

Comparison of the Thermo-Mechanical Properties of Chemically Synthesized PMMA and PTEGDMA Polymer

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ABSTRACT: The acrylic monomeric couple, methyl methacrylate (MMA)-triethylene glycol dimethacrylate (TEGDMA) was mixed and polymerized through bulk polymerization in open test tubes using three different routes. The simplest one was a monomer mixture of 70 wt % of MMA and 30 wt % of TEGDMA. The polymerization reaction was initiated by benzoyl peroxide (BPO). The second route used a casting syrup composed of 20 wt % polymethyl methacrylate (PMMA) dissolved in 80 wt % MMA. This casting syrup was mixed with 30 wt % TEGDMA to initiate the polymerization with BPO. The final synthesis route was carried out using the aforementioned chemical composition with a polymerization initiated with a mixture of BPO and

N,N dimethyl p-toluidine (DMT) at a ratio of 10 : 1. The three synthesis routes produced different types of polymers which have remarkable differences in morphology, thermal behavior, and tensile properties. Several thermal transitions were found in each type of polymer by using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Gas chromatography and Fourier transform infrared were employed to determine the cause of each thermal transition revealed. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1234–1243, 2010

Key words: thermal properties; mechanical properties; phase separation; microstructure; polymer blends

INTRODUCTION

In the past, Liu and Armeniades¹ developed a system that consisted of casting syrup made of PMMA dissolved in MMA monomer. Subsequently, the syrup was mixed with TEGDMA monomer which underwent phase separation when the polymerization reaction was carried out using a mixture of BPO and DMT as initiator. The phase separation was used to control the volume shrinkage produced after polymerization reaction.

Liu and Armeniades concluded that microdomains of PMMA and PTEGDMA were formed during a faster polymerization reaction, and those domains were produced because of the interaction between different macromolecules. Finally, a phase separation phenomenon took place. The experimental evidence to support this explanation of the phenomenon was not sufficient and the research was focused to the zero shrinkage properties of the polymers.

The MMA and TEGDMA couple is an interesting acrylic system. This monomer couple is miscible in all proportion; however, the corresponding homopolymers are not miscible.² When this system was polymerized using a conventional thermal decomposition of BPO, the polymers obtained were transparent which is an indication that a single phase copolymer could be obtained. When a quantity of PMMA is introduced in the acrylic system and the polymerization is carried out using DMT, the polymer system undergoes phase separation phenomenon as aforementioned. The possible control on the shrinkage volume makes the MMA and TEGDMA monomer system interesting because of its potential applications as a biomaterial in medicine and odontology. One of the problems to resolve when a bone or dental tissue is replaced with a polymeric biomaterial is the shrinkage volume produced after the polymerization, particularly in the cases when the material used for replacement finishes cure reaction *in situ*. The shrinkage volume produces internal stress in the materials, and subsequently, that tension could generate fissures in the material bulk and separating in the interface between the implanted material and the substrate.

This research group has been studying the phase separation mechanism produced by a fast polymerization reaction in the acrylic system made of MMA and TEGDMA monomers.^{2–5} Some properties of the

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materials obtained and their potential applications have been discussed in previous research. The microdomains formation was studied and the influence of the PMMA and TEGDMA concentrations regarding the size and morphology of those microdomains was analyzed in various previous written works.²⁻⁴ A microdomain is a group of macromolecules that are made primarily by one of the monomer used in the formulation. The chemical composition of the macromolecules in a microdomain could change at the ends of the macromolecules. On the other hand, a polymer chain segment is a portion of a macromolecule which is rich in one type of the monomers used in the formulation. The chemical composition could vary from segment to segment in the same polymer chain.

The evaluation of volume shrinkage after polymerization reactions was also discussed.² Previous researches have also contributed to the hypothesis that a polymer blend, or polymer composite is obtained through the acrylic system as a consequence of the microdomain formations. The structure of the composite appears to be complicated, and some of its properties have been evaluated and those are promising for many potential applications.²⁻⁵ Studies to obtain a better understanding of the chemical composition of microdomains and to reveal the complex structure in the polymer blend are currently being conducted.^{4,5}

The objective of this investigation was to evaluate thermal and mechanical properties of several polymers obtained using the MMA-TEGDMA acrylic system to contribute to the structural study of the polymer blend. Three different types of polymers produced using three different synthesis routes have been studied in regard to their thermal profile and tensile properties. The differences and similarities of their behavior were identified and used to understand their possible molecular structures corresponding to each type polymer. The comparison of properties of these polymers was also useful in determining the influence of the synthesis routes and the rate of polymerization reaction on the molecular structure of polymers. Furthermore, this study was valuable to understand microdomain formation mechanisms and how those microdomains influence the final properties of the polymer. In addition, the study of thermal and tensile properties was very useful to propose other potential applications for the polymers.

EXPERIMENTAL PROCEDURE

Polymer synthesis

Three different types of polymers were synthesized in this investigation; one of them was made by mix-

ing 70 wt % MMA (Sigma T-1283) and 30 wt % TEGDMA (Sigma T-5537) of liquid monomers. This formula was polymerized through thermal decomposition of 5 wt % BPO (Sigma B-2030) at 75°C. The polymer obtained by using this route is called conventional copolymer (CC) and it was synthesized as a reference material. For the second and third types of polymers synthesis, a casting syrup was prepared mixing 80 wt % PMMA (Aldrich 18, 223-0 $M_w = 120,000$) and 20 wt % MMA monomer before the polymerization reaction. The casting syrup was then mixed with 30 wt % monomer to prepare a reacting mixture.

The second type of polymer was synthesized using the thermal decomposition of BPO at 75°C. For this type of polymers 5% by weight of BPO was also used. This polymer was tagged "special copolymer" (SC). The polymer structure of SC could be simpler than that on the polymer blend and then, useful on the overall objective of this research.

The third type of polymerization was initiated at room temperature using a mixture made of BPO and DMT (Merck 822040). The latter was used as a promoter on the free radical generation reaction of BPO. The composition of these chemical substances was 5% by weight for BPO and 0.5% by weight of DMT. The amount of DMT used was minimal and possible secondary chemical reactions are not significant in these kinds of reactions.⁶ This last type of polymer was the so-called "phase-separation copolymer" (PSC), and because of the formulation used in its synthesis this polymer is a potential polymer blend. All the types of polymers were synthesized through bulk polymerization in open test tubes. During polymerizations, the test tubes were placed in a thermal bath so that the surrounding water absorbed the majority of the heat generated during polymerization reactions.

After all polymer synthesis, different curing reaction times were determined by dilatometry using the same method described in another document.² For CC the reaction took place in more than four and half hours, 280 min, in the case of SC the synthesis was a little faster than that of CC. This reaction lasted about 245 min. The fastest curing reaction was that of the synthesized PSC. Only 8 min was required to generate this polymer.

Polymer characterization

Infrared spectroscopy (FTIR)

To make certain of the differences and similarities in molecular chain structure and chemical composition of the three types of polymers, FTIR analysis was carried out on all the polymers using the diffuse reflectance technique of fine polymer powders. The

analyses and comparison of molecular chain structures helps investigators to ascertain the structure organization of the polymer blend. The polymer was cooled and ground; then the residual monomer was eliminated by heating the material in reduced pressure, and finally the powder was mixed with potassium bromide (KBr) in a mass ratio of 1 : 10, respectively. The analyses were carried out using a spectrophotometer (Bruker vector 33) with a 4 cm^{-1} resolution frequency.

Thermal behavior

Thermal behavior was one of the most important properties evaluated and analyzed in this research. This behavior was correlated to the potential molecular structure obtained with different polymerization methods; this analysis is useful for the study of polymer blend structure. All polymers were studied using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). A small portion of each type of polymer was taken from the test tube and ground into fine powders using liquid nitrogen. Approximately 10 mg of powder was used for each type of thermal analysis.

The temperatures used in this study ranged from room temperature to 450°C with a heating rate of $3^{\circ}\text{C}/\text{min}$, and a nitrogen gas flow of 80 milliliter per minute. A Perkin-Elmer DSC/TGA 7 Series was used in this thermal property analysis. Hermetic aluminum pans were used in all analyses, and baseline calibration was carried out using an empty pan. Cell constant and temperature calibration were performed using mercury and indium samples.

Gas chromatography (GC)

Determining polymer structure can be done through the study and comparison of the different polymer thermal degradation mechanisms and the identification of the gasses produced by all polymers because of an increase in temperature. Gas chromatography analyses were done to all polymers using a chromatograph GOW-MAC equipped with a thermal conductivity detector (TCD), and a 4-meter-Carboxen 1000 column which is capable of separating O_2 , CO , and CO_2 from other gasses. Hundered milligrams of the sample was used to perform each analysis and the temperature ranges used was from room temperature to 420°C with a heating rate of $3^{\circ}\text{C}/\text{min}$.

The polymers were heated from room temperature inside the chamber of the gas chromatography device, and samples of the gasses produced by polymer degradation were taken every 10 min. The O_2 concentration inside the gas chromatography chamber was kept at 20 vol % during the experiments. The conditions inside the chromatograph were not

identical with those used in the DSC and TGA experiments; finally, the amounts of CO and CO_2 produced by the polymers during chromatography experiments could be different than those obtained in the calorimetry analysis.

Tensile properties

All the polymers obtained were tested according to ASTM D638-03 tensile proofs using an Adamel Lhomargy DY22 tensile machine. All proofs were carried out using a 500 N load cell with a deformation rate of 3 mm/min at room temperature and 20% relative humidity. Within this study, groups of 10 probates of each type of polymer were analyzed. Variables such as elastic modulus, ultimate stress, breaking strength, and elongation were determined from each essay, the results were statistically processed, and the average values were obtained for all polymers. The results were compared to obtain a better understanding of the polymer blend structure and behavior.

All samples used in tensile tests were obtained by cutting acrylic sheets, which were prepared using the formulations enlisted in the polymer synthesis section. The corresponding polymerizations were performed under a pressure of about 0.6 MPa to increase the degree of monomer conversion. When the reactions were complete, processes to eliminate most of the unpolymerized monomer were done in the acrylic sheets at 80°C and the pressure of 0.13×10^{-6} MPa was reduced to prevent a decrease in tensile strength on the polymers.

Scanning electron microscopy (SEM)

The morphology, topology, porosity, and homogeneity of the polymers were observed in detail through a 5900LV Jeol scanning electron microscope using an accelerating voltage of 20 kV. All of the images were formed from the secondary electrons. Differences and similarities in morphologies and topology were recorded, analyzed and directly related to the synthesis method.

Specimens measuring 3 cm long, 1 cm wide, and 0.5 cm thick were prepared by cutting each type of polymer from the material obtained from the test tubes. The cuts were made with a circular diamond saw. Then, the specimens were placed inside a beaker containing liquid nitrogen until they reached thermal equilibrium. Finally, the specimens were carefully fractured by means of impacting, using a razor blade and a small hammer. The newly created surface formed by the rupture was sputter coated using a gold target to avoid an electrostatic charge accumulation which could produce image distortions.

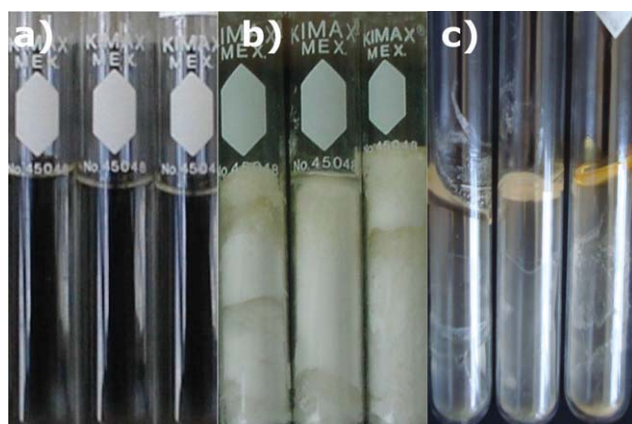


Figure 1 Photographs of three types of polymer contained in test tubes after polymerization reaction: (a) CC, (b) SC, and (c) PSC. Notice the differences in transparency. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

As a consequence of the reaction times, the macroscopic appearance of each type of polymer was quite different. Figure 1 displays photographs of the polymers inside the test tubes when the polymerization reactions were completed. It is possible to see the differences in opacity. CC was completely transparent, SC was entirely opaque, and PSC had some regions that were opaque, and others that were nearly transparent. The opaqueness in the polymers could be the result of several polymer regions obtained with different chemical compositions. Those regions also called microdomains are generated by the phase separation phenomenon, and they generate the structure of the polymer blend.¹⁻⁴

FTIR

FTIR spectra from the three types of polymer show several similarities and some differences. Most of the signals from 3000 through 4500 cm^{-1} were similar from sample to sample, for that reason those signals were not shown in the polymer spectra. Figure 2 shows a comparison between the spectra obtained from CC, SC, and PSC samples. The most remarkable difference in the spectra was the signal at 1640 cm^{-1} corresponding to C=C bond. The intensity of this signal was relatively small for CC and SC, but it was noticeably larger in the case of PSC. The existence of C=C bonds for CC and SC sample is because of a small amount of unpolymerized monomer which remains incorporated in the polymers, in spite of the process to remove it that was carried out before FTIR analyses. In the case of PSC, that signal could be produced not only by residual monomer but also by unreacted C=C bonds in TEGDMA monomer units. Because of the short cure reaction

time and low diffusion in the process to obtain PSC, the C=C bonds were unable to react and formed cross-linked polymer chains. In addition, the band at 946 cm^{-1} is produced by the bending of C—H bonds in vinyl groups. This signal could be produced by residual monomer. This band was stronger and wider for PSC and has a similar small intensity for CC and SC. The later confirms that the vinyl ester groups are more abundant in PSC as was mentioned above for the band at 1640 cm^{-1} .

The strong signals at 1440, 1250, and 1140 cm^{-1} were produced by C—O bonds. These bands were broad, especially at 1140 cm^{-1} . The width of these bands could be produced by hydrogen bondings formed naturally among hydrogen and oxygen atoms in the polymer chains; the larger number of these bonds the wider the signal. This phenomenon is similar to that commonly observed in water and alcohol molecules.^{6,7} Observing the width of the band at 1140 cm^{-1} is possible to affirm that all types of polymers formed a large number of hydrogen bondings.

DSC

Characterization by DSC of all polymers showed that thermal behavior was as different as the macroscopic appearance, and these differences were related to microstructure of polymer chain. The CC had a single glass transition temperature (T_g) at 105°C as shown in Figure 3. The single T_g was an evidence of a single phase MMA-TEGDMA copolymer, as was expected. For SC, a couple of glass transition temperatures at 103 and 146°C were registered. The first T_g value could be the contribution of both, the PMMA fraction used in the casting syrup

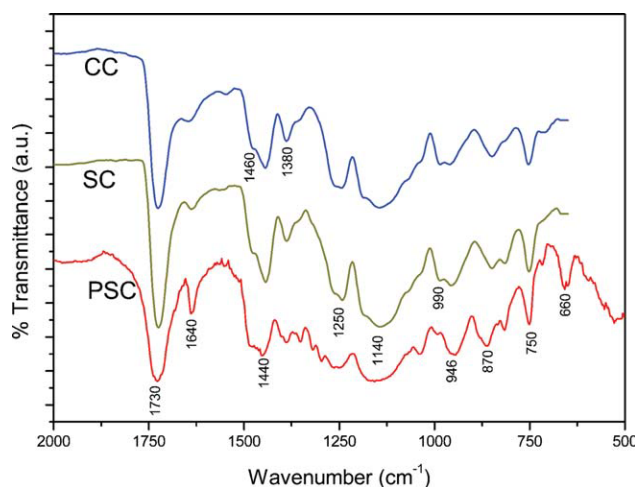


Figure 2 FTIR spectra from each type of polymer used to observe differences and similarities. The main bands are labeled. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

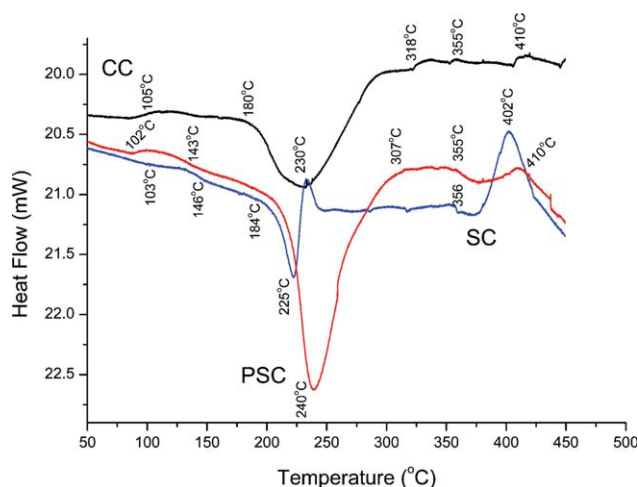


Figure 3 DSC thermograms obtained from each type of polymer. Glass transition and other important thermal transition temperatures are indicated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

(approximately 14 wt %) and the contribution of new PMMA segments formed during the polymerization reaction to obtain SC. The second glass transition temperature could be related with PTEGDMA segment in copolymer chain. According to this result, it is possible that SC had a block copolymer structure with large segments, or it is a two-phase polymer. In the case of PSC, two glass transition temperatures were also registered which are more evident than those found in SC. The first one was registered at 102°C, corresponding to the PMMA phase or domains, and the second one was at 143°C which was related to the PTEGDMA phase. The later indicates the presence of two polymer phases. This result supports the hypothesis that a polymer blend was obtained with a structure formed by microdomains.

After the said procedure, in the Figure 3 the thermograms of the three types of polymer show an endothermic peak around 230°C. For CC the peak was rather broad from 180 through 295°C. This signal is possibly because of decarboxylation and/or decarbonylation reactions.⁸ Gas chromatography confirmed the CO and CO₂ emission. For SC, the endothermic peak was significantly narrower than that registered for CC, and appeared from 184 through 228°C. This transition also corresponds to a partial degradation of the polymeric chains, decarboxylation and/or decarbonylation, similar to that observed in CC. The production of CO₂ and CO was confirmed by gas chromatography. In the case of PSC, the endothermic peak was the most intense and shows a similar width than that of CC from 196 through 307°C. Gas chromatography results indicated that the CO₂ and CO production in that tem-

perature range was less than that determined for SC, but it was similar to the one being evaluated for CC. This transition could be explained in part by the decarboxylation and decarbonylation reactions similar to CC and SC; but also, another chemical reaction took place where C=C bonds in TEGDMA monomer units react through thermal initiation. The double bond opens to form crosslinked polymer chains.

To prove the last assertion, a sample of PSC was minced into fine powders. A thermal treatment was carried out in part of the sample; it was heated from room temperature to 320°C with a heating rate of 1°C/minute. Before and after the thermal treatment, the sample was analyzed by FTIR using the same conditions for all polymers. Figure 4(a) shows both spectra obtained from PSC sample. Within this figure it is possible to observe a noticeable decrease in the signal intensities for the bands at 1640 cm⁻¹ and 946 cm⁻¹. The data herein is evidence of the chemical transformation of C=C bonds. Moreover, the bands at 1730 cm⁻¹ (C=O bonds), and 1440, 1250, and 1140 cm⁻¹ (C-O bonds) also present an

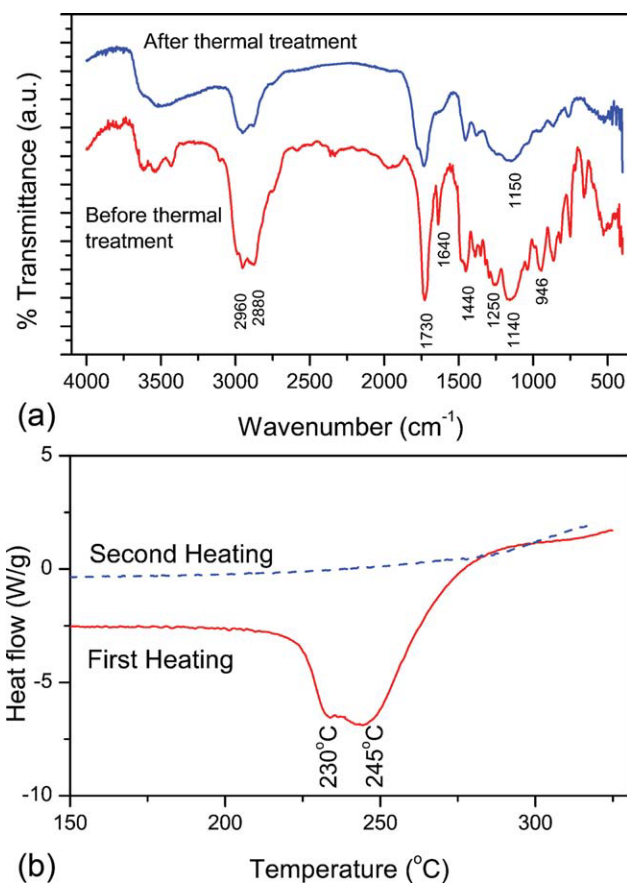


Figure 4 Characterization of PSC sample, (a) FTIR spectra before and after a thermal treatment and (b) DSC of this polymer in the temperature range from 150 through 350°C. Heating was performed twice. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

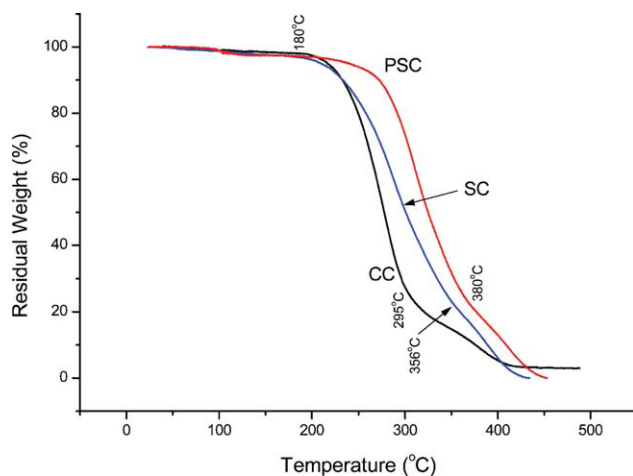


Figure 5 TGA thermograms obtained from each type of polymer. Important transition temperatures are marked. Notice the temperatures at the beginning of degradation and the residual mass percentage for each polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

intensity decrease which confirms the existence of decarboxylation and decarbonylation reactions. Besides, the band at 1150 cm^{-1} which corresponds to C—O—C groups appeared in the treated sample. The ether groups could be produced by decarboxylation and decarbonylation reactions. In addition, the rest of the PSC sample was analyzed by DSC, but this time the heating rate was $1^\circ\text{C}/\text{min}$, to obtain a better separation of the signals registered for each thermal transition. The sample was heated at room temperature up to 320°C , and then it was cooled naturally inside the DSC equipment. Finally, the sample was heated for the second time. The thermograms obtained are shown in Figure 4(b). The first heating process showed the thermal transition of the first step polymer degradation at 230°C , and then a second transition was also observed at 245°C , temperature which could be related to the chemical reaction of C=C bonds in TEGDMA monomer units. When the sample was heated for the second time, no transitions were registered in the thermogram in this temperature range. This is evidence that both transitions were irreversible because they are chemical reactions which happen only once.

In the last part of the thermograms in Figure 3, it is possible to observe the final degradation of the polymers. For CC exothermic signals appeared from 318 through 410°C . At 355°C degradation of PMMA regions took place and at 410°C degradation of PTEGDMA occurred.⁴ These signals developed the presence of small block segments in the macromolecules. These segments were produced in different stages of the polymerization because of the fact that TEGDMA is more reactive than MMA.² These regions were rather small to produce more than one T_g . For SC, a small exothermic transition appeared at 230°C . This thermal transition coincides with a maximum of CO_2 production according to gas chromatography. It is possible that 230°C is the temperature when CO_2 is released for this type of polymer. After that, a small transition appeared at 356°C which corresponds to degradation of PMMA segments. Finally, a rather intense thermal transition peak appears at 402°C , temperature which was produced for the degradation of the PTEGDMA segments.⁴ Difference in the size of the PTEGDMA segments could produce the different temperature degradation and signal intensity between CC and SC. Finally for PSC, polymer thermal degradation was completed with a couple of exothermic signals, one broad peak at 355°C and other peak at 410°C . The former was produced by the degradation of PMMA domains and other segments could be composed of a MMA-TEGDMA copolymer. The last peak is the degradation of the domains with a high content of PTEGDMA. The degradation temperature for those domains has the same value as the one that was observed for CC.

TGA

Thermograms from all polymers are shown in Figure 5. All types of polymers undergo thermal degradation in two stages. Table I summarizes the results obtained for all polymers. According to these results, PSC showed the highest temperature of the beginning of thermal degradation. This higher thermal stability could be related to the structure of microdomains in PSC and the formation of a polymer blend.

TABLE I
Temperature Range, Weight Lost Rate and Weight Lost for both Thermal Degradation Stages Observed for Each Types of Polymers by TGA

Polymer		CC	SC	PSC
1st stage	Temp. range ($^\circ\text{C}$)	180–295	186–356	196–380
	Weight lost rate (wt %/ $^\circ\text{C}$)	1.12	0.71	0.85
	Weight lost (wt %)	80	75	80
2nd stage	Temp. range ($^\circ\text{C}$)	295–440	356–430	380–450
	Weight lost rate (wt %/ $^\circ\text{C}$)	0.19	0.34	0.31
	Weight lost (wt %)	17	25	20

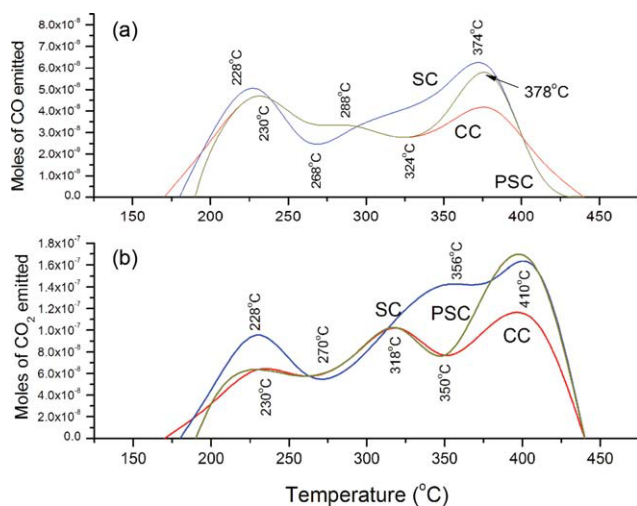


Figure 6 Emission of gasses from all the polymers during their thermal degradation as a function of temperature. (a) CO and (b) CO₂. Important temperatures are marked. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The thermogram for PSC in the first stage of degradation is similar to that for CC, although the weight lost rates are different. However, for the second step of weight loss, the thermogram for PSC is more similar to that for SC. The data herein is evidence of the complex structure of the polymer blend. The weight lost rate for PSC and SC are also comparable in the second stage. It is very possible that the SC is a block copolymer with chain segments rich in TEGDMA monomer units. The second stage of degradation for SC and PSC corresponds mainly to the degradation of PTEGDMA domains. The second stage of thermal degradation for CC is different from the other two polymers because CC lacks chain segments rich in TEGDMA monomer units, but it has a higher number of segments composed of an alternated MMA-TEGDMA copolymer.

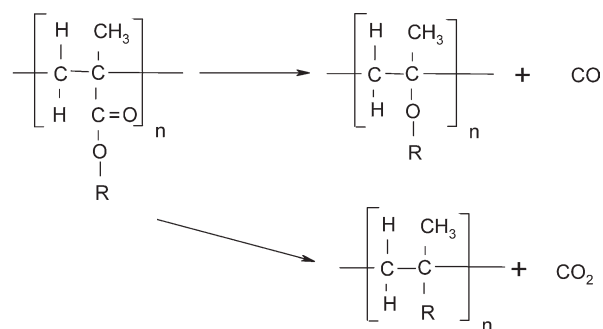
Gas chromatography

The analysis done by this technique permitted investigators to determine the CO and CO₂ quantities generated during polymer degradations. The results from this analytical technique were consistent with those obtained by DSC and TGA analyses. For all types of polymers it was possible to observe the two stages of degradation as was the case in TGA. The moles of CO and CO₂ emitted by the three types of polymers during their thermal degradation are shown in the Figure 6(a,b), respectively.

The curves of CO and CO₂ emitted for CC and PSC are similar, except in the second stage of thermal degradation, where the release of both gasses is less for CC. This result proves the supposition of

that CC lacks of chain segments rich in TEGDMA monomer units. Moreover, CC showed the most reduced production of both gasses in both thermal degradation stages, and SC and PSC had similar generation of gasses.

In the first step of thermal degradation, for all types of polymers about 230°C CO emissions had similar quantities for all polymers and CO₂ emission is greater for SC. It is possible that decarboxylation and decarbonylation reactions took place at approximately this temperature:



Where R = CH₃ or -(O-CH₂-CH₂)₃-

In the second step of all thermal polymer degradation, large CO₂ emissions were registered which were almost twice that of CO production. This last gas emission was because of the final degradation of polymer chains. When areas under the curves of CO and CO₂ emission were evaluated for each polymer, it was possible to determine the total amount of gasses emitted during thermal degradation. These results were a little different from those obtained in TGA as seen in Figure 5. The differences could be produced by the different experiment conditions used with both analytical techniques, chromatography used an environment where oxygen was present and TGA used a nitrogen flow, and the sample was hermetic packed inside an aluminum pan. Despite this, the weight loss tendencies were similar for both techniques.

SEM

Morphology observations in all types of polymers using the SEM also produced interesting results. CC sample shows a very smooth surface as can be seen in Figure 7(a). Domains were not found, neither porous nor microcraves. This morphology is evidence that this polymer has a single phase which is consistent with DSC and TGA results. The SC had a more irregular surface than that of CC. In Figure 7(b) many small holes, or porous on polymer surface can be observed. The whole morphology was very different from that of CC, and it was the consequence of a faster polymerization reaction. Formation of block copolymers in SC could be possible

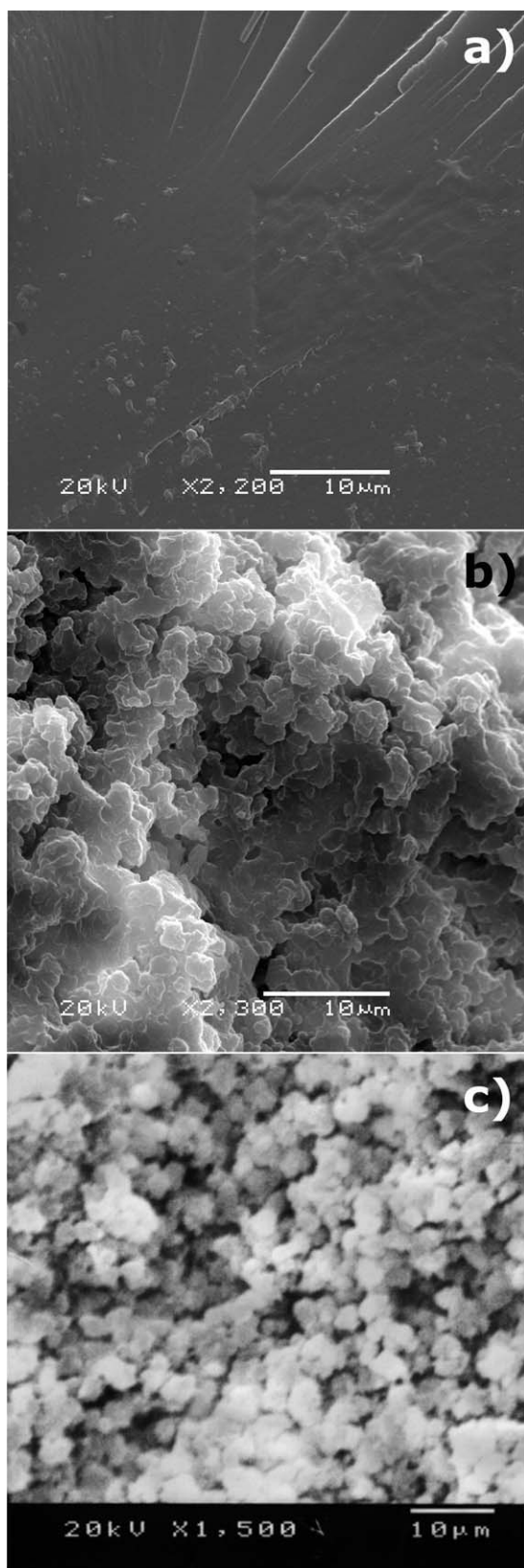


Figure 7 Secondary electron images from surfaces generated by low-temperature fractures of (a) CC, (b) SC, and (c) PSC. Differences in morphology and topology were related to the synthesis method.

observing the two glass transition temperatures registered in the DSC results. For PSC, Figure 7(c) shows a different topology from that found in the other polymers. In PSC it was possible to observe an extremely irregular surface and the material bulk appears as if it was formed by small portions of material or particle-like structures. Those particles are microdomains, and the union of these forms the structure of the polymer blend. Besides, neither cracks nor porous areas were observed in the polymer matrix; these results are similar to those reported by Liu.¹ Most of the empty spaces observed in the Figure 7(c) were produced by a separation of some particles, the microdomains, during the sample preparation process. The topology is a consequence of microdomains formation which is generated by a phase separation in the acrylic system.²⁻⁴ The phase separation was produced because of both the differences in reactivity between MMA and TEGDMA and the immiscibility between PMMA and PTEGDMA. At the beginning of the polymerization reaction to obtain PSC, PTEGDMA microdomains are formed rapidly and those microdomains interact with the PMMA polymer chains used to form the casting syrup used in the uncured formulation. Because of the polymer immiscibility, the phase separation takes place and subsequently, new PMMA microdomains are formed along with others made of PTEGDMA. At the end of the cure reaction, PTEGDMA microdomains are enclosed by several PMMA microdomains which are more abundant.

Tensile Properties

Tensile properties of all polymers specimens were processed and the average values of elasticity modulus (Y), ultimate stress (σ_m), breaking strength (σ_r), and elongation (Δl) were evaluated for each type of polymer as it is shown in Table II. The results obtained from this mechanical characterization confirm some results obtained in FTIR and DSC. Figure 8 shows selected stress-strain curves for each type of polymer. Certain selections were made observing the values listed in Table II. The most representative curve for each type of polymer has been displayed.

CC was more rigid than the other polymers, it had the highest elastic modulus and the lowest

TABLE II
Elastic Modulus, Ultimate Stress, Breaking Strength and Elongation Average Values Obtained from All Probates Tested in this Study

	Y (MPa)	σ_m (MPa)	σ_r (MPa)	Δl (mm)
CC	890	76	72	6.6
SC	720	84	82	5.7
PSC	615	120	110	6.95

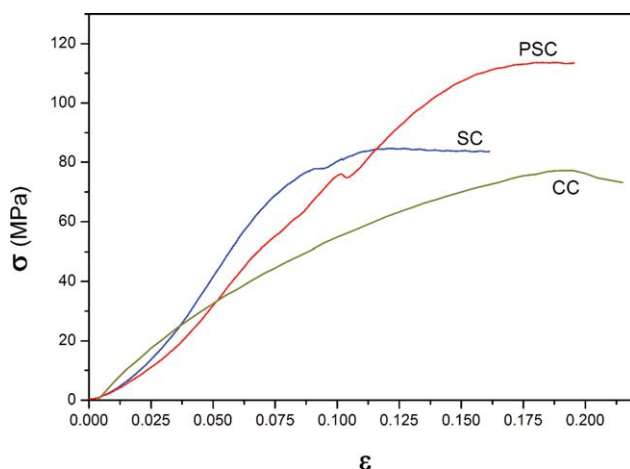


Figure 8 Selected stress–strain curves obtained in tensile tests for each type of polymer. Differences are evident in elastic modulus, deformation, and ultimate strength. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ultimate stress values. It is probable that this is because this polymer had more crosslinking bonds, but again, this polymer reached a middle elongation value between the other polymers. According to the Y values obtained (Table II), and glass transition temperatures registered (Fig. 3), SC had less crosslinked bonds than CC, and therefore the former is less rigid than the latter one. A faster polymerization reaction produced a crosslinking copolymer with a lower number of links. Moreover, SC had a higher ultimate stress value than the one for CC, yet the former reached the lowest elongation value. The last could be due to the fact that CC is a homogeneous polymer. Although it has a large number of intramacromolecular cross-linking bonds, it is possible that greater intermacromolecular sliding takes place. In the case of SC this is because of its heterogeneous material, the intermolecular sliding is less, and a shorter elongation occurs.

In the case of PSC, the polymer had the lowest elasticity modulus and the highest deformation and tensile resistance. It is possible that the fastest polymerization reaction also created a polymer with fewer cross-linking bonds. Consequently, this polymer dissipated the greatest amount of energy during its deformation. In addition, it is feasible that the structure of microdomains contributes to generate better mechanical properties for PSC. The PTEGDMA microdomains could create higher tensile resistance to the copolymer. However, the microdomains made of PMMA contribute to a larger elongation. The absence of cracks or porous areas in the PSC matrix reduces the possibility of decreasing the tensile resistance. One hypothesis about the structure obtained in PSC is the fact that the formation of a polymer blend could generate synergic

mechanical properties. The unpolymerized monomer contained in PSC decreases the tensile resistance, but in sum, the effect of the polymer blend structure is greater on the final properties, as it can be observed on the Figure 8. At the same time, previous studies regarding the kinetics to obtain PSC revealed degrees of monomer conversion of 85% or more. The use of DMT increased the efficiency of free radical generation. Simionescu established that a higher polymerization rate in addition to an increment in the efficiency of the initiator could produce higher degrees of monomer conversion.⁹ As a result it is possible that this phenomenon reduces the influence of the unpolymerized polymer on the mechanical properties of PSC. In addition, the free volume studies for the MMA + TEGDMA system previously made by these investigators⁵ not only confirms the microdomains formation but also contributes to the explanation of better degrees of monomer conversion and tensile properties of PSC.

The highest ultimate stress and elongation values could be evidence of strong interactions present among microdomains, and those domains remain united against the action of an external force. This result further support the hypothesis of copolymer segments located in the interfaces among microdomains.

In Figure 8, the small drop in the stress observed in the curve for PSC (approximately 0.1 of deformation) was due to interfacial disunions among microdomains in the bulk of the polymer blend. This last observation corroborates with the statement that a microdomain structure contributes to obtain better mechanical properties of the polymer. SC also showed a slight stress drop, and it is possible that this polymer underwent a similar disjointing among polymer chain segments.

CONCLUSIONS

The type of curing reaction affected the rate of polymerization and consequently morphology, microstructure, thermal and mechanical properties were also influenced. According to the results obtained in this research and other previously published papers by this research group, the fastest cure reaction generates a phase separation which produces a microdomain microstructure in the polymer bulk, and that microdomain structure generates a polymer blend with better thermal and tensile properties.

The characterization studies made in this research project have contributed to a better understanding of the structure present in the polymer blends obtained.

The synthesis method used to obtain PSC has the potential of being applied to synthesize polymer blends employing other acrylic monomer systems.

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