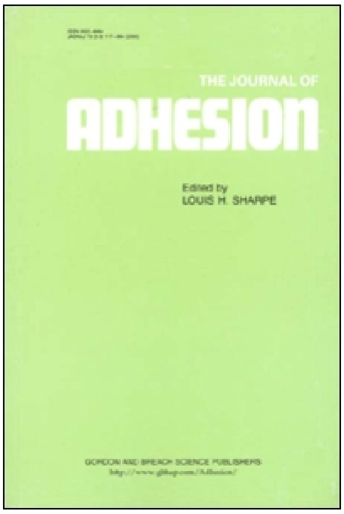

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Dynamic Mechanical Analysis of Amorphous-Phase Organization in Acrylic Polymers

M. T. Jeppesen[a]; H. Ralph Rawls[a]
[a] Division of Biomaterials, University of Texas Health Science Center, San Antonio, TX, USA

To cite this Article Jeppesen, M. T. and Rawls, H. Ralph(1994) 'Dynamic Mechanical Analysis of Amorphous-Phase Organization in Acrylic Polymers', The Journal of Adhesion, 47: 1, 191 — 199

To link to this Article: DOI: 10.1080/00218469408027099

URL: http://dx.doi.org/10.1080/00218469408027099

J. Adhesion, 1994, Vol. 47, pp. 191–199
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Dynamic Mechanical Analysis of Amorphous-Phase Organization in Acrylic Polymers*

M. T. JEPPESEN and H. RALPH RAWLS**

University of Texas Health Science Center, Division of Biomaterials,
San Antonio, TX 78284-7890, USA

(Received November 11, 1992; in final form February 8, 1993)

Factors affecting polymer network organization were studied in highly crosslinked acrylics of the type used in dental adhesive resins. The variables tested were comonomer content and processing conditions. *Bis*EMA (2,2,-*bis*[4-(2-methacryloyloxyethoxy)-phenyl]propane) and *Bis*EMA + TEGDMA (triethyleneglycol dimethacrylate) were cured with and without 25% comonomer. Comonomers had characteristics that are expected to influence intrachain organization in amorphous phases: TEGDMA, crosslinking; methyl methacrylate (MMA), monomer conversion; *iso*bornyl methacrylate (IBM), low cure shrinkage; tetrahydrofurfuryl methacrylate (THFM), antiplasticization. Dynamic mechanical analysis temperature scans were run at 0.1 Hz 2h or 24h after ambient cure, or 24h postcure after heating at 75° or 125°C. After 24h, tan δ maxima occurred in ranges centering on approximately −30°, 75° and 150°C (T_g). Heating at 125°C nearly eliminated all peaks except T_g, reduced tan δ peaks and increased T_g by 0–14°. T_g increased in the order: TEGDMA>125°C>IBM>MMA>75°C>2h>24h>THFM. The ability to crosslink, and postcure heating at 125°C, were the more important factors found to increase intrachain organization in amine-promoted, unfilled *Bis*EMA resins of the type used in dental sealants, luting cements and bulk-filling resin composite materials.

KEY WORDS acrylics; adhesion; crosslinking; dynamic mechanical analysis; glass transition; heat treatment; interphase; intrachain organization; polymer.

1 INTRODUCTION

Biomedical adhesives function well initially but deteriorate too rapidly to last the lifetime of the patient. This is particularly a problem with adhesive resins used for oral reconstruction purposes. Such materials are used as sealants, luting cements and bulk-filling adhesives. They are subjected to the severe mechanical, physical and chemical environment of the mouth and are required to maintain appearance as well as function. The major limitations on the useful lifetime of the highly crosslinked methacrylate resins used for these purposes result from four interrelated problems: 1) Shrinkage during curing, 2) incomplete curing, 3) mismatch between

---

*Presented at the International Symposium on "The Interphase" at the Sixteenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 21–26, 1993.

**Corresponding author.

the thermal expansion/contraction of the resin and the tooth, and 4) degradation in the oral environment.[1] People are living longer, keeping their teeth longer and demanding more attractive fillings. These trends are leading away from silver amalgam and creating a growing demand for long lasting, polymer-based adhesive restorations. Consequently, current products are frequently used at and beyond their performance limits. Although substantial progress has been made in finding a balance among the various technical requirements, many conflicting needs remain, particularly those related to long term performance.

An increase in intrachain network organization generally enhances thermodynamic stability and, hence, durability. Thus, resin adhesives should be improved by increased organization within the polymer network. Polymer microstructure can range from crystalline to totally random-coil (amorphous) within the same material. Further, the amorphous phase is usually not homogeneous. Rather, it consists of varying degrees of chain alignment all of which are less ordered than the lowest energy, crystalline state. This condition can be characterized by the degree of inter- and intrachain order in the amorphous state, which is mainly determined by the composition and structure of the polymer, presence of plasticizing components, filler content and temperature. A premise of this investigation is that improvements in the performance of the highly crosslinked, thermosetting resins used in dental adhesives can be gained through strategies that increase polymer network organization. This is because more highly ordered structures are more thermodynamically stable structures and, therefore, inherently more durable.

Network organization is dependent on the degree of chain-to-chain segmental alignment, crosslinking, presence of pendent groups, filler loading, residual stresses and other factors that influence segmental organization.[2] Dynamic mechanical thermal analysis (DMA) is a particularly sensitive method for studying these factors. DMA subjects a specimen to a cyclic (*i.e.*, dynamic) force and measures the response of several parameters as a function of either frequency or temperature. In particular, the mechanical energy lost as heat (E″) and the recoverable mechanical energy stored in the material (E′) can be measured as temperature is increased. The ratio E″/E′ is defined as the loss tangent, tan δ. Tan δ is sensitive to microstructure and always exhibits a maximum at T_g, the glass transition.[3]

An increase in glass transition temperature and lowered intensity of tan δ peaks are evidence of increased polymer network organization. Demarest and Greener[3] recently showed that, in acrylics, T_g increases in proportion to the volume fraction, V_f, of a high aspect-ratio mica filler. This was explained as a result of an increase in polymer-segment organization in the ***interphase*** between the filler surface and the bulk of the matrix polymer. In general, as T_g increases, the performance properties of dental adhesives can be expected to improve.[4] The relatively low T_g values observed for most dental adhesives have been attributed to incomplete conversion of diacrylate monomer and the formation of pendent methacrylate groups.[4] This results in incomplete crosslinking and a network inherently plasticized and susceptible to oxidative degradation.[4,5] Thus, in order to improve properties significantly, a better organized polymer chain network is needed at the molecular level.[6] This is particularly true in the interphase regions at the filler-matrix and tissue-matrix interfaces,[3] which are critical for adhesive performance.

The aim of this investigation was to examine several experimental resin formulations to determine how comonomer composition influences T_g and the intensity of the loss tangent, tan δ, in the absence of filler. Other important factors that are also expected to influence adhesive performance, such as filler loading, size and shape of filler, hydrolytic stability and environmental degradation, are planned for later studies. Through these investigations we expect to gain insights into the mechanisms that influence polymer organization in the amorphous-phases and interphases of resin adhesive structures. Our ultimate objective is to use these insights to develop stronger, more durable biomedical adhesive materials. The results reported here represent the initial step in this plan.

2 EXPERIMENTAL METHODS

Materials

A series of experimental compositions were prepared such that each contained a particular comonomer that could potentially influence polymer network organization. The monomers and other components used to prepare the experimental compositions are shown in Table I. Two basic compositions, one based on *Bis*EMA (2,2,-*bis*[4-(2-methacryloyloxyethoxy)-phenyl]propane) and the other on *Bis*EMA + TEGDMA (2:1, w/w) were cured with and without 25% w/w of various comonomers. Comonomers had reported characteristics that indicated a potential to affect network organization: triethyleneglycol dimethacrylate (TEGDMA = **T,** crosslinking), methyl methacrylate (MMA = **M,** monomer conversion), *iso*-bornyl methacrylate (IBM = **I,** low cure shrinkage[7]), tetrahydrofurfuryl

TABLE I
Compositions of experimental resin formulations

Components$^+$	**50% *Bis*EMA** (E:T:C: = 2:1:1)*				**75% *Bis*EMA** (E:C = 3:1)*				**100% *Bis*EMA** (E:C = 3:0)
Weight %									
*Bis*EMA	50	50	50	50	75	75	75	75	100
TEGDMA	50	25	25	25	25				
IBM		25				25			
THFMA			25				25		
MMA				25				25	
Molar %									
*Bis*EMA	61	64	67	70	83	86	89	93	100
TEGDMA	39	20	21	22	17				
IBM		16				14			
THFMA			12				11		
MMA				8				7	

*Underlined letter in component name identifies abbreviations used: E = *Bis*EMA, C = variable comonomer = T (TEGDMA), I (IBM), F (THFMA) or M (MMA).

$^+$Other components used in all formulations: 5.8% BP (BP = 70% active), 0.68% DHEPT, BP/DHEPT = 9 w/w = initiator/accelerator ratio. This produced a 3–5 min setting time for all formulations.

methacrylate (THFM = **F**, antiplasticization[8]). Benzoyl peroxide (BP) and dihydroxyethyl *p*-toluidine (DHEPT) were used, respectively, as initiator and accelerator.

Methods

Four factors relating to composition (conversion of acrylate groups, antiplasticizing, cure shrinkage and crosslinking) and two processing factors (time for ambient cure and temperature of postcure heating) were studied. These factors are known, or have potential, for strongly influencing polymer organization in composite systems. Model compositions were prepared having components that exhibit useful or attainable extremes (*i.e.*, they either enhance or depress the effect) for each of these variables (Table I). These were tested to identify those having the greater influence on tan δ. As shown in Table I, *Bis*EMA was the major ingredient and three sets of comonomer formulations were used. These were 100%, 75% and 50% w/w *Bis*EMA plus comonomers (T and/or I, F, M, as shown). Factors that were varied as a consequence of changes in the comonomer composition were: crosslinking, degree of conversion, antiplasticizing effect (high T_g comonomer), and molar volume per methacrylate group (cure shrinkage).

Test specimens were prepared by mixing ingredients and curing them in 1 × 3 × 20 mm molds. A Perkin-Elmer DMA-7 dynamic mechanical thermal analyzer (DMA) was used to determine glass transition temperature, T_g, from peak values of tan δ.[9] The extent of cure was routinely estimated by hardness measurements with a Durometer D-scale indenter. A DMA measurement consisted of scanning at 0.1 Hz and 3 deg/min to a temperature of approximately 200°C. Initial survey scans starting at −100°C showed that the transitions of greatest interest occurred above 0°C, which was used as the starting point for most of the subsequent temperature scans. DMA scans were run either 2h or 24h after ambient cure with BP/DHEPT (5.8 wt %/0.68 wt %), or 24h postcure followed by heating at either 75° or 125°C. Postcure-treatment specimens were held at either 75° or 125°C for a time (approximately 10 minutes) sufficient for the storage modulus, E′, to increase to a plateau value. These specimens were then cooled and scanned to about 200°C in the same manner as the others. The 75°C postcure temperature was chosen because, following ambient cure, a transition occurred in this region that appeared to be due to incompletely converted monomer (which would plasticize the polymer and lower T_g). This was evident from survey scans in which the transition shifted to a higher temperature upon scanning a specimen for a second time. The 125°C postcure treatment was chosen because the 75°C treatment revealed a transition in this region (*e.g.*, see Fig. 1).

3 RESULTS

Typical results are shown in Figs. 1 and 3, and are summarized in Figs. 2, 4 and 5. At 24h after initiation of cure, transitions occurred in ranges centering on approximately −30°, 75° and 150°C (150° is due to the glass transition, T_g). Heating at 75°

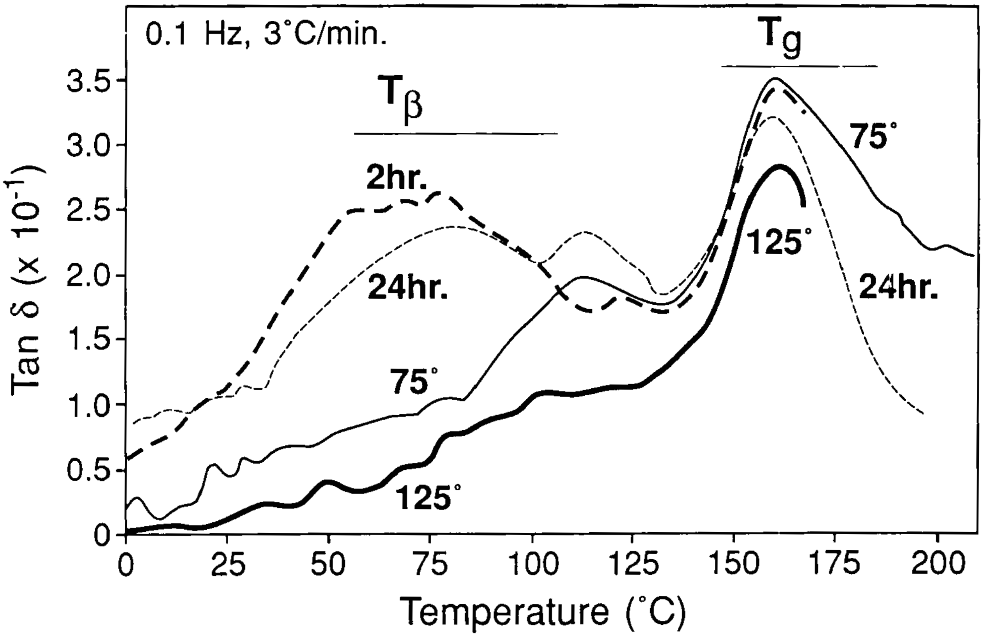

FIGURE 1 Effect of Processing on Loss Tangent (Tan δ) in *Bis*EMA-TEGDMA-IBM Resins (E:T:I = 2:1:1). I = Isobornyl methacrylate.

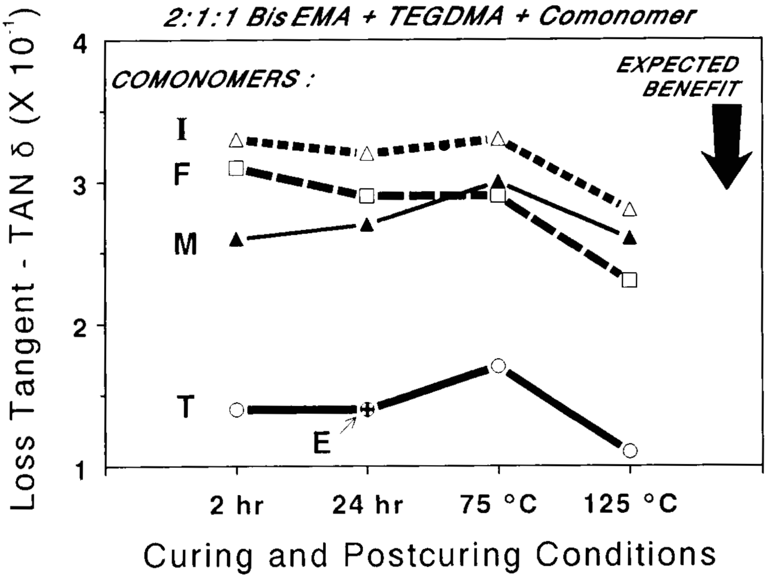

FIGURE 2 Effect of Processing Conditions on Loss Tangent at the T_g of *Bis*EMA-TEGDMA Terpolymer Resins. E:T:C = 2:1:1 where C = T, I, F, M or E (see Table I).

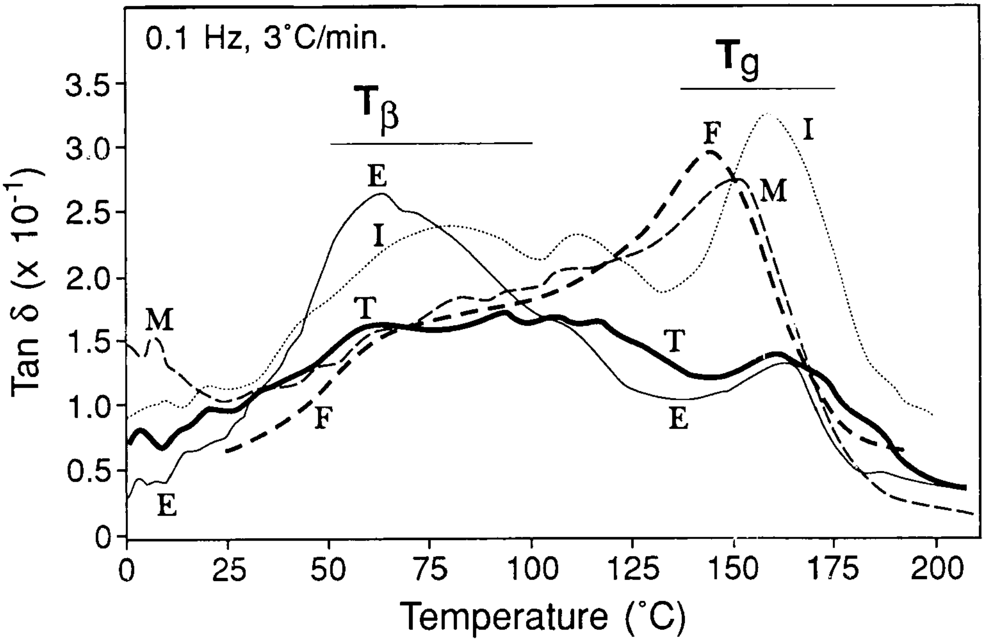

FIGURE 3 Effect of Comonomer on Loss Tangent (Tan δ) in E:T:C=2:1:1 Resins After 24h Ambient-cure. See Table I for comonomer identification.

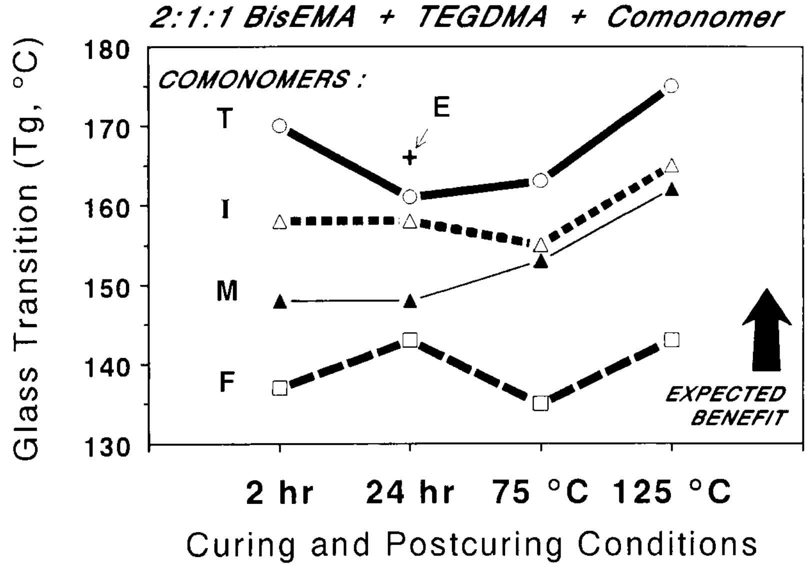

FIGURE 4 Effect of Processing Conditions on T_g of *Bis*EMA-TEGDMA Terpolymer Resins. E:T:C=2:1:1 where C=T, I, F, M or E (see Table I).

increased modulus, reduced the $-30°$ and 75° peaks and shifted the 75° and T_g peaks approximately $+30°$ and $\pm 3°$, respectively. As shown in Figs. 1 and 4, heating at 125° nearly eliminated all peaks except T_g, and reduced and shifted T_g between zero and $+14$ degrees. Figs. 3, 4 and 5 show that the effect of the comonomer was to increase T_g in the order: TEGDMA>IBM≥MMA>THFM. In Figs. 2, 3 and 5 it can be seen that comonomer decreased the intensity of tan δ at T_g in the order: TEGDMA>MMA≥THFM>IBM. These effects, as a function of both the type and concentration of comonomer, are illustrated in Figure 5.

4 DISCUSSION

Inspection of the figures reveals the following:

1. A transition occurs in the 60°–160°C range and another in the 135°–175°C range. The loss tangent (tan δ) at these transitions decreases in intensity and shifts to higher temperatures in response to the presence of specific comonomers and various processing conditions.
2. The 60°–160°C transition is probably due to plasticized polymer and/or polymer segments or domains containing pendent chains from unreacted acrylic end groups, since it decreases with both time after curing and postcure heat-treatment temperature.
3. The transition at 135°–175°C is an α-transition (*i.e.*, T_g) in which amorphous phase(s) change from a glassy to a flexible state.

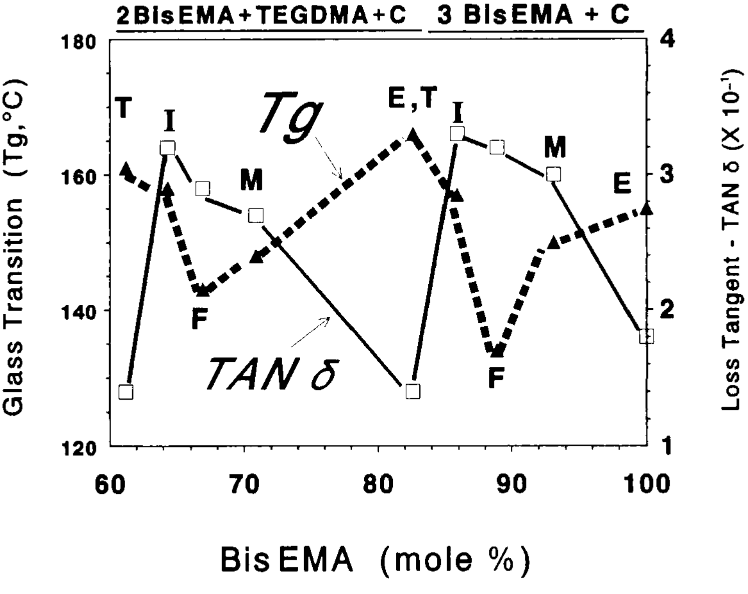

FIGURE 5 Effect of Comonomer on T_g and Tan δ in E:T:C = 2:1:1 and E:C = 3:1, 24h Ambient-cure Resins. See Table I for comonomer identification.

4. Heating at 125°C had the strongest effect on elevating T_g and reducing tan δ in both transition regions, while heating at 75°C had a smaller, but similar, effect which was more dependent upon comonomer composition.
5. Only crosslinking comonomers, TEGDMA and *Bis*EMA, had a major effect on both maximizing T_g and minimizing loss tangent (tan δ).
6. Concentration of comonomers had very little effect in the 25%–50% w/w (7%–39% molar) range.
7. Among the non-crosslinking comonomers, IBM has the strongest effect on elevating T_g but the weakest effect on reducing tan δ, while THFMA is the least effective in elevating T_g.
8. MMA shows evidence of increasing the degree of monomer conversion at ambient temperature.
9. Between 2h and 24h ambient cure time, very little change occurred except for the copolymer with 50% w/w TEGDMA (E:T:T=2:1:1, Table I). For this composition T_g was 170°C after 2h and decreased to 161°C after 24h. From the current results we have no explanation for this.

Overall, the factors found to influence changes in T_g and tan δ in amine-promoted, unfilled *Bis*EMA resins, in decreasing order of effect, are:

Crosslinking comonomers (TEGDMA and *Bis*EMA)	A
125° postcure heating	B
Comonomer producing high T_g (IBM)	C
Comonomer with high conversion efficiency (MMA)	C
75°C postcure heating	D
2 hour ambient-cure	E
24 hour ambient-cure	E
Antiplasticizing comonomer (THFMA)	F

The effects labeled with the same letter (A, B *etc.*) are not significantly different at $p<0.05$ (Student's t-test). The strong-effect extreme of this relationship is characterized by an elevated T_g and depressed tan δ peaks in both transition regions. The weak-effect extreme is characterized by a depressed T_g and elevated tan δ in both transition regions. Interestingly, within the range of factors studied, the optimum composition was found to include those factors that are utilized with many commercial resin composites used as adhesive tooth-filling materials. Also, resin composites used as inlays to restore decayed teeth have been found to display optimized mechanical properties when cured in the 100°–150°C range[10] and optimum 3-body wear resistance when cured at 125°C.[11]

On the basis of the observed elevations in T_g and decreases in loss tangent, we conclude that crosslinking monomers and post-cure heating at 125°C have the stronger effects on intrachain organization in unfilled *Bis*EMA-based acrylic resins cured under ambient conditions. We would also predict that, other factors being equal, the performance of acrylic adhesive materials can be optimized by selecting crosslinking comonomers and postcure heating conditions that minimize tan δ and maximize T_g. These and other factors, filler and coupling agent characteristics in particular, will be the subject of future studies.

Acknowledgements

Thanks are due to the Dental Materials Group of the American Association for Dental Research for a student research fellowship (MTJ) and to the Esschem, Rohm and Haas, and Sartomer companies for donation of monomers and reactants.

References

1. R. A. Draughn, R. L. Bowen and J. P. Moffa in *Restorative Dental Materials, An Overview*, Vol. I, J. Reese & T. Valega, Eds. (Quintessence, London, 1985), pp. 75–107.
2. A. Bernes and C. LaCabanne in *Order in the Amorphous State of Polymers*, S. E. Keinath, Ed. (Plenum, NY, 1987), pp. 305–326.
3. V. Demarest & E. Greener, *J. Dent. Res.* **65,** 829 (Abst. 928) (1986).
4. W. D. Cook in *Posterior Composite Resin Restorative Materials*, G. Vanherle & D. C. Smith, Eds. (Peter Szulc Pub. Co., Holland, 1985), pp. 273–287.
5. I. E. Ruyter, *Adv. Dent. Res.* **2,** 122–129 (1988).
6. P. L. Fan in *Posterior Composite Resin Restorative Materials*, G. Vanherle & D. C. Smith, Eds. (Peter Szulc Pub. Co., Holland, 1985), pp. 287–296.
7. R. L. Clark, *Biomaterials* **10,** 630–633 (1989).
8. K. W. M. Davy and M. Braden, *Biomaterials* **12,** 406–410 (1991).
9. T. W. Wilson and D. T. Turner, *J. Dent. Res.* **66,** 1032–1035 (1987).
10. E. Asmussen and A. Peutzfeldt, *Scand. J. Dent. Res.* **98,** 564–567 (1990).
11. S. L. Wendt, Jr., *Quintessence Int.* **20,** 259–263 (1989).