Synthesis of Shrinkage-Controlled Acrylic Copolymers

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ABSTRACT: Acrylic copolymer systems consisting of methyl methacrylate and triethylene glycol dimethacrylate with different chemical compositions were synthesized through bulk polymerization using *N,N*-dimethyl-*p*-toluidine as an acelerator to obtain nonshrinkable polymers. The use of the tertiary amine on this formulation produces an increase on the volume of the material due to a phase separation in the copolymer, which compensates the volume reduction upon curing. The specific volumes of all materials were determined by volume dilatometry using a dilatometer specially constructed for this purpose. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 586–591, 2000

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INTRODUCTION

Curing shrinkage is a consequence of the polymerization reaction, and it is an important property of polymers that causes several problems on the properties and final appearance of the material.[1] A large number of methods have been tried aiming to control this effect. Some of those approaches are very expensive and limited because the monomer used in the polymerization reaction has a very complex molecular structure, such as spiro monomers.[2] Other methods employ additives dispersed in the uncured resin and their volume compensate curing shrinkage, but the resulting mechanical properties of the polymer are worse than those of the polymer without these additives.[3–5] A new method to control cure shrinkage was developed by Liu and Armeniades[6] and it consists of an acrylic system, which, when polymerized at a high polymerization rate, undergoes phase separation into microdomains. This phase separation is responsible for the control of curing shrinkage. The system they originally studied was PMMA-TEGDMA, and reported shrinkage changes as a function of composition measured by pycnometry. Also, their SEM micrographs revealed segregation effect to which they attributed the observed shrinkage changes. However, neither details on the possible mechanism nor careful quantification of the shrinkage was provide in that pioneering work.

The purpose of this work is to report a new family of acrylic copolymers synthesized with different chemical compositions, with phase separation produced at different degrees. The aim was also to find the optimal composition and reaction conditions at which, the phase separation minimizes the curing shrinkage.

EXPERIMENTAL

Synthesis of Polymers

For the synthesis of the polymeric materials first, casting syrups were prepared employing polymethyl methacrylate (PMMA) (average M_w 120,000) and methyl methacrylate (MMA) monomer in concentrations of 10, 20, and 30% by weight of the polymer. Each of the casting syrups

Table I   Formulation of the Different Mixtures Used to Synthesize Controlled-Shrinkable Polymers

Casting Syrup (g) (At certain concentration)	TEGDMA (g)	TEGDMA %
40	0	0
36	4	10
32	8	20
28	12	30
26	14	35
24	16	40
20	20	50
16	24	60
12	28	70
8	32	80
4	36	90
0	40	100

was mixed with triethylene glycol dimethacrylate (TEGDMA) monomer in different proportions from 0 to 100% by weight, as shown in Table I, and 36 reacting mixtures were obtained with different chemical compositions. Each of the mixtures was mixed separately with a mechanical stirrer until a single phase was obtained. Then the mixtures were bottled and stored under refrigeration until the polymerization reactions were completed.

When a polymerization reaction was carried out, 5 g of one of the 36 reacting mixtures were withdrawn and placed inside a test tube with an 8-mm diameter and 50 mm long. Then 50 mg (1% by weight) of benzoil peroxide (BPO) were added as initiator. The mixture was mixed until the BPO was completely dissolved, and then the solution was placed in a thermal bath at 70°C to start the reaction. When the viscosity was obviously increased by visual inspection, the test tube was taken of from the bath and the reaction was completed at room temperature. This process, called "conventional reaction" was done with all of the reacting mixtures.

An alternative method to carry out the polymerization consisted in taking other 5 g of mixture in a test tube and then add 50 mg of BPO; when the benzoil peroxide was dissolved it was added 5 mg (0.1% by weight) of *N,N*-dimethyl-*p*-toluidine (DMPT), and the reaction began and was completed at room temperature. This type of reaction, called "fast reaction," was also done with all the reacting mixtures.

Dilatometry Measurements

The dilatometer used in this work was constructed specially to determine the specific volumes of all the polymers before and after the curing reaction. The construction of the dilatometer was based on the original design by Snow and Armistead,[7] employing Pyrex glass. The dimensions of all its parts were the same as those in the original design. The apparatus consists of three main parts, a detachable bulb, a graduated precision capillary, and a filling aparatus. Only one change was made from Snow's design, which was the use of a Teflon stopcock instead of a PTFE valve. That change was made to obtain a higher rate of flow on the mercury, which was used as a confining fluid.

A special treatment was done on the internal surface of dilatometer bulb to avoid the adhesion of the forming polymer to the bulb, and was carried out before calibration. The calibration was made to determine the volume capacity of the bulb, the capillary diameter, and its uniformity along its length. Both processes, the bulb surface treatment and calibration, were performed as described by Snow.

To carry out the dilatometry measures, it was necessary to degas the reacting mixtures before each experiment. From one of the mixtures 20 g were placed into a small round-bottom flask, which was, in turn, placed in a preheated bath at 60°C; then the pressure was gradually decreased down to 300 mTorr, and magnetic stirring was used during all the operation. The degassing process lasted 10 min. It is advisable to use a condenser to prevent MMA losses by volatility. All the reacting mixtures were degassed one by one using this procedure, and the process was done a few minutes prior to each specific volume determination.

To begin the determination, the bulb was filled with the degassed mixture and then weighed to know the amount of mixture used in the experiment. Thus, 1% by weight of BPO previously degassed was added to the mixture and dissolved, the bulb of dilatometer was rapidly connected to dilatometer, which was previously assembled and weighed separately; the dilatometer was rapidly filled with mercury under vacuum of 300 mTorr. This operation was carried out on a balance to determine the volume of mercury used in the experiment. The specific volume of the corresponding reacting mixture was determined imme-

diately, reading the height of the mercury column in the capillary at room temperature (26°C).

The bulb attached to the dilatometer was put in a thermal bath at 70°C to begin the polymerization reaction. The heating was suspended when the viscosity of the mixture had sufficiently increased, and the reaction finished at room temperature. The monomer conversion percentage was determined as a function of time by determining the density directly related to conversion, based on previous reactions employed as a calibration method. Those calibrating reactions were, in turn, calibrated by high-resolution picnometry. Once the reaction was over, the reaction time was determined, and when the bulb reached the temperature of 26°C, the specific volume of the polymer was obtained. Finally, the polymer was withdrawn from the bulb and the dilatometer was ready to perform another determination. The above procedure was used with the polymers made through conventional reactions, and it was applied to all the reacting mixtures.

To determine the specific volumes of the polymer made by fast reaction, the dilatometer bulb was filled with one of the degassed mixtures and weighed. Then, 1% by weight of BPO previously degassed was added to the bulb and dissolved. Then, 0.1% by weight of DMPT was added and the bulb was immediately attached to the dilatometer and the specific volume of the mixture was determined at 26°C. The polymerization reaction began within few seconds at room temperature. This fast reaction produces a large amount of heat in a short time, causing a strong increase in temperature on the bulb. To avoid monomer evaporation, when the bulb temperature reached 70°C a cold bath was employed, and it was removed when the temperature did not increase further. The reaction finished at room temperature and the specific volume of the polymer was obtained at 26°C. The monomer conversion percentage and the reaction time were also obtained by evaluating the apparent viscosity of the mixture. Once the mix polymerizes, there exists a marked increase in viscosity. This procedure was applied to all the mixtures. If a bubble appeared during any of the different specific volume determinations, the experiment was aborted, the bulb cleaned, and other amount of mixture was added to bulb to begin a new determination.
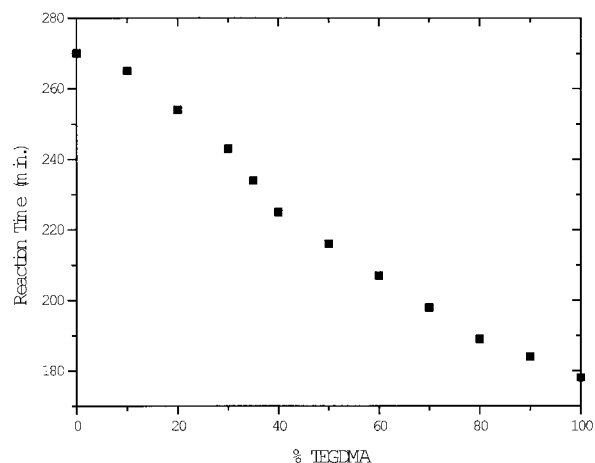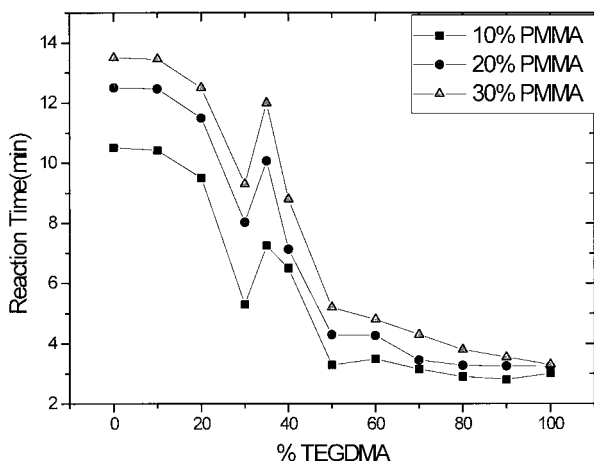

Figure 1 Plot of the variation f the reation time as a function of the TEGDMA content for polymers containing casting syrup at 20% of PMMA and synthesized through conventional reactions.

RESULTS AND DISCUSSION

The TEGDMA content has an influence on the reaction time. In Figure 1 it is possible to observe the variation of the reaction time as a function of the chemical composition for conventional reactions. The curve shows a simple variation: when the TEGDMA content is increased, the reaction time decreased. The plot only shows the results obtained for reaction employing casting syrup with 20% of PMMA, but similar variations were observed for compositions with syrups at 10 and 30% of polymer.

In the case of fast reactions, the variation of the reaction time is more complicated than that of the former case. At low concentration of TEGDMA, the reaction time decreases when the concentration of the monomer reaches 30%; then, at a content of 35%, the reaction time has a large increment, and subsequently, the time is reduced with the increase of the monomer (Fig. 2). This behavior is due to the phase separation and the formation of microdomains.
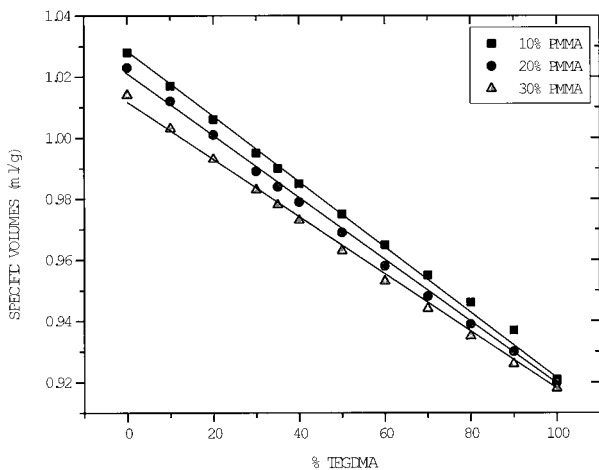
The effect of the chemical composition on the polymers volume is shown in the Figures 3 and 4. In Figure 3, the dependence of the specific volumes of uncured polymers mixtures with the TEGDMA concentration for different PMMA contents can be observed. For these systems, the specific volume decreases linearly with the TEGDMA concentration for samples with different PMMA content; this is a consequence of the higher density of the TEGDMA monomer. The
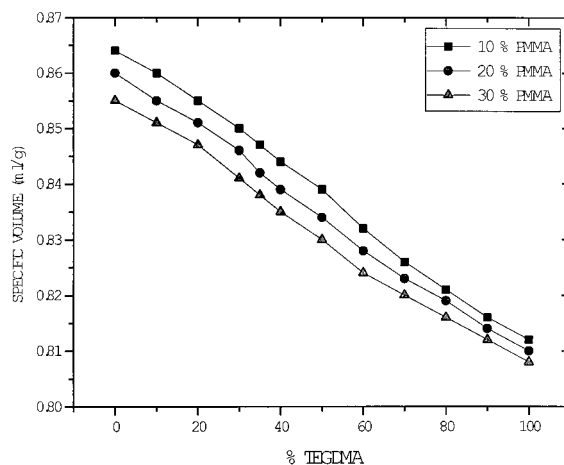
Figure 2 Plot of the variation of the reaction time as a function of TEGDMA content for polymers containing casting syrup at different concentrations of PMMA synthesized through fact reactions.

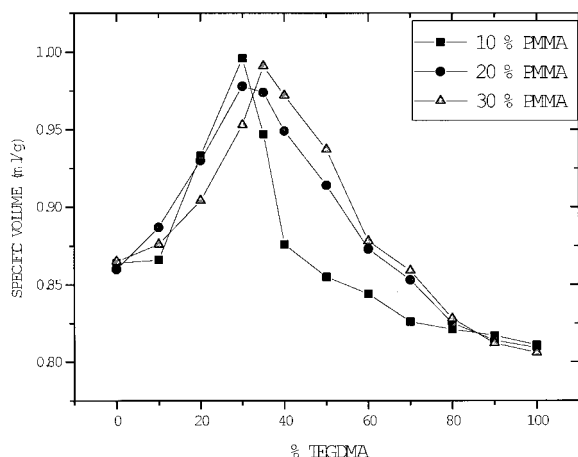
Figure 4 Variation of the specific volume as a function of TEGDMA concentration for all the polymers synthesized through conventional reactions.

linear dependence of the specific volume with the TEGDMA content means that an excess volume of mixing during this mixing process does not exist. It is also possible to see the influence of the PMMA concentration on the specific volume: when PMMA content in the syrups is increased, the specific volume decreases. This effect naturally decreases with the increment of TEGDMA concentration.

For samples with 10 and 30% of PMMA, these curves are similar to each other, one slightly below the other; however, for samples with 20% PMMA, the straight line has a slightly smaller

slope than the other two, indicating that for this PMMA content, the density of the mixtures is less influential. Desptie the apparently small difference among slopes, this effect is significant, because it reveals that the specific volume variation is not responsible for the phase separation effect.

When the samples were obtained by conventional polymerization reaction, the dependence of the specific volume with the TEGDMA content is no longer a straight line, indicating, as was previously mentioned, the effect of the specific composition on the final properties of the blends. These results are shown in Figure 4. For comparison purposes, these experimental data were adjusted using both a straight line and curve fitting. As observed there, the fitting is nonlinear. Samples of the three different content of PMMA are shown. It is possible to observe how the PMMA content contributes to obtain a smaller volume reduction of the polymers.

The variation of the specific volumes for the polymer made by fast reactions is rather complex. At low TEGDMA contents, the specific volumes of these polymers are very similar to those of conventional polymers, but at a concentration of about 20%, the specific volume begins to increase, and reaches their highest values at about 35% of TEGDMA. At this concentration, the polymers have the same specific volume as their respective mixtures. In other words, the system has reach a zero shrinkage situation, for all practical purposes. After this concentration, the specific volume begins to decrease, and at 70% has values again very similar to those of the conventional
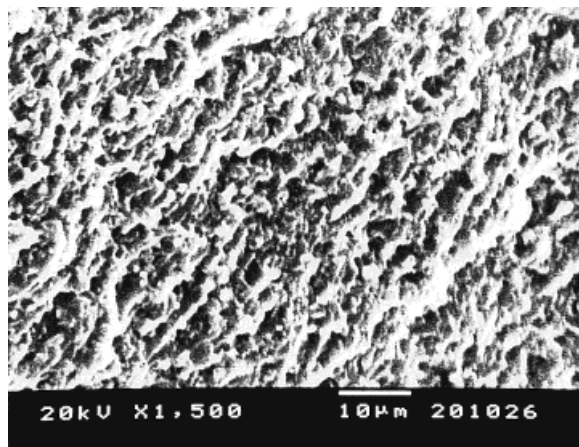

Figure 3 Variation of the specific volume as a function fo TEGDMA concentration for all the uncured reacting mixtures.

Figure 5 Variation of the specific volume as a function of TEDGMA concentration for all the polymers synthesized through fast reactions.
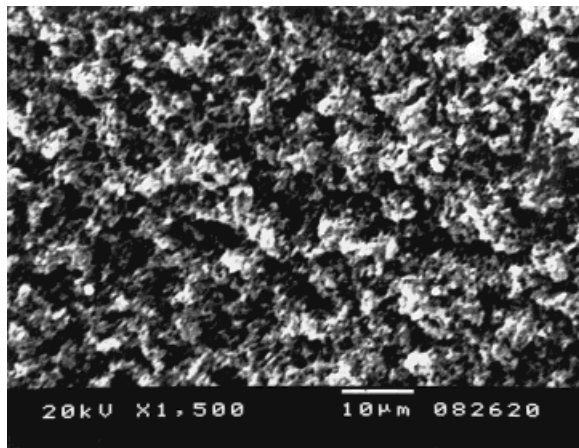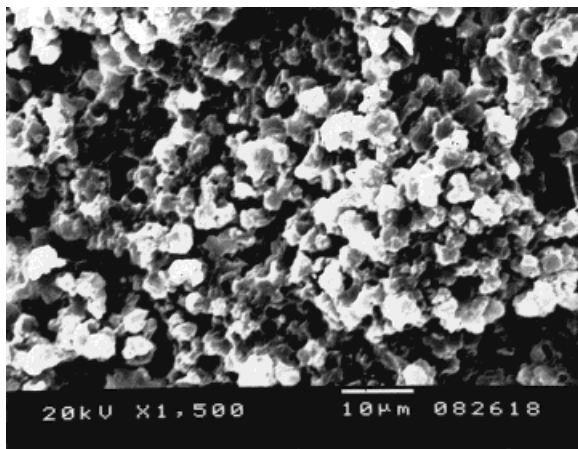

Figure 6 Micrograph of a polymer containing casting syrup 20% wt. of PMMA and 10% wt. of TEGDMA. Notice the small particle content in the polymer bulk. It is possible to suppose that the particles are PTEGDMA, and the bulk is PMMA.

polymers. In this last range of TEGDMA content in the mixture from 20 to 70% by weight, the phase separation is present in the material, the increasing TEGDMA concentration produces a separation more and more evident with the highest degree occurring when the two components of the chemical composition are present in the optimal amount. Subsequently, although the TEGDMA content continues to increase, the concentration of the casting syrup decreases at the same proportion, and it causes the separation to become smaller and smaller until it eventually disappears completely. Figure 5 shows this variation. Here, it is possible to see an influence of the PMMA concentration of the syrup on the size range within which the phase separation is present: the higher the PMMA concentration, the wider this range would become. Other evidence of this influence of the TEGDMA content on the phase separation was obtained by scanning electron microscopy; Figures 6, 7, and 8 show micrographs of polymers containing casting syrup at 20% of PMMA with TEGDMA contents of 10, 30, and 70% by weight, respectively. It is possible to observe the increase on the size of the microdomains as the TEGDMA concentration increases, and after the 35% of the monomer, the size of microdomains begins to decrease as the monomer increases. A more detailed study of the influence of the TEGDMA content on he morphology and microstructure of the polymer will be presented in a separate article.[8]

From the last plot one can conclude that is possible to control, at least to some extent, the

degree of shrinkage of the acrylic copolymers, allowing adjustment to this variable to some specific value to meet some requirements of the polymer molding process. This idea can be extended to produce polymers with a controllable thermal expansion coefficient by just mixing appropriated pairs of polymers. These can be produced as polymer blends or composites where, in the later case, the internal stresses produced into the material can be used as a mechanical sensor.

Figure 7 Micrograph of the polymer containing casting syrup 20% wt. of PMMA and 30% wt. of TEGDMA. In this polymer, the TEDGMA concentration is such that it produces a morphology of large microdomains, and it is not possible to differ between particles of PMMA and PTEGDMA.

Figure 8 Micrograph of a polymer containing 20% wt. of PMMA in the syrup and 70% wt. of TEGDMA. Here, it is possible to observe again, small particles contained in the polymer bulk. This time, the particles are PMMA, and the bulk is PTEGDMA.

CONCLUSIONS

A novel acrylic copolymer material was produced with a controllable shrinkage effect by using PMMA and TEGDMA components. The best copolymer composition, which produces the small-est volume shrinkage, was at 20% wt. of PMMA with 35% wt of TEGDMA. This work opens the attractive possibility of producing other shrinkage-controlled polymeric systems.

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