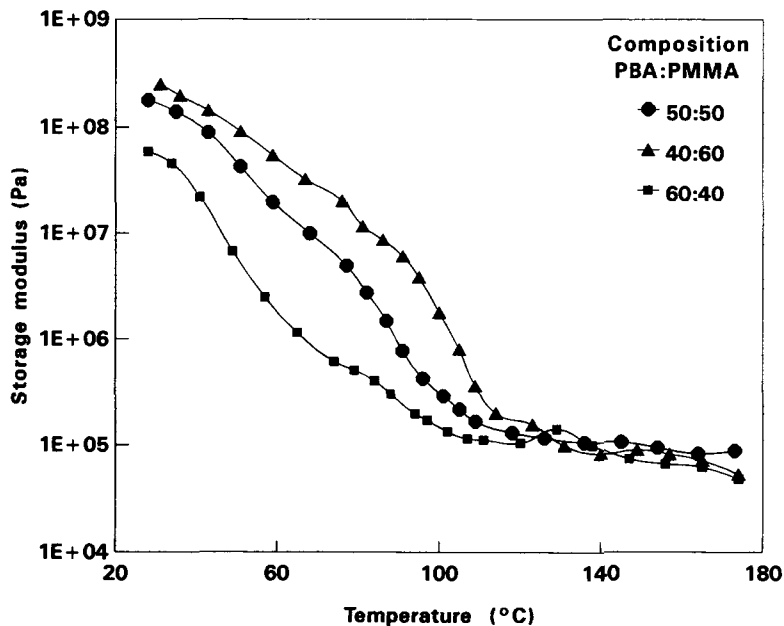
Figure 5   Storage modulus–temperature curves for gradient polymers with different overall composition.

this is an indication of the presence of copolymers of different composition.

In Figure 6, the effect of composition and thickness of the gradient layer on mechanical properties is presented. As expected, if the PBA content in the particle is increased, the material becomes more elastic. By comparing the curves for the polymers

having a gradient layer representing 66.6% by weight (Fig. 4) with curves for the polymer with a gradient layer representing 50% by weight, it can be seen that decreasing the size of the gradient layer causes the material to become more rigid, indicating, again, the higher influence of the shell.

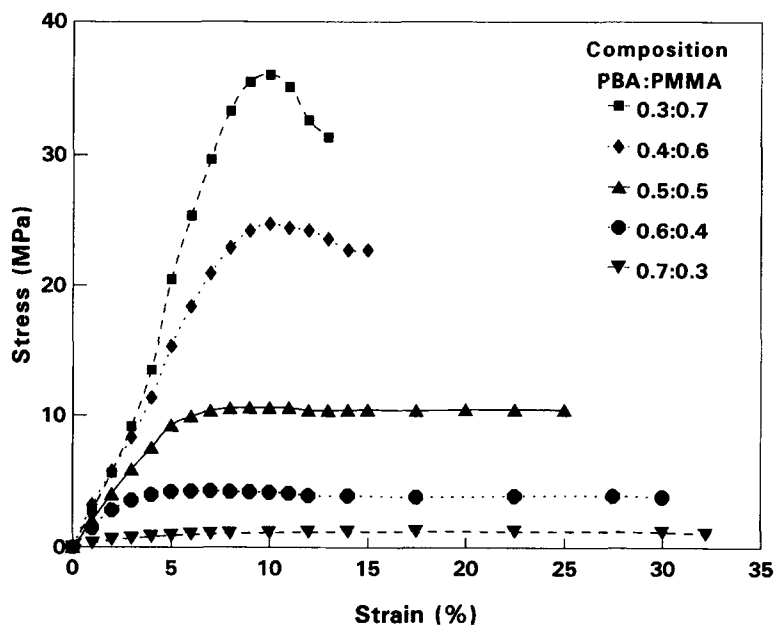Stress–strain   curves   for   soft-core–hard-shell

Figure 6   Effect of gradient layer thickness: (——–) 66.6% weight of particle; (· · ·) 50% weight of particle; (– – –) 33.3% weight of particle.
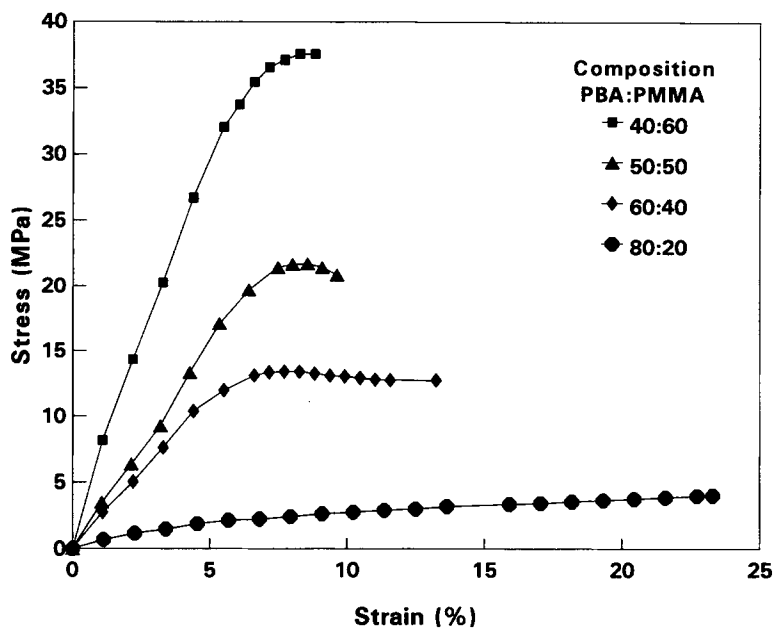
Figure 7 Stress–strain curves for soft-core–hard-shell polymers with different overall composition.

polymers of different composition are presented in Figure 7. This figure and Table III show that a higher Young's modulus, higher ultimate strength, and lower elongation at break are obtained with the polymers with higher PMMA content. Because PBA has a very low T_g, the polymer with the higher amount of PBA behaves as an elastomer. Mechanical data (Table III) for hard-core–soft-shell poly-

mers of different composition show a similar behavior to that of the soft core–hard shell. For a given PMMA content, the hard-shell polymers present a higher Young's modulus and higher tensile strength, because when forming the plates (at least for the polymers with a content of 50% or more of PMMA), the continuous phase is formed by the PMMA. It has been reported that the continuous matrix has a
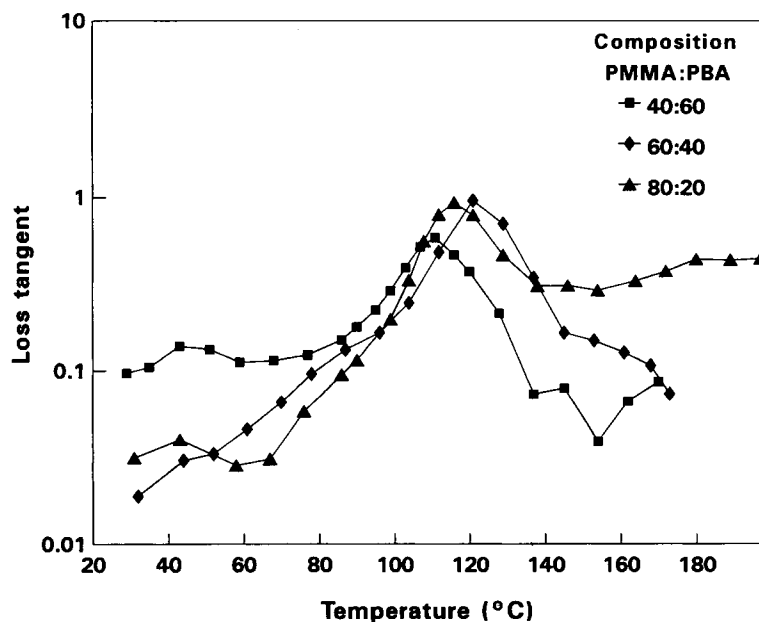

Figure 8 Loss tangent as a function of temperature for hard-core–soft-shell polymers.
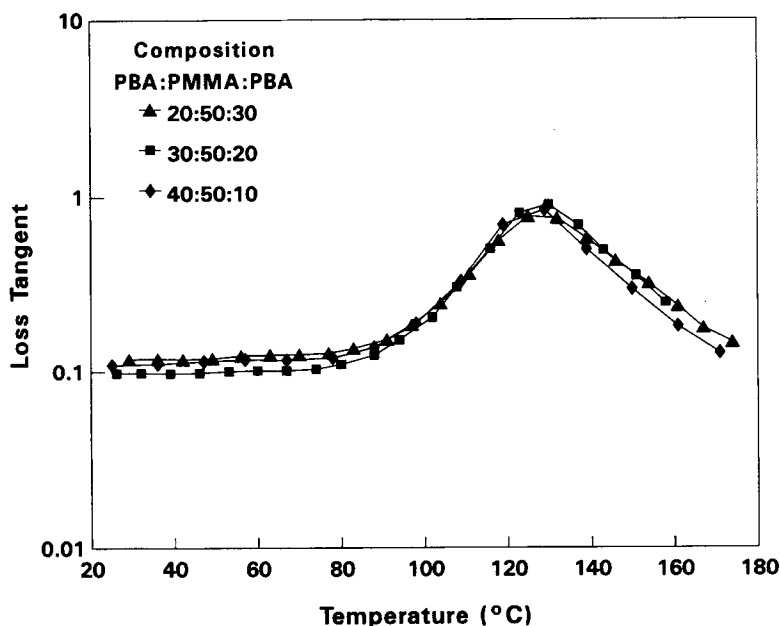
Figure 9   Loss tangent-temperature curves for three layers polymers: soft/rigid/soft.

greater effect on tensile properties than does the disperse phase.[2]

Curves for loss tangent as a function of temperature for core-shell polymers show in the range studied (20–170°C) only one narrow peak (Fig. 8), indicating that the PMMA was segregated. DSC studies showed only two transition temperatures: one at −45°C and the other at 120°C. These data confirm the presence of two distinct phases.

In Figure 9, it can be seen that varying the thickness of the multilayer polymers does not affect their behavior. Only one T_g detected by rheometry corresponded to PMMA. Two T_g values were found by DSC: one corresponding to the PMMA and the other to PBA.

CONCLUSIONS

Using multistage polymerization, polymers with a broad range of properties may be obtained by modifying composition and particle structure. The presence of the copolymer zone can increase the impact resistance of the material. Gradient polymers of PBA/PMMA are a good option in many applications since they combine good impact resistance with a relatively high Young's modulus. For the multilayer polymers, the shell material is more important in determining mechanical properties.

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