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CURE SHRINKAGE CONTROL OF POLYMERIZATION SYSTEMS

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ABSTRACT

CURE SHRINKAGE CONTROL OF POLYMERIZATION SYSTEMS

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Cure shrinkage is an inherent property of polymerizing systems due to the conversion of secondary bonds between monomer (or prepolymer) molecules to primary bonds, which have smaller interatomic distances. Cure shrinkage is highly undesirable: it impairs dimensional control and causes poor surface finish in molded polymers; it also generates setting stresses in highly filled systems. Previous methods for cure shrinkage control require special materials and conditions or entail the formation of voids. In this investigation, two processes were developed for producing polymer systems with zero shrinkage or slight expansion: (a) use of ammonia-modified montmorillonite as additive; and (b) microphase separation.

The first method utilizes the dilatation of specially-modified montmorillonite (MMT) particles to counteract resin polymerization shrinkage. The MMT particles are first processed by replacing part of their hydration water with ammonia (which forms coordination bonds with SiO₂ in
the mineral crystal) then dispersed into the resin. During cure at ambient temperatures the polymerization exotherm raises the temperature to 60-80°C, breaking the SiO₂-NH₃ bonds; however the liberated gaseous ammonia cannot escape outside the resin-embedded MMT particles and forces them to dilate to more than twice their original size. By controlling the amount of ammonia-modified MMT added to the resin (in amounts of 6-10%) we obtain cured systems that show zero shrinkage and have no setting stresses. This can increase their strength by ca. 20-40%.

The second method achieves cure shrinkage control by microphase separation. Certain multicomponent acrylic systems, when polymerized rapidly, separate into microdomains of different phases with a corresponding reduction in cure shrinkage. We attribute this phenomenon to lower efficiency in molecular chain packing at the interphase boundaries; the phase separation itself is attributed to local, diffusion-controlled composition changes during rapid cure. Accumulation of the local volume increase at the microphase boundaries gives rise to the observed reduction in cure shrinkage.
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CHAPTER I. BACKGROUND

1. CURE-SHRINKAGE AND SETTING STRESSES IN POLYMERIC MATERIALS

1.1. Cure Shrinkage

Cure-shrinkage is an inherent property of most systems that undergo polymerization. It results from the conversion of secondary bonds between the monomer (and/or prepolymer) molecules to primary (covalent) bonds within the macromolecular chains. Secondary bonds between discrete monomer molecules have characteristic distances of 4-5 Å. During polymerization these bonds convert to primary bonds, which in carbon-carbon chains have a distance of 1.54 Å. This conversion brings about an overall decrease in volume of the polymerizing system, the cure shrinkage. Different polymers have different extents of cure-shrinkage, depending primarily on the size of their monomer molecules: for example, unsaturated polyesters show cure-shrinkages of 5% to 6%, epoxy 2% to 3%, and polyurethane systems 3% to 4%; worst of all are acrylic resins, such as methyl methacrylate which shows cure-shrinkage of 21%. In general, other things being equal, the larger the molecular weight of the monomer molecule, the smaller the cure-shrinkage. For this reason, the use of prepolymer will reduce the actual shrinkage during the final polymerization.
This inherent property of cure-shrinkage handicaps the processing and applications of polymeric materials, especially particle-filled polymer composites, in which the cure shrinkage generates dimensional changes, as well as setting stresses.

1.2. Setting Stresses in Particle-Filled Composites

1.2.1. Setting Stresses in Polymer Concretes and Mortars

Polymer concrete is a composite material consisting of mineral aggregate and filler, held together with small quantities of organic resin which hardens via polymerization. Most commercial polymer concrete systems use epoxies, unsaturated polyester/styrene or acrylic resins as binders. In all cases it is the polymerization and/or crosslinking of the organic resin that causes the setting of polymer concrete. The aggregate and filler are sand and gravel identical to that used with ordinary Portland cement concrete, but without any water.

In systems where the liquid resin forms a continuous phase, such as fiber-reinforced composites, cure shrinkage forces are accommodated during the pre-gel part of the polymerization by a volume reduction in the resin, the setting shrinkage. However, most polymer concrete systems, contain so much filler and aggregate that it occupies 70 to 75 percent of the total volume, and the solid particles are nearly
close-packed. The resin is largely confined to the small interstices between particles, which cannot change in volume. In these spaces the resin is forced to polymerize at constant volume; consequently the cure shrinkage forces are not relieved and give rise to local tensile stresses, which increase as the system cures. These are setting stresses. The process is shown schematically in Fig. I-1.2.1.

The existence of setting stresses in commercial polymer concrete formulations is evidenced by their modest tensile strength and flexural strength and their poor creep resistance. The presence of setting stresses in a cured polymer concrete system can be assessed roughly by comparing its actual cure shrinkage with the theoretical shrinkage, based on the inherent cure shrinkage of the resin and its volume fraction. Thus a polyester polymer concrete containing 30 percent by volume resin with 8 percent inherent shrinkage should shrink 2.4 percent in order to be free of setting stresses. However, most commercial polyester polymer concretes show less than 1 percent shrinkage, indicating the presence of substantial setting stresses.

Both setting shrinkage and setting stresses are highly undesirable. Shrinkage during cure may impair moldability, dimensional stability, and appearance of the product. Setting stresses reduce the ultimate strength and significantly impair
Fig. I-1.2.1: Polymerization shrinkage and setting stresses in polymer concrete system.
the creep resistance of the composite. Currently setting stresses are controlled by the use of low-shrinkage resins in combination with widely graded aggregate and substantial amounts of fines. However, current polymer concrete systems suffer from reduced strength, due to setting stresses. Other materials that are adversely affected by cure-shrinkage and setting stresses include polymer based dental restorative composites, and polymer formulations used for the restoration and preservation of antique structures.

1.2.2. Cure Shrinkage and Setting Stresses in Dental Composite Restorations

For many years, amalgam has been used as the main material for dental fillings. Recently there have been concerns about the toxicity of amalgam, not so much to the patients, but to the dentists and technicians who work daily with the liquid mercury used in the preparation of amalgam and are exposed to mercury vapour, which is very toxic. Therefore, there is a strong interest in developing polymer composites as dental filling materials. Theoretically, polymer composites can match or surpass the physical properties of amalgam, but they have their own limitations, one of which is cure shrinkage.

Dental restorative composite resins are composed of three components: organic resin, fillers and polymerization initiators. NMR analysis (Vankerhven, 1981) showed that most
commercial dental filling materials contained in their resin phase BIS-GMA, iso-BIS-GMA, and triethylene glycol dimethacrylate (TEGDMA). BIS-GMA is a combination of epoxy and methacrylic resin with dimethacrylate reactive sites. It is the reaction product of bisphenol A with glycidyl methacrylate. Bis-GMA is very viscous, consequently, in order to achieve a suitable viscosity in which to incorporate fillers, BIS-GMA is thinned with a variety of other monomers of which the most commonly used have been TEGDMA and diethylene glycol dimethacrylate. Commercial dental restorative materials are cured either chemically (by means of initiator/promoter systems that generate free radicals when mixed at ambient temperature) or by irradiation with ultraviolet light. Chemically cured systems are packaged as two separate components (paste-paste, paste-liquid, or powder-liquid), one containing the initiator, the other the promoter. The two components when mixed polymerize in situ. Radiation cured materials are usually in the form of a single paste which contains the necessary initiators and promoters. Polymerization is activated by the insertion of a special ultraviolet light source in the patient's mouth.

Numerous types of fillers have been used in dental composite resins. Based on the manufacturing technique and average particle size, these fillers can be divided in three categories: traditional macrofillers with size range of 1 to 5μ;
microfillers with sizes less than 1μ; and a combination of those two. There is a downward trend in filler particle size has over the last few years.

In the absence of adequate bonding (micromechanical retention to etched enamel or chemical adhesion to dentin or both), polymerization shrinkage of a composite restoration will result in compromised adaptation of the restoration to the cavity (Asmussen, 1975. Tani, 1985. Hansen, 1982. Hansen, 1983.). The microleakage occurring as a result eventually leads to marginal staining, marginal degradation, secondary caries, and postoperative sensitivity, including pulp pathosis (Phillips, 1965). Under ordinary conditions polymerization shrinkage always results in the formation of a gap between a central filling and the cavity walls, thus allowing ingress of bacteria, and other chemical substances into the cavity. The ingress of bacteria at the tooth/restoration interface is the main factor responsible for the pulpal reactions (Brannstrom, 1986). If adequate bonding does exist between the composite and the cavity surface, polymerization shrinkage will cause internal stresses to develop in the restoration due to the contraction forces. (Hegdahl, 1977. Davidson, 1984. Bowen, 1986. Bowen, 1967. Fan, 1985).

In current restorative dental composites, the filler occupies 50 to 70 volume per cent of the total composite
volume and the particles are nearly close-packed. The resin does not form a continuous phase but is largely confined to the small interstices between solid particles, which cannot change in volume. The shrinkage forces developed in these spaces during polymerization are not relieved and give rise to local tensile stresses, which increase as the system cures. Reported values for these stresses range 2.4 MPa for conventional composites (Bowen, 1967), 2.8 to 3.9 MPa for conventional and microfilled composites (Davidson, 1984), to 5.5 to 7.3 MPa for conventional and 6.1 to 6.4 MPa for microfilled composites (Bowen, 1982).


There is some uncertainty concerning the extent of the effect of polymerization shrinkage on the marginal seal of the restoration. Some investigators have implicated
polymerization shrinkage as the cause of fractured restoration margins (Baush, 1982. Asmussen, 1975. Bowen, 1982. Lambrechts, 1982. Lee, 1977). Others suggest that in practice the stresses generated during polymerization shrinkage are relieved to a certain extent by flow of the composite (Davidson, 1984). Composite materials will sorb water from the environment for at least 16 weeks after polymerization has occurred, resulting in a volumetric hygroscopic expansion (Pearson, 1979). It has been suggested that this expansion of may aid in sealing the cavity (Asmusen, 1972). However, since the linear polymerization shrinkage is 0.23 to 0.36 per cent and the average amount of hygroscopic expansion is 0.07 to 0.08 percent, a residual shrinkage of 0.10 to 0.29 per cent results after one year (Lee, 1969. Bowen, 1982. Dickson, 1979. Craig, 1985). Though there is some disagreement about the exact nature and degree of the resulting defects, polymerization shrinkage is considered to be the most serious limitation of composite resin dental restorative materials (Davidson, 1985).

The adverse effects of polymerization shrinkage can be overcome in "adhesive cavity preparations" if the enamel etch technique is used and a bonding agent applied (Luscher, 1977. Porte, 1984. Lutz 1985). However, posterior composites should be suitable to replace existing Class II amalgam restorations in which the cavity design has the conventional proximal box. In this case damage due to polymerization
shrinkage cannot be overcome even when the enamel is etched and a dentin bonding agent is used.

It has been demonstrated that a non-shrinking or expanding composite restorative would optimize the marginal adaptation of composite restorations even if incremental techniques were not utilized, i.e. the restorative composite could be replaced and cured in one step (Lutz, 1985).

The volume change of polymer-based restorative material during cure is commonly measured by dilatometry (Bandyyopadhyay, 1982). Measurements of volumetric shrinkage of commercial restorative composite resins ranged from 1.67 to 5.68 volume percent shrinkage (Goldman, 1983). The highest results overall tend to be for the powder-liquid materials. Photopolymerized materials appear to shrink the least with the paste-paste materials being the intermediate.

In chemically activated composite resins, the shrinkage is directed to the center of the restoration. Photoactivated materials, however, contract toward the outer surface of the restoration. In both cases setting stresses are developed in the restoration. These stresses are likely to cause microcracks and possibly marginal gaps between the restoration and the cavity wall. The observed space at the cavity wall to restoration interface when there is little or no adhesion is
smaller than the values calculated from volumetric shrinkage simply because a substantial amount of shrinkage may occur perpendicular to the surface rather than directly away from the cavity wall.

The degree of marginal leakage is strongly influenced by polymerization shrinkage (Tani, 1985). Four factors are believed to be of major importance in causing the observed shrinkage, (1) The amount of reacting monomer; (2) The type of reacting monomer; (3) The degree of cure; (4) The amount of air incorporated in the material (Goldman, 1983).

A large amount of the cure shrinkage occurs in the viscous and early plastic state of the polymerization process. This part of the shrinkage has no clinical significance because it is possible to restore the cavity by exerting pressure on the matrix.

Studies over the past decade have revealed that the marginal gap caused by initial polymerization shrinkage is often not eliminated by acid etching or volumetric expansion due to water uptake. The wall-to-wall contraction was not affected by the filler content to certain extent (Asmussen, 1975).

Adhesion of the setting material to the cavity wall results
in internal stress ranging from 700 to 1000 psi (Bowen, 1983), causing microcracks and premature failure of the composite resin restoration (Jorhensen, 1975). It is clear that the polymerization shrinkage is one of the main factors that determines the life span of a composite resin restoration (Bausch, 1982)
2. CURE SHRINKAGE CONTROL: WORK REPORTED FROM OTHER LABORATORIES

2.1 Chemical Elimination of Cure Shrinkage

Bailey (1973) proposed the use of bicyclo and spiro type compounds as zero shrinkage or expanding monomers. Ring-opening polymerization usually involves somewhat less shrinkage than either addition or condensation polymerization, because for every polymer bond that is formed involving a shift from a Van der Waals' distance to a covalent distance, a bond is broken in the cyclic monomer involving a shift from a covalent distance to a near Van der Waals' distance. If therefore, monomers were utilized in which two or more bonds were broken for every new bond that is formed in the polymerization process, zero shrinkage or even expansion would be possible. Using suitable bicyclo or spiro compounds, Bailey formulated systems which expand on polymerization. Among the monomers that indeed give essentially zero shrinkage or some expansion on polymerization are the spiro ortho esters, such as 2,4,6-trioxaspiro (4,4) nonane, spiro orthocarbonates and bicyclo ketal lactones.

A more fruitful approach appeared to be the study of bicyclic compounds. In bicyclic monomers, for every bond that goes from a Van der Waals' distance to a covalent distance, at least two bonds would go from a covalent distance to a near
Fig.I-2.1: Ring opening polymerization (From Bailey).
Van der Waals' distance. Fig.1-2.1 shows such a system. In this system, cyclopentene, which undergoes a 15% shrinkage when it was converted to the polycyclopentenomer, would undergo a 20% shrinkage when converted to its saturated dimer. If a catalysts were available for the polymerization of saturated dimer to the same polycyclopentenomer, a 6% expansion would be predicted. Similarly, if the cyclopentene is converted to adamantane, a 26% shrinkage would result, and if adamantane could somehow be converted to the same Polycyclopentenomer, a 17% expansion in volume would be calculated. Unfortunately, the catalyst which would make these conversions possible are presently not known.

This is a conceptually elegant method of cure shrinkage control; however, it has serious practical disadvantages which limit its applications.

2.2 "Low profile" Additives for Shrinkage Control of Unsaturated Polyester Resin Systems.

Unsaturated polyester resins which are copolymerized with styrene account for about 60% of the thermoset polymers used in the United States and the most widely used thermosets in polymer composites. They offer a good balance of properties, are relatively inexpensive and are amenable to most fabrication processes.
When the conventional unsaturated polyester/styrene systems were first used in fiber-reinforced materials, their applications were limited by a number of problems, the most important being poor surface quality; this rough surface showed a "high profile" pattern when it was scanned by a surface-profilometer (Figure 1-2.2.1(a), Atkins, 1982). Fibers often showed through, and an inordinate amount of labor was required to obtain acceptably smooth decorative prepaint finishes by operations such as dry sanding of the surface. Other problems included warpage or "sinks" on the surface of molded parts and inability to mold to exact dimensions. These problems were attributed to the high polymerization shrinkage during the cure. As the polyester crosslinks with styrene, it shrinks away from the mold walls, creating internal stresses that lead to surface and structural flaws. Fig. 1-2.2.2 (Kroekel, 1978) shows a typical shrinkage measurement of unsaturated polyester system, the final cure shrinkage was as much as 7%.

The addition of certain thermoplastic materials to the unsaturated polyester resin was found to compensate the cure-shrinkage or even produce a slightly expanding system (Figure 1-2.2.3, Kroekel, 1978), thereby solving most of the problems and giving smooth surface to the final products which would show "Low Profile" scanning pattern on surface profilometer (Fig. 1-2.2.1(b), Atkins, 1982). These thermoplastics were called "low profile additives" (LPA).
A. SMC part without low-profile additive

ARITHMETIC AVERAGE SCALE 100

B. SMC part with low-profile additive

ARITHMETIC AVERAGE SCALE 100

Fig. I-2.2.1: "High profile" and "Low profile" scanning patterns (From Atkins).
Fig. I-2.2.2: Dialometric shrinkage measurement with conventional resin (From Barlkus and Kroekel)
Fig. I-2.2.3: Dialometric shrinkage measurement with low profile resins (From Barlkus and Kroekel).
Currently the use of LPA the predominant method in the plastics industry for producing zero-shrinkage molding from composites based on unsaturated polyester resins. These highly filled (glass fiber, calcium carbonate, etc.) systems are usually compression molded to form a variety of automotive parts, from hood scoops and fender extensions to front end panels.

A typical low shrinkage/low profile polyester resin contains three components: a highly reactive unsaturated polyester; a thermoplastic polymer as a LPA; and styrene. Many different kinds of thermoplastics are employed as LPA, such as vinyl acetate polymers, acrylic polymers, polystyrene, and polycaprolactone (Hsu and Lee, 1989). Among them, elastomeric thermoplastics containing unsaturated double bonds are considered more efficient both for enhancing the polymerization rate and for imparting good impact resistance to the cured compounds. The overall composites usually contain about 20-25% resin, 45-50% particulate filler (calcium carbonate, etc.) and 25-30% chopped glass fiber, and small amounts of catalysts, chemical thickening agents, and release agents. The compounded low-shrinkage systems are cured under typical molding conditions (500 psi, 300 °F). Under these cure conditions, LPA can essentially eliminate the polymerization shrinkage.
There are two types of LPA-containing low-shrinkage polyester resin systems: two-phase and one phase systems. In two-phase systems, the components of the raw resin are not completely soluble in each other and even after thorough mixing they form a two-phase dispersion consisting of 50-100 micron liquid globules in a continuous medium (Pattison, 1974); the continuous phase contains unsaturated polyester while the liquid globules contain both thermoplastic additive and unsaturated polyester dissolved in monomer. These systems retain their two-phase form throughout their polymerization. In one-phase systems, the components of raw resin are completely soluble in each other forming a homogeneous, single phase. Phase separation occurs during polymerization.

The degree of improvement in shrinkage control depends on the structure of the thermoplastic additives, its molecular weight, the amount used, and the structure of the unsaturated polyester resin. However, with proper attention to these factors a "zero-shrinkage" composite can be formulated to yield moldings with excellent surface smoothness, no part warpage, and precise dimensional stability.

Since there are some similarities in between industrial LPA containing resins and the systems developed in this project where cure shrinkage is controlled by phase separation, the previous work on LPA systems is discussed here in some detail.
2.2.1. Review of Previous Work

Kroekel (1970) developed an acrylic-modified unsaturated polyester/monomer LPA system in the early 70s. Two components comprise this system, both being in medium viscosity liquid form. They are incompatible and must be blended just before use. Thermoplastic polymers useful in the compositions include homopolymer of methyl methacrylate, ethyl methacrylate, methyl acrylate, etc. The molecular weight of these thermoplastics may vary widely. The preferred molecular weights range from 25,000 to 500,000. The thermoplastic polymer should be present in amounts from 5 to 20 parts by weight based on the total component resin system. A typical composition of the resin is as follows: unsaturated polyester 37.5 wt%, thermoplastic polymer 12.5 wt%, styrene 50.0 wt%. This system is cured without filler using 1% t-butyl peroctoate by weight as initiator, under positive pressure of 400 psi at 250°F in a press. Use of the plastic LPA causes this resin system to cure with a 2.9% expansion (Fig. I-2.2.3).

This "low shrinkage" polyester system is available from Rohm and Haas under commercial name Paraplex P-19. Volume changes are similar to those shown by conventional resin up to the point where cure shrinkage begins. Here a second peak occurs which has not been observed with conventional polyester resins. Bartkus and Kroekel (1970) believe that this peak and
its magnitude are directly related to the low shrinkage or expansion tendencies in P-19 molding compositions. Increasing temperature and/or decreasing pressure can increase the height of this peak while decreasing temperature and/or increasing pressure can eliminate it.

Okada and Konaka (1982) proposed the use of both single-phase and two-phase low profile systems in polymer concrete. Two kinds of unsaturated polyester resins and four kinds of thermoplastic polymers, low shrinkage thermoplastic additives, were used in their study. The unsaturated polyesters were orthophthalate-based rigid polyesters of different reactivity in solution with styrene monomer. Polyvinyl acetate (PVAc) was compatible as an LPA with both of the above polyesters and a homogeneous single-phase system of polyester-thermoplastic LPA was obtained. Two phase systems were obtained with polystyrene. In the two phase systems, styrene copolymer grafted with saturated polyester was added as stabilizer. For the two phase system, low shrinkage was more easily obtained by the low molecular weight polystyrene, compared with conventional grade polystyrene.

Atkins et al (1982) developed LPA's based on polyvinyl acetate and polycaprolactone (Union Carbide low profile additives LP-40, LP-60, and LP-90). These materials gave excellent shrinkage control and dimensional stability over a
range of polyester resins. In addition they provide flexibility to the very rigid polyester required for good results with acrylic based thermoplastics.

These "third generation" developments led to automotive/truck Class A surface systems with phthalic modified polyesters for improved toughness. The high dimensional stablity of these composites has allowed expansion of the industry into housings of electrical business machines. Also, the existence of these materials has allowed the development of several proprietary tougher polyesters by resin manufacturers.

The "fourth generation" LPA resins emerged in 1980s. Atkins (1988) presented systems that meet the needs for super Class-A surface qualities for use on automotive exterior panels. These compounds allow for actual linear expansion of 0.01 to 0.05 percent resulting in molding with exceptional mold reproduction and surface smoothness.

Fukushi et al (1987) developed a unique method using styrene-vinyl acetate block copolymer as a LPA for unsaturated polyesters. The curing process of the resin was observed under SEM. Dispersed in a styrene solution, the polystyrene segments were outside and poly(vinyl acetate) segment were inside of the micelles. When the copolymer-styrene solution was mixed
with unsaturated polyester, phase inversion took place, turning the poly(vinyl acetate) segment to the outside. At final curing stage, phase inversion again took place and copolymer micelles with outside polystyrene segment separated as spheres (Fig I-2.2.4). Voids were formed in this process for prevention of cure-shrinkage. There is an advantage in using block copolymer as LPA: by having polystyrene segments outside, dissolved in styrene monomer, the bonding between the separate microdomains is enhanced and so are the mechanical properties of the cured systems.

All of the above methods fall under the so-called "low-profile" polyester resins. Walker (1971) enumerated many of the factors that appear to be related to development of low profile character as follows:

1. Use of LPA's reduces the gross shrinkage of the molded part and may even result in zero shrinkage or an overall expansion.

2. With LPA's, castings are opaque and show areas containing a multitude of microvoids.

3. Very reactive polyester systems are used, and a substantial polymerization exotherm seems necessary for effective performance.

4. Effective systems contain a larger proportion of styrene than usually required.

5. Material such as t-butyl catechol which inhibit
不飽和ポリエステル樹脂の新しい低収縮化剤及び電子顕微鏡による作用の観察

\[ \text{(a)} \quad \text{St solution of poly(St-b-VAc)} \]
\[ \text{(b)} \quad \text{Mixture of St solution of poly(St-b-VAc) and unsat. polyester} \]
\[ \text{(c)} \quad \text{After curing} \]

Fig.I-2.2.4: Phase reversion of poly(St-b-VAc) in unsaturated polyester.
homopolyerization (e.g. of styrene) reduce the low profile effect.

(6) While there appear to be specific constraints on the nature of the polyester portion of the system, a wide latitude on the nature of the thermoplastic additive is allowable.

Significant improvement in part quality accrues through the use of low-profile polyesters due to the eliminating of cure-shrinkage. Some of the advantages obtained are:

(1) Excellent surface quality, the surface of the mold can be essentially reproduced;

(2) Accurate reproduction of mold dimensions which permits the molding of parts to very close tolerances and is especially important in electrical and mechanical applications;

(3) Elimination of warpage;

(4) Minimization of internal cracks and voids.

Several mechanisms have been proposed for cure-shrinkage control by using low-profile additives:

Okada and Konaka (1982) proposed a mechanism for both single and two-phase low-profile systems. On the fracture surfaces of test pieces from two-phase systems with polystyrene as LPA, spherical voids were observed. The cure shrinkage control and void formation was deduced as follows:
(1) Copolymerization began to take place in the matrix phase, while styrene monomer in the spherically dispersed low shrinkage additive phase did not react, as styrene homopolymerization rate is slower than copolymerization rate.

(2) Styrene and other components expanded as the temperature at peak exotherm increased, and counteracted the shrinkage. However, phenomenon similar to this must occur in the original polyester resin without low shrinkage additive as well.

(3) As styrene monomer was consumed in the matrix phase, monomer migration from the dispersed phase to the matrix phase occurred. With the rising temperature, the vapor pressure of styrene increased and the vaporized styrene expanded to cancel out the cure shrinkage. Then it was assumed that vacancies in the dispersed phase were produced as the styrene vaporized.

(4) As the expansion became comparable to the curing shrinkage, the strain became maximum at peak exothermic temperature, and the thermal shrinkage started.

The mechanism in the single-phase systems was somewhat similar: In the progress of curing, the crosslinking polyester gel domains grew and adhered to each other, and LPA separation occurred. The separated phase was no longer spherical but
formed complex shaped droplets. During polymerization, styrene monomer migrated from the dispersed phase to the continuous matrix phase and vaporized. As the vapor pressure of styrene increased, the pressure concentrated on the sharp edges of the dispersed phase, and caused microcracks and expansion.

Boos et al. (1973), using dilatometry, calorimetry and swelling experiments suggested that the total volume changes during crosslinking are mainly controlled by temperature. They showed in their work that at high enough temperatures even a conventional polyester system does not shrink. Hence, the function of the thermoplastic low shrinkage additive is to lower the crosslinking temperature at which no shrink or even expansion occurs. This effect can be also accomplished by using other additives having high thermal expansion coefficients or by using initiators with different decomposition temperatures.

Bartkus and Kroekel (1970) proposed possible cure shrinkage control mechanisms of "optical heterogeneity and boiling monomer" for the two-phase low-profile polyester system Paraplex P-19 (Rohm and Haas Co.). First, it is important to notice the fact that for those two-phase systems the polymerization rates of the two liquid resin phases differ widely. The continuous phase, contains the unsaturated polyester and monomer, crosslinks rapidly at normal molding conditions and liberates considerable exothermic heat. The
dispersed droplets, by contrast, cure more slowly because the principal reaction is homopolymerization of the monomer. Because of the great disparity of the phases the dispersed droplets, while still essentially liquid, are subjected to the high temperature produced by the polymerization of the reactive continuous phase. Furthermore, the continuous phase gels and becomes crosslinked in the early stages of its reaction.

Several possible sequences of events can be visualized during the early cure stages.

(1) The free monomer, which most certainly is present in the droplets during the exothermic reaction of the continuous phase, may tend to boil and exert enough pressure to counteract the shrinkage of the matrix leaving foam-like occlusion when cure is complete.

However, at the actual molding temperatures (140-150°C) and pressure (1000 psig), it seems unlikely that monomer would volatilize (at 200°C, the vapor pressure of monomer styrene is 50 psig).

(2) When subjected to the high temperature generated during the rapid polymerization of the continuous phase, the dispersed liquid droplets expand thermally and tend to
counteract or compensate for the polymerization shrinkage occurring in the continuous phase. The droplets, in this thermally expanded state are frozen in, and when polymerization and shrinkage subsequently occur in the droplets, microscopic voids form and a foam-like appearance develops.

(3) The less reactive dispersed droplets may act as reservoirs for monomer which migrates from the discontinuous to the continuous phase to supply the demand of the highly linking reaction, again leaving tiny voids and a foam-like appearance in the droplet.

Other studies of the two-phase low profile polyester systems have modifications in the Bartkus and Kroekel's theory. Pattison. et al. (1974) have proposed a mechanism of "strain relief through stress cracking" in which they stipulate that the unreacted styrene monomer thermally expands to compensate for the loss of volume due to polymerization shrinkage. At the same time, as the cure progresses, shrinkage causes local stresses to develop in the system; these increase to such an extent that microcracks are formed to relieve them. Such stress cracking will propagate through the weakest part of the material, being either in the thermoplastic additive phase or at the interface between the dispersed phase and the continuous phase. Consequently voids will form to compensate for the loss of volume due to polymerization
shrinkage. A similar explanation has been offered by Rabenold (1972), except his work includes the proposal that the large excess of styrene monomer (compared to conventional molding resins) can result in styrene homopolymerization inside the thermoplastic.

Walker (1971) also suggests that void formation is critical to polymerization shrinkage control.

The mechanisms proposed by Bartkus and Kroekel (1970) fail to account for the low shrinkage observed in homogeneous, single-phase system (i.e. a low profile resin, in which the thermoplastic additive is compatible with the polyester before cure begins). Pattison's theory (1974) was based on the study of a polyester system which consists of two phases in the uncured liquid stage.

Pattison et al. (1975) studied single-phase low profile resin systems (thermoplastic totally soluble in polyester before molding ) and proposed a modified "strain relief through stress cracking" mechanism for one-phase system. This one phase system was based on a polyester resin from phthalic anhydride, maleic anhydride, and propylene glycol, employing poly(vinyl acetate) as the LPA, Upon curing under heat and pressure this clear homogeneous liquid mixture becomes white and opaque. Its composition is as follows: unsaturated
Polyester 28 wt%, poly (vinyl acetate) 12 wt%, and styrene 60 wt%.

The initial liquid mixture of styrene, unsaturated polyester, and LPA is clear and homogeneous. On heating to ca.130°C, there is simultaneous copolymerization of the unsaturated polyester and styrene, resulting in contraction of the polymerizing compounds and a counteracting thermal expansion of styrene monomer. At 130°C, the crosslinking polymerization has progressed to a point where beads of crosslinked resin separate from the styrene-LPA solution. As the polymerization continues, styrene is consumed leaving a matrix of low-profile polyester. During this phase of the cure, polymerization is effecting a contracting stress, and there is little styrene monomer present to counteract it by thermal expansion. As these stresses increase, they are relieved by crack formation that progresses through the weak matrix of low-profile additive. This obviates the need for relief of the internal stress by macroscopic contraction of the molding as a whole, as observed in the ordinary crosslinking polyester system.

None of the mechanisms discussed above addresses the question of the effectiveness of various types of thermoplastic resins, when used as low profile additives. Atkins (1976, 1973, 1982, 1988) has asserted that the ability of various types of
thermoplastic resins to control shrinkage is closely related to their thermal expansion coefficient. He observed that the effectiveness of a low profile additive increases with increasing values of its thermal expansion coefficient. Atkins noted however that, in order for a thermoplastic resin to function effectively as a low profile additive, it must be incompatible; it must precipitate from the styrene-crosslinked polyester matrix during the cure.

Atkins studied three thermoplastic additives in two unsaturated polyesters: poly(vinyl acetate), a methyl methacrylate-ethyl acrylate copolymer, and polystyrene. The polyesters were based on (1) maleic anhydride and propylene glycol, and (2) isophthalic acid, maleic anhydride and propylene glycol.

In both unsaturated polyester resins the shrinkage control was best with the poly(vinyl acetate), next best with the acrylic based thermoplastic, and considerably worse with polystyrene. Still shrinkage with the polystyrene was much less than with no thermoplastic present. Scanning electron microscope examination of each cured resin matrix in the absence of fillers and reinforcements was conducted, at magnification x500 it showed the presence of voids <1 micron in diameter.
Atkins considered that the thermal expansion of the thermoplastic compensated for the cure-shrinkage, as illustrated in Fig.1-2.2.5. The differences in ability of thermoplastics to control cure-shrinkage is explained by Atkins by the thermal coefficients of expansion of these thermoplastics. A graph of the specific volume of the thermoplastic versus temperature is given in Fig. 1-2.2.6. At every temperature, it is evident that the poly (vinyl acetate) occupies more volume than the acrylic polymer because of its higher thermal coefficient of expansion. This evidence suggests that the differences in thermal expansion coefficient between the thermoplastic LPA and the polymerizing matrix is important to its ability to control cure shrinkage. Obviously, the thermoplastic LPA must become chemically incompatible with the thermosetting systems before this effect can be realized.

Polystyrene has greater specific volume at any temperature than either poly (vinyl acetate) or the acrylic material, as it is shown in Fig. 1-2.2.6. Yet it is not nearly as effective as either of these materials. Some explanation for this can be seen in the microscopic examination of this material with polyesters (1) and (2). Particularly with polyester (2) the matrix appears visibly compatible and no voids are evident even at a magnification of 5000. Yet some incompatibility was noted by torsion pendulum studies.
Fig.I-2.2.5: Polyester shrinkage and the low-profile phenomenon. (From Atkins)
Fig.I-2.2.6: Volume-temperature relationship of PMMA, PVA, and polystyrene. (From Atkins)
The relative compatibility here is suggested to be influenced by polarity. Before cross-linking, the unsaturated polyester is reasonably polar (dipole moment 2.0-2.5), while after crosslinking the introduction of styrene segments lowers the polarity (e.g. dipole moment approximately 0.8). Both poly(vinyl acetate) and the acrylic polymer are polar (dipole moments 1.6 and 1.3), while polystyrene is relatively nonpolar (dipole moment 0.3). Therefore, as the polyester crosslinks, the polar thermoplastic has a greater driving force to become incompatible and thus to be available for expansion to compensate for polymerization shrinkage. Conversely, the polystyrene, being nonpolar, has less of a tendency to become incompatible with the thermoplastic system; therefore, lesser amounts of it are available for expansion and compensation of cure shrinkage.

Atkins et al feel that void formation is due to styrene homopolymerization in the thermoplastic phase and shrinkage of the thermoplastic phase away from the thermoset phase during cooling of the matrix from peak exotherm. The greater compatibility of the polystyrene systems also yields uniform colors, while use of the more polar additives normally will not allow this approach.

Siegmann et al. (1978) studied low profile behavior of both single-phase and two-phase unsaturated polyester systems and
proposed the following mechanism:

(1) For a two-phase system, (where the initial system exists as a two-phase mixture at room temperature) the continuous phase consists of the polyester, styrene and some of the thermoplastic additive; the dispersed phase consists of the thermoplastic additive and polyester in styrene.

(2) Upon heating crosslinking begins to take place in the continuous phase while the dispersed phase remains fluid since crosslinking in the latter is much slower. As a result the concentration of unreacted styrene in the continuous phase decreases with time, causing some migration of styrene from the dispersed droplets into the continuous phase. Crosslinking of the continuous phase would cause the system to shrink but thermal expansion of the monomeric styrene and thermoplastic additive, plus the styrene vapor pressure act to cancel out the shrinkage.

(3) As the reaction in the dispersed phase begins, the polyester which has been crosslinked is no longer soluble in styrene and thus precipitates out.

(4) On further heating, polymerization in the dispersed phase continues, homopolymerization of styrene causes shrinkage of the droplet. The overall shrinkage tendencies coupled with the
different thermal expansions create stresses within the droplets. The stresses increase upon further heating. The high unsaturation of the polyester generates a rigid material and causes, as a result of the developed stresses, microcracking rather than elastic deformation. These microcracks create voids which compensate for the polymerization shrinkage.

It is therefore seen that there are two main mechanisms operating to reduce the shrinkage: (a) Polymerization shrinkage of the continuous phase is compensated by vapor pressure of styrene and the thermal expansion of the other constituents; (b) Polymerization shrinkage of the dispersed phase is compensated by void formation in the dispersed phase.

Walker (1971) assumes also void formation but he adds that the mechanism may be expansion of the voids under the influence of the styrene vapor pressure. However, surface tension considerations would predict much smaller voids than observed.

In their excellent paper Hsu and Lee (Hsu and Lee, 1989) described the structure formation in the cure of Low-Shrinkage unsaturated polyesters, but did not offer any explanation of the cure-shrinkage mechanism. They pictured the LPA resin system before cure as a system of many coiled polyester chains swollen with styrene. Chemical reactions may occur inside,
outside, and at the surface of the coils. During the styrene-unsaturated polyester copolymerization, long-chain molecules were formed by connecting styrene monomer and polyester molecules in both inter- and intramolecular reactions (Fig. 1-2.2.7). Because of the intramolecular crosslinking between the pendant C=C bonds of the polyester molecules, these long chain molecules tend to form spherical-type "microgel globular particles", 0.5 to 1.0 µ in diameter (Fig.1-2.2.8). The final structure of the resin is determined very early in the reaction. After that, further reaction is predominantly intramolecular cyclization, which increases the overall conversion and the local crosslinking density, but does not seem to much enhance the mechanical properties of the whole sample. They found that there were relatively small differences in reaction kinetics, rheological changes, and gel conversion for resin with or without LPA which means that the formation of micro globules does not affect the reaction mechanism very much, although it provides a means for the reduction of cure shrinkage.

2.2.2 Limitations of the LPA Methods

Although the use of LPA eliminates cure-shrinkage for polyester resin systems and improves the qualities of the molding products, it has several limitations and is not the final solution for cure-shrinkage of polymeric materials. Some disadvantages of this method are:
Fig.I-2.2.7: Schematic of copolymerization reaction. UPE coils occupy a larger space at higher temperatures. The "=" symbolizes styrene.(From Hsu and Lee)
Fig. I-2.2.8: SEM micrographs show globule formation at all conversions: (a) 1%, (b) 5% to 10%, (c) 60%, and (d) 82% conversion. (From Hsu and Lee)
(1) Elevated temperature and high pressure are required; (Bartkus and Kroekel, 1970), systems that have zero shrinkage when cured under typical molding conditions (300 °F and 500 psig) show the usual polyester cure shrinkage when polymerized at ambient temperature and pressure. Commercial LPA systems are formulated for use in matched metal die molding where cure is accomplished by heat and pressure. These systems will not function at low temperatures (Barkus, 1971).

(2) Low profile systems developed so far are restricted to unsaturated polyester resins.

(3) The cured products are not free of voids and in extreme cases have foam-like appearance. In fact, microscopic void formation is critical to polymerization shrinkage control (Walker, 1971).

(4) The presence of microcracks and voids in these systems lowers the strength of the cured composite.

2.3. Other Cure-Chrinkage Control Methods in Polymer Concrete Systems

Several other methods have been proposed or producing low or zero-shrinkage resin systems for polymer concretes. Skeist (1958) discusses the use of high-molecular weight liquid prepolymer. Those materials undergo less change in density as they polymerize into solids. The use of thiokol-epoxy blends is an example of this type. He also discusses the so-called "pore method" which is well-known in plastic technology. The special
foaming agents are used as the source of gas which produces a cellular structure of material. A good example is the polymerization of diisocyanates in the presence of small amounts of water, which generates CO$_2$, thus producing a cellular structure. The pore method in polymer concrete has been used among others by Liveremont (1972), Putlayev et al (1973) and Irtuganova et al (1972). The common disadvantage of all these methods is the reduced strength of the resulting material due to high porosity.

Czanecki (1982) obtained expansive polymer concrete by using various volatile organic liquids adsorbed into the pores of zeolites which were dispersed in the raw resin; the curing exotherm expels the volatile molecules from the zeolite pores thus generating zero-shrinkage or expanding polymer concrete. This method again produces porous cured systems with significantly impaired strength.

Ohama and Nawata (1987) used thermoplastic resins as shrinkage reducing agents for PMMA concrete. They investigated the setting shrinkage of PMMA concrete with several thermoplastic resins such as poly(methyl methacrylate), polystyrene, polyisobutyl methacrylate, poly(vinyl acetate), and styrene-vinyl acetate block copolymer as cure-shrinkage control agents. The test results revealed that such thermoplastic resins did not give a suitable reduction in the
setting shrinkage of PMMA concrete. But the combination of unsaturated polyester, polystyrene, poly(isobutyl methacrylate) (PIBMA) and crosslinking agent TMPTMA can act as an very effective shrinkage reducing agent in the temperature range of 20°C to -20°C.

A reduction of setting shrinkage is caused by the synergistic effects of the expansive action of PIBMA and the cross-linking action of unsaturated polyester. Resin system immediately after mixing exist as a two-phase mixture with a continuous phase consists of unsaturated polyester, MMA, TMPTMA, and some of the PIBMA. The dispersed phase does of PIBMA and MMA. Polymerization in the continuous phase begins with shrinkage, while no reaction occurs in the dispersed phase. As the exothermic temperature of PMMA concrete rises in the progress of the polymerization, the thermal expansion of the dispersed phase with PIBMA and monomeric MMA occurs and acts to cancel out the shrinkage of the continuous phase.

Compared to the systems discussed in 2.2, the resin system Ohama and Nawata used has a composition of a rather typical low-profile resin system. The mechanism they proposed is very close to the mechanism proposed by Atkins et al. No investigation of void formation was mentioned in Ohama and Nawata' work. However, Data of mechanical property tests show that the compressive strength of maximum expansion (59
NM/M$^2$) is considerably lower than the maximum compressive strength at little shrinkage (87 NM/M$^2$).
3. CURE SHRINKAGE CONTROL: PREVIOUS WORK AT RICE UNIVERSITY

3.1. The Concept of Dilating Additives: MMT-PC

The methods for combatting setting shrinkage discussed above have several serious drawbacks. These include loss of strength in the cured composite (a major disadvantage), the need for specialty chemicals, applicability to a single type of resin (LPA systems), etc.

In an effort to overcome these drawbacks Dr. Armeniades and his research group at Rice University explored the utilization of special dilating additives that would counteract cure shrinkage. In particular they sought to utilize porous mineral additives which would admix easily with many different polymerization systems and would utilize the exothermic character of polymerization reactions to undergo an increase in volume, which would counteract polymerization shrinkage without generating voids inside the cured system. The mineral montmorillonite (MMT) in its hydrated form was found to possess such properties and has been successfully used to develop polymer concretes and mortars that show zero cure shrinkage (or cure expansion) with an increase in strength. These systems are referred to as montmorillonite polymer concrete (MMT-PC) and form the foundation for a substantial part of the research discussed in this Thesis. Consequently the
chemistry and cure shrinkage control of MMT-PC systems will be described in some detail in the following sections.

3.2 Formulation and Properties of MMT-PC

Zero shrinkage and expanding PC systems based on unsaturated polyesters, epoxy, and acrylic resins have been prepared by Armeniades and Haque (1986, 1987). These systems contain small amount (1-8%) of hydrated (natural) MMT dispersed into the raw resins in the form of very fine powder. The mineral interacts with the resin during the cure, giving rise to an increase in volume. Depending on the amount of MMT added and the cure temperature, systems that show zero shrinkage or expansion can be obtained upon curing. These MMT-PC systems are remarkable in that they achieve zero shrinkage properties with a significant increase in strength when compared to the same PC formulations without MMT.

Montmorillonite is a hydrated alumino-silicate clay with a laminar crystal structure that includes up to 4 layers of semi-ordered water between the metal-oxide layers of the basic crystal. In the naturally occurring mineral this water is gradually released when the MMT is heated from 95 to 140 °C (Theng, 1974). The addition of very small amount of MMT in the resin (in the order of 1-2%) is sufficient to produce zero-shrinkage PC; higher MMT content give systems that expand with cure as shown in Fig.1-3.2.1. If these expanding
Fig. I-3.2.1: Thermomechanical Analysis data showing the Volume Changes Manifested during (A) the Cure of Unsaturated Polyester Resin; (B) the Dehydration of Pure MMT; (C) the Cure of Polyester Resin with 8% MMT.
systems are forced to cure at constant volume they generate considerable hydrostatic pressure. Investigation of MMT-PC systems with Differential Scanning Calorimetry, Gas chromatography and light-Microscopy has confirmed that cure expansion occurs when the polymerization exotherm raises the temperature of the curing system above 100°C. At these temperatures the coordination bonds that hold the hydration water in the MMT crystal structure are broken and water vapor is formed. However, at this point in the polymerization process the resin adsorbed onto the surface of the MMT particles has formed a viscous, rapidly solidifying layer that envelops the mineral particles and presents the escape of the hydration water, which causes the particle to double or treble in size. This MMT dilatation counteracts polymerization shrinkage of the resin, thereby relieving setting stresses and with higher MMT contents, produces cure-expanding systems (Haque and Armeniades, 1986, 1987).

The most important aspect of MMT-PC systems is their significantly higher strength, compared to the respective conventional PC. This is most pronounced in the zero-shrinkage systems, which achieve strengths up to 30% greater than the corresponding PC systems without MMT (Fig. 1-3.2.2). The strength enhancement is most probably due to the minimization of setting stresses when the cure-shrinkage forces are eliminated. It should be noted, however, that the
Fig.I-3.2.2: Compressive, Flexural, and Splitting Tensile Strength Measurements on Unpromoted MMT-PC systems with different MMT contents.
previous zero-shrinkage PC systems, prepared by others using methods mentioned before, showed a reduction in strength, which could be attributed to the formation of low-strength domains when a second phase precipitated from solution or was released from molecular sieves. It appears, therefore, that in zero-shrinkage MMT-PC systems the relief of setting stresses is achieved without disruption of continuity in the polymer-network/aggregate system. This has been confirmed by Transmission Light Microscopy of MMT-resin section as well as Scanning Electron Microscopy of fracture surfaces of MMT-PC.

The integral structure of the cured MMT-PC systems is due to the tendency of MMT to adsorb organic molecules and incorporate these species into its intercrystalline layers.

X-ray diffraction measurements of MMT dispersions in various raw resins show an increase in the interlayer spacings of the MMT crystals when the mineral is admixed into epoxy resins, polyester and methyl methacrylate monomer (Haque and Armeniades, 1986). These measurements are in agreement with earlier findings that certain organic molecules (alcohols, ketones, esters), when mixed with MMT enter the interlayer spacing of the mineral (Theng, 1974).
CHAPTER II. SCOPE OF THIS RESEARCH

1. CHEMICAL MODIFICATION OF MMT TO CONTROL CURE SHRINKAGE AT TEMPERATURES CLOSE TO AMBIENT

The methods developed by Haque and Armeniades (Haque and Armeniades, 1986, 1987) for controlling cure shrinkage and eliminating setting stresses by use of hydrated MMT, although novel and effective, have significant limitations. They require the cure temperature to reach ca. 120°C at peak exotherm in order to trigger the dehydration process that dilates the mineral particles. This limits the use of MMT to oven cured systems and has prevented to-date the utilization of MMT-PC for large, field erected structures. In addition, due to the disparity in thermal expansion coefficients between resin and aggregate, the high-temperature cures subject the PC systems to thermal stresses, which may not disappear when the cured composites return to ambient temperature.

It should be possible to overcome the 100°C cure threshold of MMT-PC systems by replacing some of the hydration water in MMT with lower-boiling inorganic or organic liquids, capable of penetrating the MMT lattice, such as ammonia, various amines, acetone, etc. This approach is based on previous work (Haque, 1986) which has shown that many liquids of medium-to-high polarity can enter the interlayer spacing of the MMT crystal with other species present in the crystal. Achievement of a
lower temperature cure would significantly enhance the usefulness of MMT-PC.

The main objective of this research at the outset was the chemical modification of MMT for the purpose of effecting dilatation of MMT particles in the 50-80°C temperature range so that the modified mineral could be used as a cure-shrinkage control additive in polymeric systems curing at ambient temperatures. This objective was successfully attained with the preparation of ammonia-modified MMT. The chemistry, activation mechanism, and properties of zero shrinkage and expanding PC systems containing ammonia-MMT are discussed in Chapter IV. A multicomponent acrylic resin was selected as the experimental system for these studies, because of its low viscosity, low molecular weight and most of all because the cure-shrinkage of acrylic monomers and dimers is the worst among resin systems.

2. ALTERNATIVE METHODS OF CURE SHRINKAGE CONTROL

In the course of our work with multicomponent acrylic resin systems we observed that certain formulations, when made to polymerize rapidly, undergo phase separation and show also decreased cure shrinkage. Experiments over a wide range of concentrations of the major components of the raw resin revealed that the observed decrease in cure shrinkage depended on the size of the phase microdomains and the complexity of
phase boundaries. The investigation of this phenomenon is discussed in Chapter V and a hypothesis is proposed for its explanation.
CHAPTER III. MATERIALS AND METHODS

1. CHEMICALS

1.1. Monomers and Dimers

Several acrylic monomers and dimers were used for the studies:

Methyl methacrylate (MMA) was supplied by the Du Pont Company. It is a clear, low viscosity monomer, with high volatility and a sharp, pungent odor; It is easily polymerized at temperature ranging from 0 to 100°F when combined with the proper initiator(s), crosslinking agents, and accelerators. In this work, MMA was cured at ambient temperature in the presence of acrylic dimers as well as dissolved poly(methyl methacrylate).

Two acrylic dimers were used: Triethylene Glycol Dimethacrylate (TEGDMA) obtained as Satomer 205 from Sartomer Co. and Diethylene Glycol Dimethacrylate (DEGDMA) obtained as "Sartomer 231". Both are clear liquids with mild odor, high boiling point and low viscosity. They are both difunctional due to their two acrylic double-bonds. Therefore they can act as crosslinking agents, thus enhancing mechanical properties of composite. By mixing Satomer resin with MMA, the volatility and unpleasant odor of MMA are substantially reduced since both Sartomer dimers have low vapor pressures.
Linear poly(methyl methacrylate) (PMMA) in powder form was supplied by the Du Pont Co. as "Elvacite 2013". The PMMA powder was dissolved into MMA before cure to enhance viscosity and further reduce the unpleasant odor of MMA. The presence of long macromolecular chain of PMMA also played an important role in the phase separation process that effected cure shrinkage-control.

BIS-GMA (2,2-Bis [4-(2-hydroxy -3- methacryloyl oxypropoxy) phenyl] propane) used in dental restorative composites was supplied by Freeman Chemical Co.. BIS-GMA is a highly viscous, clear, light colored liquid thermosetting resin, widely used in dental restorative composites. It copolymerizes readily with other monomers and gives little cure-shrinkage due to its high molecular weight. The molecular structure of, BIS-GMA, Triethylene Glycol Dimethacrylate, and Diethylene Glycol Dimethacrylate are shown in Fig. III-1.1.

1.2. Initiator and Promoter

The acrylic resins used in this study were polymerized by free-radical processes. Benzoyl peroxide (BPO, Pennwalt Corp., Piffard, NY) was used as initiator, in the form of paste, containing 40% BPO. It was added to the resins just prior to mixing with fillers such as aggregates for polymer mortar and hydroxyapatite for dental restorative composites. In all the formulations used in this research BPO was accelerated
Fig.III-1.1: Chemical structure of TEGDMA and Bis-GMA.
(promoted) by the addition of N,N'‐dimethyl‐p‐toluidene (DMPT, Pennwalt Corp., Piffard, NY), which is a clear highly toxic liquid. The promoter was mixed with the resin (0.3% by weight) prior to the addition of BPO.

1.3 Fillers

River sand was supplied by Clemtex. Ltd., Houston., TX., in grades of 8 to 100 mesh according to ASTM C-136. A typical gradation curve is shown in Fig 4.4.2. (Zeilenga, 1983). The polymer mortar formulations used in this work contained 77-85 % by weight aggregate in polymer mortar resulting in a stiff but workable mixture. The use of aggregates reduced the peak exotherm temperature during cure. Since 85 % of the polymer mortar system is mineral aggregate, much of the exotherm is dissipated in just heating the aggregate particles.

Hydroxyapatite (Sagma) and Fluoroapatite (Ward's scientific, Inc) were used as fillers for dental restorative composites. Hydroxyapatite is the main component of human tooth. Fluoroapatite has the same structure as hydroxyapatite with the hydroxyl group replaced by fluoride group. Fluoroapatite powder was crushed from transparent Durango Apatite crystal. Both fillers were in the form of fine white powders with particle size ranging from 20 to 200 microns.

1.4. Coupling Agent
Fig.III-1.3: Sieve Analysis of Fine Cement Sand and Silica Sand, ASTM C33 Grading Specification for Fine Aggregates, and Ideal Curves of Fuller.
Coupling agents are used as molecular bridges at the interface between two immiscible substances usually but not limited to an inorganic filler and an organic or polymer matrix.

The silane coupling agent 3-Methacryloxypropyl-trimethoxy silane supplied by PolyScience was used in the polymer mortar formulations. Silane coupling agents monomeric silanes of the general structure $R'-Si(OR)_3$ in which two distinct centers of reactivity exist. The first site, $R'$, is a common organofunctional group such as amine, vinyl, epoxy, methacryloxy, mercapto, etc, bonded to the silicon atom by a short alkyl chain. The second reactive site is centered around the silicon atom and consists of hydrolyzable alkoxy groups $Si(OR)_3$.

In use, the alkoxy groups hydrolyze to form silanols ($Si-OH$) which can react or otherwise condense in the presence of active silica, clay, wollastonite, or metal oxide surfaces. At the other end of the silane molecule, the functional organic groups react with suitable groups in the organic matrix resin. To be effective in a given composite, they must be reactive to some degree with both the organic and the inorganic components. In practice, the silane can be applied to the filler in a separate pretreatment step, or it can be added directly to the resin and will migrate to the resin/filler interface during processing. In this work the silane was added directly to the
1. Formation of silanol.

\[
3H_2O + R-Si-\overset{OCH_3}{\text{OCH}_3} \rightarrow R-Si-OH + 3CH_3OH
\]

Trimethoxyalkylsilane  Alkylsilanol

2. Formation of siloxane linkage between silanol and MMT surface.

\[
\begin{align*}
&\text{R-Si-OH} + \text{HO-Si-}^- \rightarrow \text{R-Si-O-Si-}^- \\
&\text{Filler solid surface} \quad \text{Siloxane linkage}
\end{align*}
\]

3. Formation of siloxane linkages between silanol molecules at the MMT surfaces.

\[
\begin{align*}
&\text{R-Si-O-Si}^- + 2\text{RSi(OH)}_3 \rightarrow \text{R-Si-O-Si}^- \\
&\text{OH} \quad \text{OH} \quad \text{OH}
\end{align*}
\]

The formation of hydrogen bonds between silanol and the MMT surface can be illustrated as follows.

\[
\begin{align*}
&\text{R-Si(OH)}_3 + \text{HO-Si-}^- \rightarrow \text{R-Si-O-Si-}^- \\
&\text{OH} \quad \text{OH} \quad \text{OH}
\end{align*}
\]

Fig.III-1.4.1: The function of silane coupling agent in polymer concrete system.
resin. It has been found that silane coupling agents increase the physical, mechanical, and processing characteristics of highly filled engineering plastics (Sterman and Marsden, 1965, 1966; Ranney, et al., 1972).

Several titanate and zirconate coupling agents (Kenrich Petrochemicals, Inc.) were tried on dental composites. Among them, LZ 33 (neopentyl (dially) oxy, trimethacryl Zirconate) had best impact on mechanical properties for the acrylic resin based dental composite with Hydroxyapatite and Fluoroapatite as fillers. The structure of LZ 33 is shown in Fig. III-1.4.2.

1.5. Sample preparations

1.5.1 Polymer Mortar and Polymer Cements

The following sequence of steps was used to prepare polymer mortar and polymer cement systems: (1) PMMA was dissolved in MMA, then the solution was mixed with Sartomer 205 and 231, (2) the initiator, promoter, and coupling agent were dissolved into the resin, (3) MMT (for polymer cement) or MMT and aggregate (for polymer concrete and mortar) were blended into resin. Fig. III-1.5.1 is the formulation of polymer cement.

The polymer mortar mixture was then placed into teflon molds for test specimen preparation. The molds were filled in
neopentyl(diallyl)oxy, trimethacryl zirconate

\[
\begin{align*}
\text{CH}_2 = & \text{CH} - \text{CH}_2 \text{O} - \text{CH}_2 \\
\text{CH}_3 - & \text{CH}_2 - \text{C} - \text{CH}_7 - \text{O} \text{ Zr}(\text{O} - \text{C} - \text{C} = \text{CH}_2)_3 \\
\text{CH}_2 = & \text{CH} - \text{CH}_2 \text{O} - \text{CH}_2
\end{align*}
\]

*Fig. III-1.4.2: Chemical structure of LZ33.*
### COMPOSITION OF ACRYLIC SYSTEMS

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acrylic Cement</strong></td>
<td></td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>33.65</td>
</tr>
<tr>
<td>triethylene glycol dimethacrylate (Sartomer 205)</td>
<td>25.24</td>
</tr>
<tr>
<td>diethylene glycol dimethacrylate (Sartomer 231)</td>
<td>16.88</td>
</tr>
<tr>
<td>poly (methyl methacrylate)</td>
<td>8.00</td>
</tr>
<tr>
<td>fumed silica (Cab-O-Sil)</td>
<td>1.05</td>
</tr>
<tr>
<td>benzoyl peroxide (40% paste)</td>
<td>1.00</td>
</tr>
<tr>
<td>N,N'dimethyl p-toluidene</td>
<td>0.33</td>
</tr>
<tr>
<td>3-methacryloxypropyltrimethoxy silane</td>
<td>0.85</td>
</tr>
<tr>
<td>kaolinite</td>
<td>0-to-13.00</td>
</tr>
<tr>
<td>ammonia-modified montmorillonite</td>
<td>0-to-13.00</td>
</tr>
<tr>
<td><strong>Mineral Aggregate</strong></td>
<td></td>
</tr>
<tr>
<td>#1 Sand (8-20 mesh size)</td>
<td>15.0</td>
</tr>
<tr>
<td>#3 Sand (16-40 mesh size)</td>
<td>25.0</td>
</tr>
<tr>
<td>#6 Sand (60-100 mesh size)</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Fig. III-1.5.1: Formulation of polymer cement and polymer concrete.
successive layers, and tamped with a steel rod. Excess material was removed by scraping the open mold top surface with a steel straight edge. The molds were then left at ambient temperature for curing. After curing, the specimens were allowed to cool down to room temperature before demolding. The polymer cement mixtures were poured directly into glass or plastic molds and cured at room temperature.

1.5.2. Dental Restoration Composites

The dental composite resin was prepared by first dissolving the powdered PMMA into the liquid MMA and then adding the remaining resins: BIS-GMA, Sartomer 205, and Sartomer 231. Once the resins were thoroughly mixed with the magnetic stirrer, the BPO initiator and DMPT promoter were added and mixed for 60 seconds. The ammonia modified MMT powder was then added to the liquid resin and thoroughly mixed for an additional 30 seconds with the magnetic mixer. Finally, the coupling agent (LZ 33) was added. The formulation was then poured into a polypropylene test tube until slightly overflowing. A fitted, countersunk cover was placed over the open end of the mold, extruding the excess resin. Constant pressure was applied to the cover during curing to eliminate porosity. After the resin cured for 30 minutes at room temperature, the polypropylene mold was broken and the cured composite rod removed. The ends of the composite rod were removed using a low-concentration diamond wafering blade in a
low-speed saw (Isomet), leaving a cylindrical composite sample 16.0 mm long and 8.0 mm in diameter with parallel flat ends. These samples were used for both compressive tests and hardness tests.

1.5.3. Phase Separation Studies

Samples for phase separation studies were prepared by first dissolving under continuous stirring powdered PMMA into liquid MMA at weight ratios of PMMA/MMA= 30/70. TEGDMA was then added at different proportions to the PMMA/MMA solution. Once the resin mixtures were thoroughly mixed for 60 seconds with the magnetic stirrer, the initiator (BPO) and promoter (DMPT) were added and mixed for 60 seconds. The formulation was then poured into glass test tubes 75 mm long and 8 mm in diameter and polymerized at room temperature.
2. MEASUREMENT OF MECHANICAL AND OTHER PROPERTIES

2.1. Physical and Mechanical Properties

2.1.1. Cure-shrinkage/Expansion Measurements

Shrinkage or expansion of polymer cement and dental restoration composites were measured using a micrometer slide cathetometer (Model M9440-300P, Gaertner Scientific Corp., Chicago). The mixed formulation was poured into a glass test tube with a length of 75.0 mm and internal diameter of 8.0 mm. The test tube was rigidly attached in a vertical orientation to a ring stand and the formulation leveled even with the mouth of the tube. The cathetometer was placed adjacent to the suspended test tube and focused on the mouth (i.e. the top of the polymerization formulation). The resin system as formulated cures at room temperature (22°C) for 7-10 minutes, depending on the amount of filler, promoter and initiator used. The formulation was allowed to cure at room temperature for 30 minutes, at which time the vertical extrusion or intrusion of the set formulation in the test tube was measured with the micrometer slide cathetometer. The vertical change was used to calculate the percent expansion or contraction relative to the premeasured internal length of the test tube.

2.1.2. Compressive and Splitting Tensile Strength

Cylindrical dental composite samples 16 mm long and 8 mm
in diameter with parallel flat ends were used for compressive tests. Each sample was placed in a universal testing machine (Model TT-C, Instron Corp., Canton, MA) and loaded under compression at a cross-head speed of 0.01 in/min until fracture. The compression yield point and the compressive strength at fracture were determined from the load/strain curves of the chart recorder.

Compressive tests for polymer mortar followed the ASTM C-116 Standard. Cylindrical specimens 7.62 cm diameter by 10.16 cm length (3"x4") were loaded axially on an Instron universal testing machine at a cross-head speed of 0.01 in/min until failure. The (engineering) compressive strength was obtained by dividing the loading-at-fracture by the specimen cross section.

Splitting tensile tests for polymer mortar were performed on the same size cylindrical specimens in accordance with the ANSI/ASTM C-496 Standard. The cylinders were subjected to transverse crushing loadings at a cross-head speed of 0.01 in/min. The splitting tensile strength $T$ was given by:

$T = \frac{2P}{3.14 DL}$

Where $P$ is the load at fracture, $D$ is the specimen diameter and $L$ its length.

2.1.3. Flexural Tests
These were performed also on the Instron testing machine, in accordance with the ANSI/ASTM D-790 Standard. Bar shaped specimens 21.59x3.81x1.27 cm (8.5 x1.5 x 0.5 inches) were subjected to 3-point flexural loading at a constant rate until failure. Their flexural strength was calculated from:

\[ F = \frac{3PL}{2bd^2} \]

Where \( L \) is the span between supports and \( b \) the respective width and depth of the specimen.

2.1.4. Hardness test

The cylindrical dental composite sample 16.0 mm long and 8.0 mm in diameter was used for hardness test before the compressive strength tests. The flat side surface was smoothed using 600 grit silicon carbide backed paper and then polished with 6 micron diamond polishing paste (Metadi, Buehler Ltd.) in an automatic metallographic polisher (Automet, Buehler Ltd.). Five Knoop hardness measurements were made on this polished surface using as automatic microhardness machine (Model DM-400 FT, Leco Corp.) under 200 g load.

2.1.5. X-ray Diffraction

Changes in the crystal structure of MMT were investigate by X-ray diffraction in an automated Phillips Diffractometer (X-ray diffraction unit, type 12045, with a Phillips wide range goniometer type 42201); these were connected to an Apple II computer, which was programed for regression analysis,
extended spectrum display, and curve fitting.

Montmorillonite in powdered form was compacted into the cavity of a metal specimen holder, which was then mounted in the diffractometer. When MMT was modified by ammonia, the same metal plate specimen holder was used, but the top was covered with X-ray quality mylar film.

2.1.6 Scanning Electron Microscopy

The flat surface of dental composite sample 16.0 mm long and 8.0 mm in diameter was mounted and polished as described in III-2.1.7.1. It was then highly polished with 0.05 micrometer size deagglomerated alumina (Gamma Micropolish II, Buehler Ltd., Lake Bluff, IL.). After rinsing with ethanol and ultrasonically cleaning in a bath of Freon 113 for two minutes, the sample was sputter coated with gold and examined for porosity using scanning electron microscopy (SEM, Model JSM820, JEOL Ltd.).

2.1.7. Phase Separation Studies

2.1.7.1. Optical microscopy

In the optical microscope an image is produced by the interaction of light and an object or specimen. The image can reveal fine detail in or on the specimen at a range of magnifications from 2x to 2000x. Resolution on the order of 0.5
μ is possible, limited by the nature of the specimen, the quality of the microscope optics and ultimately the wavelength of light. The O.M. studies of this work were conducted on a Zeiss microscope.

Polishing is an important step for this microscopic work. Polishing specimens can produce artifacts at each stage of the preparation. Cutting the specimen and final polishing are the steps with the greatest potential for artifacts. The initial cutting can cause the formation of microcracks which can be misinterpreted as voids or cracks in the specimen. In order to limit such cracking, the specimen should be rough cut several inches from the surface of interest and then cut more carefully, with a water cooled diamond saw, near that region. Grinding should be done with gentle pressure on the mount and should never be done dry. Each successive grit should be removed. Cleaning of the specimen is also important as larger grits or polishes on the specimen can contaminate the fine polishing cloth. A 30 seconds ultrasonic rinse in water followed by drying off with a can of Freon gas is adequate to remove the grit. As the specimen is ground on each of the successively finer papers, it is turned 90 degree so that the new scratches are clearly visible compared to coarser scratches being replaced. Water flowing over the grinding papers keeps the specimen from heating up and also carries the debris away. Polishing is conducted using graded alumina suspensions in
water (1, 0.3 μ), chromium oxide slurries or diamond paste suspended in oils.

In this work, thin slice disc specimens 8.0 mm in diameter and 0.5 mm in thickness were cut by a low speed diamond saw from cylindrical copolymerized specimens, prepared by the procedures of in III-1.5.3. A layer about 3 mm thick of fast cure-epoxy was spread on the surface of a glass slide, thin disc specimen was then mounted on glass slide, and moderate pressure was applied on the top of the disc specimen by a thin rod 2 mm in diameter to make the disc specimen totally immersed in the epoxy layer. Care was taken to make the thin epoxy layer between the glass slide and disc specimen as thin as possible and to excluded air bubbles in the thin epoxy layer between the glass slides and the disc specimen. The mounted thin disc specimen was left at room temperature for over 24 hours to harden; then it was polished down to a thickness of 30 to 40 μ, first by 600 grit silicon carbide backed paper, then with one micron size Al₂O₃, and finally smoothed with 0.3 μ diamond polishing paste (Metadi, Buehler ltd., Lake Bluff, IL) in an automatic metallographic polisher. After polishing, samples were quickly rinsed with ethanol and ultrasonically cleaned in a bath of Freon 113.

To obtain further information about the phase separation process, another type of microscopy study was carried out. A
droplet of uncured resin with the specified composition was cured between two thin glass cover slides in a hot stage, attached to a Polarizing Microscope. This is a microscope with a polarizer located below the condenser, and an analyzer located above the objective. When ordinary light passes the polarizer, its electromagnetic waves become oriented along the polarizer axis with the polarizer and analyzer parallel to each other, the light transmitted by the first polarizer is also transmitted by the second. When the second polarizer is rotated 90 degrees (crossed with the first polarizer), no light gets through. When viewed between crossed polarizers, isotropic matters will be dark. Anisotropic, or birefringent matter can be picked up in the crossed polarized light field since the transmitted polarized light is twisted (or partially twisted) by the anisotropic matter before its light reaches the second polarizer. Therefore some light is transmitted through the second, crossed polarizer.

2.1.7.2 Density measurements

Densities of both the liquid uncured resins and the solid cured systems were measured on a Specific Gravity Chain balance (Troemner Inc., model S-100, Phila., PA). The balance has a accuracy to 0.0001 g/cc. All measurements were carried out at 20°C. The specific gravity of solid was calculated by following equation:

Specific gravity (g/cc) = (W1-W2)/[(W1-W2)-(W3-W4)]
W1: reading of basket in air without sample.
W2: reading of basket in air with sample in it.
W3: reading of basket in water without sample.
W4: reading of basket in water with sample in it.

2.1.7.3 X-ray Diffraction, Infrared Spectroscopy

Phase separation in the cured system was investigated by X-ray diffraction (same X-ray diffractometer used in 5.2). A droplet of uncured resin of zero-shrinkage formulation was cured between thin cover glass slides. By controlling the curing temperature, (hence the resulting cure rate) two different cured films were obtained: one was opaque due to phase separation, the other remained transparent (single phase). The top cover glass was removed by a surgical knife before the cured film was mounted on the X-ray diffractometer.

Cured systems with and without phase separation were also investigated by infrared spectrometry. The KBr disk method was employed since the cured system with phase separation was crosslinked and could not be put in solution.
CHAPTER IV: RESULTS AND DISCUSSION

1. CHEMISTRY OF MONTMORILLONITE

1.1. Crystal Structure

Montmorillonite is a phyllosilicate clay mineral of the smectite group. The generally accepted structure shown in Fig.2.1.1., was first proposed by Hofmann, Endel and Wilm (1933), modified by later suggestions of Marshall (1935), Maegdefrau and Hofmann (1937), and Hendricks (1942). According to this concept MMT is composed of an octahedral alumina sheet, sandwiched between two sheets of inward-pointing linked silica tetrahedra. These sheets are so arranged that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to adjacent layers are oxygens instead of hydroxyls. The layers are continuous in the a and b directions and are stacked one above the other in the c direction. Due to the fact that the alumina sheet is sandwiched between two silica sheets (2:1 type mineral), Oxygen layers of each unit are adjacent. Consequently there is a very weak bond and an excellent cleavage between them. MMT shows extensive interlayer expansion (swelling) due to its structure. Water and other polar molecules can enter between the unit layers, causing the crystal to expand in the c-direction. Most naturally occurring montmorillonites contain
Fig. IV-1.1: schematic representation of the MMT crystal structure.
large amounts of water.

1.2. MMT-Water Interaction

Water is present in MMT usually in two forms: (1) absorbed water, present in pores, on surfaces, and around the edges, (2) interlayer water, semiordered between the crystalline layers. Type 1 water requires generally very little energy for its removal, which can be accomplished by drying with a dessicant at room temperature. Type 2 water requires substantial energy (i.e. higher temperature) for its removal (Grim, 1968).

Swelling of MMT due to water uptake occurs in two stages. Water is adsorbed in successive monolayers on the mineral surfaces and pushes the particles or layers of MMT apart. In this stage, the principal driving force in the adsorption energy of the water layers on the clay surface. The increase in c-spacing with increasing in interlayer adsorption is shown in Table IV-1.2. Most naturally occurring montmorillonite contain between 3 and 4 water interlayers.

In the secondary stage, the swelling is due to doublelayer repulsion, whereby the particles or layers may be pushed further apart. This is also known as the osmotic swelling stage. In the primary stage, the layers part during the adsorption of water molecules, and cations originally located
Table IV-1.2: Effect of Hydration Water Content on the Interlayer Spacing of Pure MMT Crystal.

<table>
<thead>
<tr>
<th>No. of water layers</th>
<th>Total thickness of water layer (A)</th>
<th>C-spacing of crystal (A)</th>
<th>Density of ordered water (gm/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
<td>12.5</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>14.5</td>
<td>1.01</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>17.5</td>
<td>0.95</td>
</tr>
<tr>
<td>4</td>
<td>10.5</td>
<td>20.5</td>
<td>0.96</td>
</tr>
</tbody>
</table>
in the tetrahedral holes of the dry mineral leave the holes during water adsorption. The expansion in the c-direction in the primary stage in thus due to: (a) hydration of the interlayer cations, and (b) hydration of the exposed clay surfaces. The relative importance of these two types of interaction in the primary stage is debatable. Nagelschmidt (1936) and Barshad (1955) suggested that during the initial adsorption of water on MMT, the water molecules remain on the outer surfaces, whereas Marshall (1936) and Mering (1946) maintain that a uniform hydration of all exchangeable cations occurs first. Another model which represents a compromise between the above two extreme approaches was proposed by Hendriks et al. (1940). They suggested that in the primary stage, the Ca+ ions are hydrated first, whereas in the Na-clay the initial adsorption of water molecules is on the external surfaces. Low et al. (1970) have found out that during the adsorption of water, the b dimension of the unit cell changes also. This change is attributed to forces exerted by hydrogen-bonded water molecules in epitaxial arrangement with tetrahedral oxygen atoms. The effect is strongest at monolayer coverage and decreases with subsequent layers.

In the primary stage the net energy of interaction is not only due to the hydration energy but also due to van der Waals attraction between the layers and electrostatic interaction of charged surfaces and cations. At any given
stage of hydration, the cations either remain embedded in the hexagonal holes of the silica sheets, as they are in the dry state of the clay, or they leave the holes and assume positions midway between the layers. In the first case, the electrostatic interaction is a repulsion, in the second case an attraction.

It is known that when ions remain associated with the layer surfaces, the electrostatic repulsion is small and to some extent compensates for the small van der Waals attraction. Hence the overall force is a net repulsion, primarily due to hydration energy of the surface. This surface hydration energy is partly due to hydrogen bond formation between absorbed water molecules and surface oxygen atoms, and partly due to interaction of the water dipoles with the cations assume midway positions, the attractive energy will be substantial, which results in high hydration energy (electrostatic attraction + small van der Waals attraction). But in this arrangement, the relatively large cation-dipole interaction energy is available through cation hydration, although not even the full bulk cation hydration energy is involved in the confinement of interlayer space.

The water molecules held directly on the surfaces of MMT particles are in a state different from that of liquid water (Low, 1961). They have an ice-like arrangement and
are present mostly on the flat surface of MMT particles, with a thin film one the surface of the pores and where adjacent MMT particles come together. The presence of this water in an organized arrangement has been explained by several workers on the basis of dipole character of water molecules. Terzaghi (1928) suggested that the initial layer of water consists of water molecules all oriented in the same direction. The positive ends of the water point towards the negatively charged MMT surface, while the negative ends extend outward which itself acts as a surface of negative charge on which can be built another layer of completely oriented water molecules. Owing to the fact that the water molecules possess thermal energy and tend to be in a state of continuous motion, a definite oriented thickness is always maintained, with the degree of orientation decreasing outward as the relative effect of thermal motion becomes greater. Low (1961) considered the charge distribution of water molecules as a tetrahedron with two positive and two negative corners. The resultant centers of positive electricity lie between the protons whereas the resultant centers of negative electricity lie near the oxygen nuclei on the side next to the protons. When two water molecules approach each other, there is electrostatic attraction between the positive tetrahedral corner of one molecule and the negative tetrahedral corner of the other; that is, there is an electrical interaction between the proton of the former and the lone electron of the
latter. Since the proton of the hydrogen is involved, the bond is called hydrogen bond. Each water molecule forms four hydrogen bonds in each tetrahedral corner. This results in each molecule being hydrogen-bonded to four neighboring water molecules which surround it tetrahedrally. In ice, the water molecules which exist in fixed positions, with each molecule tetrahedrally coordinated to four others. When ice melts, there is an increase in density; similarly the high degree of hydrogen bonding decrease temperature.

Owing to the fact that the surface of MMT are made up of either oxygen atoms or hydroxyl groups arranged in a hexagonal pattern and the crystal lattice contains excess electrons (due to isomorphous substitution), the water molecules adjacent to the MMT surfaces form a covalent hydrogen bond with the oxygen atoms of the surface. The existence of covalent bonds alters the electron distribution in these molecules which then form additional covalent bonds with other molecules in the same and next layers. Due to the directional properties of the bonds, the bonded water molecules are arranged in a tetrahedral fashion.

Hendricks and Jefferson (1938) suggested that a water layer is composed of water molecules joined into hexagonal groups of an extended hexagonal net; as shown in the projections in Fig. IV-1.2.1. and Fig IV-1.2.2. This is due
partly as a result of tetrahedral distribution of charge about a water molecule, two corners of the tetrahedron being occupied by hydrogen atoms and the other two corners by an excess of electrons. Each side of the hexagon corresponds to a hydrogen bond, with the hydrogen of one water molecule being directed towards the negative charge of the neighboring molecule. One-fourth of the hydrogen atoms, or a hydrogen atom of half of the water molecules, are not involved in bonding within the net. The net is tied to the surface of the clay minerals by the attraction between those hydrogen atoms not involved in bonding within the net and the surface oxygen layer of the clay mineral unit. When the surface of the clay mineral contains hydroxyl groups, some of the hydroxyl are free for bonding through hydrogen to oxygen atoms in the water layer.

A second mechanism by which water is attracted to a MMT surface is by hydration of exchangeable cations. Due to isomorphous substitution on oxygen ions of octahedral net, there is a negative charge on the MMT surface. This causes the first water molecule to be sorbed precisely on these oxygen ions with the formation of a hydrogen bond of the long hydroxyl type. Due to the formation of a hydroxyl bond, the hydrogen of a water molecule is drawn onto an oxygen ion of the octahedron causing saturation of the oxygen valency, which, with subsequent hydration, cause displacement of the
Fig.IV-1.2.1: Arrangement of Oxygens and Hydrogens in Water net, after Hendricks and Jefferson (1938).
Fig.IV-1.2.2: Configuration of Water Net Proposed by Hendricks and Jefferson (1938) Showing the Bonding through Hydrogen to the adjacent Clay Mineral Surfaces.
sorbed cations. The second hydrogen of these water molecules form active centers in the development of hydrate layers. Further sorption of water is followed by coordination of the sorbed cations. Fig. 2.2.3 shows the structure of MMT with all the bonds formed by the interlayer water (Eirish and Tretyakova, 1970).

It has been observed (Brindley and Hoffmann, 1962) that aliphatic molecules with strongly polar groups are oriented in such a way that the zigzag plane is parallel to the silicate sheet and those molecules without polar group perpendicular to the silicate sheet. Greene-Kelly (1955) observed that at low concentrations, the aromatic rings of the organic compounds are oriented parallel to the silicate sheets, but at higher concentrations become perpendicular to the silicate sheets. Emerson observed the formation of O-H…..O-Si hydroge bonds between adsorbed alcohol molecules and surface oxygen ions; but it has been found that cation-dipole interactions are more important than the surface -molecules O-H….O type bonding for adsorption.
2. MODIFICATION OF MONTMORILLONITE

2.1. Process for Exchange of H₂O with NH₃

The procedure for replacing part of the hydration water in naturally occurring MMT with ammonia starts with utilizing partial vacuum (0.04-0.05 MPa absolute pressure) with continuous agitation of the MMT powder to remove hydration water at temperature from 40 to 100 °C. Partial dehydration of the mineral is followed by introduction of gaseous ammonia at slightly higher pressures (0.07-0.08 MPa absolute Pressure) and equilibration of the modified mineral for a minimum of 1 hour while the system cools, prior to venting to the atmosphere. The amounts of water lost and ammonia gained at different temperatures were monitored by weighing the MMT before and after exposure to gaseous NH₃; the corresponding structural changes were assessed by X-ray diffraction measurements of the interlayer spacing (C-spacing) in MMT structure. The bench-scale setup for the introduction of NH₃ in MMT is shown in Fig. IV-2.1.

2.2. H₂O and NH₃ Contents of Modified MMT

Table IV-2.2. shows C-spacing X-ray diffractometry measurements of the systems in the replacement of MMT hydration water with ammonia at different temperatures. It can be seen that as temperature increases, the amount of
Fig.IV-2.1: Apparatus for preparation of ammonia-MMT.
<table>
<thead>
<tr>
<th>MMT Temp. (*C)</th>
<th>$H_2O$ lost (g/100gMMT)</th>
<th>c-spacing (Å)</th>
<th>NH$_3$ gained (g/100gMMT)</th>
<th>c-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ambient (25)</td>
<td>0.0000</td>
<td>12.9986</td>
<td>4.6973</td>
<td>12.6233</td>
</tr>
<tr>
<td>40</td>
<td>0.1752</td>
<td>11.7556</td>
<td>5.0354</td>
<td>12.5052</td>
</tr>
<tr>
<td>60</td>
<td>1.1117</td>
<td>10.2816</td>
<td>4.8654</td>
<td>12.5028</td>
</tr>
<tr>
<td>100</td>
<td>3.3365</td>
<td>10.0712</td>
<td>3.9422</td>
<td>12.3458</td>
</tr>
</tbody>
</table>

Table IV-2.2: Substitution of hydration water in MMT with ammonia at different temperatures.
interlayer hydration water lost increases when temperature increases, and the C-spacing, (the spacing between adjacent oxide layers in MMT crystal), decreases. When ammonia is introduced into the system the C-spacing is restored to the level of the original hydrated crystals. Thus indicates that the spaces left by the lost hydration water are now refilled by ammonia. Due to the similarity in molecular size between water and ammonia, the C-spacing is about the same when the interlayer is occupied by ammonia molecules compared to hydration water molecules. There is a broad maximum in the amount of ammonia gained by the mineral at temperatures from 40°C to 60°C under 0.05 MPa absolute pressure. At higher temperatures, the extent of water removal is sufficient to effect complete dehydration, thus collapsing the interlayer spacing to an extent that allows direct bonding between the neighboring silica layers. This impedes the ingress of ammonia molecules and reduces the number of sites, to which these species can attach via coordinate bonding. Consequently the amount of ammonia gained by the mineral decreases. We chose 50°C as the optimal temperature for this preparation. The material obtained by this process is stable at temperatures up to ca. 50°C. At higher temperatures there is gradual release of ammonia, which increases in both rate and extent, becoming most pronounced at 75-80°C. Measurements of the amounts of ammonia released at different temperatures in the 50-80°C range indicate that the ammonia-modified MMT should effect
cure-shrinkage control in polymerization systems that attain peak exotherm temperature of at least 60°C.
3. PROPERTIES OF POLYMER MORTAR AND POLYMER CEMENT WITH NH$_3$-MMT

3.1. Cure Shrinkage and Expansion

Fig IV-3.1.1. shows the amount of cure-shrinkage observed in acrylic mortar specimens with different contents of ammonia-modified MMT, cured at ambient temperature (25 °C) for 30 minutes, with peak exotherms of ca. 80 °C (Curve A). These systems show a zero cure-shrinkage range at 7-10 percent MMT by weight of resin. Similar measurements are shown in curve B for specimens, prepared with natural MMT and cured at 85 °C, with peak exotherms of 130-140 °C.

These data indicate that ammonia-modified MMT is less efficient in counteracting cure shrinkage than natural MMT, 7-10 percent by weight being required to produce zero shrinkage systems, as compared to 3 per cent. This is not surprising since only part of the hydration interlayer water is replaced with ammonia in ammonia-modified MMT. However, the greater volatility of ammonia causes the modified MMT particles to dilate at much lower temperatures (60-80°C, compared to 120-140°C for natural MMT).

3.2. Cure Shrinkage Control Mechanism

In order to confirm that the cure-shrinkage control action of ammonia-modified MMT involved dilatation of the individual
Fig. IV-3.1.1: Cure shrinkage and expansion of polymer cement systems at different MMT content.
MMT particles and to ascertain whether the process entails the release of volatiles outside the mineral particles, we examined the interior surfaces of several cast specimens by means of Scanning Electron Microscopy. These specimens were prepared from the acrylic cement formulations shown in Table 4.6. using ammonia-modified MMT with a narrow particle size distribution, obtained by screening the mineral particles between a 325 and 400 mesh sieve. They were subjected to two different cure regimes: 30 minutes at 25°C (conditions generating peak exotherms of 80-85°C which fully release the ammonia from ammonia-modified MMT) and 24 hours at 5°C (conditions at which the exotherm does not exceed ambient temperature and the mineral remains inert). The specimen surfaces were prepared by cutting with a diamond saw, followed by careful polishing, and viewed at low magnifications (ca 300x). Over 100 particles were measured. The average diameter of the activated MMT particles (in the specimens cured at 25°C) was 21.56 μ average, compared to 15.94 μ average for the inert MMT particles (in the 5°C-cured specimens). This is a 35% increase in average particle diameter and corresponds to over 100% increase in the volume of the activated MMT particles.

These experiments indicate that the mechanism of cure shrinkage control with MMT is the same as with the natural MMT mineral: it involves dilatation of the MMT particles, caused
by gaseous ammonia, which is liberated from the interlayer space of the crystal but remains trapped inside the MMT particles embedded in the polymerizing resin. The process is shown schematically in Figure IV-3.2.1 and IV-3.2.2. The ammonia release is due to the disruption of the coordination bonds with the SiO₂ layers. This is an endothermic reaction, which occurs to progressively higher extents over the temperature range of 60-80°C. The heat for this reaction is supplied by the polymerization exotherm of the resin. Consequently the temperature, reached by the curing system at peak exotherm is an important parameter in determining the amount of cure shrinkage shown by a system with a given MMT content, since it establishes the amount of generated volatiles and the resulting dilatation of the MMT particles. For example, a polymerization system that exceeds 80°C at peak exotherm, will achieve maximum dilatation of the ammonia-modified MMT particles and thus will require less MMT to reach zero cure shrinkage, compared to a similar system with a peak exotherm of only 70°C, which would experience lower particle dilatation. For every resin system with a specific chemical composition the peak exotherm temperature is affected by several variables: the polymerization rate (controlled by the ambient temperature and the amounts of initiator and promoter in the resin), the relative mass of reactive and inert components in the system (resin-to-filler ratio), and the rate of unsteady-state heat transfer from the
Fig. IV-3.2.1: Structure of MMT particle.
Fig.IV-3.2.2: The dilatation process of MMT particle.
curing specimen which is controlled by its size and shape, as well as the material and temperature of its mold. It should, therefore, be noted that the data shown in Fig. IV-3.3 are specific for the specimen formulations, sizes, shapes, and molding conditions, indicated in Table IV-3.2. Nevertheless, the reported measurements establish the effectiveness of ammonia-modified MMT in eliminating cure shrinkage in acrylic resin systems at ambient temperature polymerizations.

3.3. Strengths of the Cured Systems

Table IV-3.3 shows the compressive, flexural, and splitting tensile strengths of the acrylic cement and mortar specimens containing 8.5 and 7 per cent ammonia-modified MMT respectively. These are zero-shrinkage systems in which the setting stresses should be minimum. They are compared with corresponding "ordinary" acrylic compositions, in which the MMT has been replaced with an inert clay (kaolinate). In these systems the resin shows cure shrinkage of ca. 2.5 percent and the highly filled mortar is expected to develop setting stresses. Indeed the strengths of the zero-shrinkage systems are significantly higher than those of the corresponding "ordinary" systems. As expected the greatest strength enhancement is seen in the flexural and splitting tensile strengths.
TYPES OF COMPOSITES INVESTIGATED

**Acrylic Cement:** resin system w/initiator and promoter and varying amounts of NH$_3$/MMT

**Acrylic Mortar:**
- Acrylic cement: 17 weight \%
- Mineral Aggregate: 83 weight \%

SPECIMEN SIZE AND SHAPE:

Cylinders, 16 mm in diameter by 30 mm long.

---

Fig.IV-3.2: Size and shape of the systems investigated.
<table>
<thead>
<tr>
<th>Composition of specimens</th>
<th>Compressive Strength (MN/m(^2))</th>
<th>Splitting Tensile Strength (MN/m(^2))</th>
<th>Flexural Strength (MN/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic cement w/8.5% NH(_3)/MMT</td>
<td>99.56±11.12</td>
<td>13.06±1.48</td>
<td>41.97±3.58</td>
</tr>
<tr>
<td>Acrylic cement w/kaolinite</td>
<td>82.45±5.45</td>
<td>9.23±1.44</td>
<td>32.76±1.4</td>
</tr>
<tr>
<td>Difference</td>
<td>21%</td>
<td>42%</td>
<td>28%</td>
</tr>
<tr>
<td>Acrylic mortar w/7% NH(_3)/MMT</td>
<td>50.06±3.08</td>
<td>6.37±0.35</td>
<td>27.55±1.94</td>
</tr>
<tr>
<td>Acrylic mortar w/7% kaolinite</td>
<td>44.27±1.56</td>
<td>5.32±0.49</td>
<td>19.48±0.82</td>
</tr>
<tr>
<td>Difference</td>
<td>13%</td>
<td>20%</td>
<td>41%</td>
</tr>
</tbody>
</table>

Fig.IV-3.3: Strengths of cured acrylic cements and mortars.
4. PROPERTIES OF DENTAL RESTORATIVE COMPOSITES

4.1. Cure Shrinkage

Table IV-4.1 shows the average values and (standard deviations) of linear polymerization shrinkage/expansion obtained from specimens, prepared according to section III 5.2. These values were calculated on the basis of the 75.0 mm initial specimen length. Fig. IV-4.1 is a plot of the per cent linear change during polymerization as a function of weight per cent ammonia-modified MMT added to the unfilled resin system. Zero polymerization shrinkage occurs in the BIS-GMA system when 4 to 5 per cent ammonia-modified MMT is added.

Chemically cured resins have been used as direct dental restoratives for many years. The amount of heat released due to the polymerization exotherm of a volume of resin the size of a typical restoration has not been demonstrated to adversely affect pulp vitality. The experimental resin system evaluated in this study cures at ambient temperatures in 7-10 minutes, with peak exothermal temperature of 75-80 °C. The mechanism of cure shrinkage control with both natural and NH3/MMT utilizes the dilatation of the MMT particles. This dilatation is caused by the release of H2O vapor or NH3 gas from the layered crystals inside the MMT particles embedded in the polymerizing resin. This is an endothermic reaction which occurs
Fig.IV-4.1: Percent volume change of dental resin at different MMT content.
<table>
<thead>
<tr>
<th>Percent MMT</th>
<th>Dimensional Change (mm)*</th>
<th>Percent Volume Change **</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>- 1.1252 [0.0008]</td>
<td>- 1.50</td>
</tr>
<tr>
<td>2</td>
<td>- 0.4506 [0.0005]</td>
<td>- 0.60</td>
</tr>
<tr>
<td>4</td>
<td>0.0076 [0.0005]</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>- 0.0372 [0.0008]</td>
<td>- 0.05</td>
</tr>
<tr>
<td>8</td>
<td>- 0.1126 [0.0005]</td>
<td>- 0.15</td>
</tr>
</tbody>
</table>

* N = 5. Standard deviations are in brackets.

** Based on initial length of 75.0 mm.

Table IV-4.1: Percent volume change of BIS-GMA resin system at different MMT contents.
progressively over a temperature range: 100-145°C for water and 45-80°C for ammonia. The heat for this reaction is supplied by the polymerization of the resin. Consequently, the temperature of the curing system at peak exotherm is an important additional parameter in determining the amount of cure shrinkage (or dilatation) shown by a system with a given MMT content since it establishes the amount of generated volatiles and the resulting degree of dilatation of the MMT particles.

For every resin system with a specific composition, the peak exotherm temperature is affected by several variables: the polymerization rate (controlled by the initiation temperature and the amount of initiator and promoter in the resin), the relative amounts of reactive and inert mass in the system (resin to filler ratio), and the rate of unsteady-state heat transfer from the curing specimen to its surroundings, which depends on specimen size and shapes used. Controlling polymerization shrinkage in composite samples the size of typical dental restorations would require recalculation of the amount of MH₃/MMT to be added. This is because significantly less exotherm would be present in a small sample (compared to the sample used in this study), and the shape of a restoration is geometrically unlike the cylindrical samples prepared.

4.2. Mechanical properties
The mean values and standard deviations of compression yield point, compression strength at fracture and Knoop hardness determined for the composite formulations are presented in Table IV-4.2.2. The Tukey HSD interval at the 95 percent confidence interval is 859 psi for the compressive yield point, 1234 psi for compressive strength, and 0.8 kg/mm$^2$ for Knoop hardness. Using this interval to compare pairs of means, vertical lines in Table IV-4.2.2. indicate no significant difference ($p < 0.05$). There was no significant interaction.

Porosity was not detected in any of the composite samples with SEM up to a magnification of 10,000x. A SEM photomicrograph of experimental composite number 6 at 1000x magnification is presented in Fig. IV-4.2.1.

The 32,087 psi compressive strength of Group 6 experimental composite, containing 30 percent HA filler and 15 percent FA filler, compare favorably with that reported for dental composite resins, 34,000 to 34,400 psi. (Phillips, 1982. Craig, 1989). The filler in a composite has the greatest impact on the mechanical properties and typical dental composites currently commercially available to the practicing dentist contain about 80+ weight per cent filler (Craig, 1985). The filler system used for the experimental composite in this study, hydroxyapatite and fluoroapatite, is not used in dental
<table>
<thead>
<tr>
<th>Component</th>
<th>Experimental Composite Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Bis-GMA</td>
<td>27.13*</td>
</tr>
<tr>
<td>MMA</td>
<td>36.17</td>
</tr>
<tr>
<td>PMMA</td>
<td>9.04</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>9.74</td>
</tr>
<tr>
<td>DEGDMA</td>
<td>9.74</td>
</tr>
<tr>
<td>BPO</td>
<td>0.42</td>
</tr>
<tr>
<td>DMPT</td>
<td>0.28</td>
</tr>
<tr>
<td>LZ33</td>
<td>3.48</td>
</tr>
<tr>
<td>MMT</td>
<td>4.00</td>
</tr>
<tr>
<td>Filler</td>
<td>0.00</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

* Values in grams

Table IV-4.2.1: Formulation of experimental composites.
Fig. IV-4.2.1: SEM picture of dental composite.
<table>
<thead>
<tr>
<th>Experimental Composite Number</th>
<th>Filler Content (Weight Percent)</th>
<th>Compressive Yield Point (psi)</th>
<th>Compressive Strength (psi)</th>
<th>Knoop Hardness Number (kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>13,680 [240]*</td>
<td>**</td>
<td>18.8 [0.4]</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>14,672 [640]</td>
<td>**</td>
<td>19.2 [0.3]</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>16,780 [160]</td>
<td>**</td>
<td>19.5 [0.2]</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>18,280 [220]</td>
<td>22,380 [630]</td>
<td>22.2 [0.2]</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>18,650 [120]</td>
<td>30,460 [420]</td>
<td>24.2 [0.5]</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>19,894 [169]</td>
<td>32,087 [398]</td>
<td>25.1 [0.5]</td>
</tr>
</tbody>
</table>

* Standard deviations are in brackets. Vertical lines represent no significant differences (p<0.05). The Tukey interval at the 95% confidence interval is: 860 psi for compressive yield point, 1200 psi for compressive strength, and 0.8 kg/mm² for Knoop hardness.

** Samples with less than 30 weight percent filler did not fracture on compression.

Table IV-4.2.2: Mechanical properties of experimental composites.
composites and has a wide range of particle shapes and sizes, as seen in Figure 8.2. The compressive strength of the experimental composite would be significantly larger if the filler content and particle size distribution used were comparable to that of present day dental composites. This would be due to the elimination of internal stresses, which are present in commercial dental composites because of the polymerization shrinkage.

The compressive strength is also affected by the type and amount of the coupling agent used, polymer crosslinking density, and the curing condition. A zirconate coupling agent was used (LZ 33) specifically formulated for the type of filler and resin in this study. This coupling agent, due to its multi-functional groups molecular structure, acts as a coupling agent between the inorganic fillers and the organic groups as well as a crosslinking agent among the organic groups (Monte, 1985). Vinyl silane coupling agents are more appropriate if silica (quartz or glass) fillers are used.

Knoop hardness values range between 25 kg/mm² for microfilled composite resins and 55 kg/mm² (Monte, 1985). The values obtained for the experimental composite ranged between 18.8 and 25.1 kg/mm² for Group1 and 6, respectively. The lower values for the experimental composites are due to the low filler content as compared to commercially available
dental composites. The usefulness of hardness numbers is of questionable value in predicting the abrasion resistance for any material.

Porosity was not visually detected in any of the experimental composites up to the resolution limits of the SEM, about 10,000x magnification. The experimental composites resin deteriorated rapidly at that magnification due to the high energy electron beam, which prevented taking a high magnification photomicrograph without artifact.

The ammonia gas that is released within the NH$_3$/MMT particles interlayers does not escape from the particles into the surrounding resin. Rather, it is retained within the NH$_3$/MMT particles and is responsible for their expansion, which counters the polymerization shrinkage of the resin. If the gaseous ammonia were released from the NH$_3$/MMT particles into the resin, porosity would have been detected in the cured composites during SEM examination and polymerization shrinkage would not have been successfully controlled.

This work has demonstrated that constant volume polymerization can be attained with the BIS-GMA resin by addition of precise amounts of NH$_3$/MMT. However, further study will be necessary before this system can be applied to
dental composites. The NH$_3$/MMT system depends on the resin polymerization exotherm, which depends on the volume of resin curing. Since the volume of typical Class II composite restoration is much smaller than the volume tested in this study, the exotherm will be different and the amount of NH$_3$/MMT necessary for polymerization control will be different.

Microleakage of a NH$_3$/MMT modified dental composite in extracted teeth should be measured, as should the amount of heat transferred to the pulp chamber of extracted teeth during cure of NH$_3$/MMT modified experimental composite. It should be determined if traces of ammonia are released from a MH$_3$/MMT modified experimental composite during or after cure.
CHAPTER V. RESULTS AND DISCUSSION: CURE SHRINKAGE CONTROL BY PHASE SEPARATION

1. ACRYLIC SYSTEMS CURING WITH PHASE SEPARATION

1.1 Cure Shrinkage and Phase Separation

The acrylic systems used in this study contain two copolymerizing components: (a) triethylene glycol dimethacrylate (TEGDMA), and (b) methyl methacrylate (MMA), containing 30% by weight linear poly(methyl methacrylate) (PMMA). The two components were mixed in different proportions and their densities were measured throughout the range of compositions before and after cure. In all proportions the uncured systems are mutually soluble forming a single, transparent phase. Two types of cure were effected: slow cure over a 12-hour period at ambient temperature; and fast cure, obtained at ambient temperatures by increasing the amount of initiator and promoter.

The densities of all these systems (raw resins, slow-cured, and fast-cured) are plotted in Fig V-1.1. The data along line A show the linear increase in density of the uncured system with increasing TEGDMA content. When all of these systems are allowed to cure slowly (over a 12-hour period) they maintained a single phase, forming transparent polymer and showing considerable shrinkage (line B). At 0% TEGDMA
Fig.V-1.1: Densities of acrylic systems consisting of TEGDMA & a 30% solution of PMMA in MMA.
Curve A: uncured systems (single phase)
Curve B: cured over 12-hour period (single phase)
Curve C: cured within 5 minutes.
the cure shrinkage is 17.5%. Shrinkage decreases linearly with TEGDMA content, becoming 14.4% at 100% TEGDMA. Throughout this range the measured cure shrinkages are consistent with calculated values from the molecular weights of the respective monomers and polymers. When systems containing 20-70% TEGDMA are polymerized rapidly a second phase precipitates during the cure and the polymerization shrinkage decreases considerably. Curve C shows the densities of systems with cure times of 5 minutes or less. At the mid points of this composition range (30 to 40% TEGDMA) cure shrinkage is eliminated and a small (ca. 0.5%) increase in volume is observed in the cured systems. The resulting polymers are white and opaque due to the large number of interdispersed microphases.

1.2 Effect of Chemical Composition

Fig.V-1.2.1 is a photograph of a set of rapidly polymerized systems covering the entire range of TEGDMA contents at increments of 10%. That is, the first one on the left contains 0% TEGDMA, the second 10%, and so forth, with the last one being pure TEGDMA. At 0% TEGDMA the system is simply PMMA, containing preexisting as well as newly formed linear polymer. It maintains a single phase throughout its cure and shows the expected cure shrinkage of 14.6% (70% of the 21% shrinkage of MMA-PMMA since the monomer contains 30% dissolved polymer). In the second sample, containing 10% TEGDMA the rapidly cured
Fig. V-1.2.1: Rapidly polymerized systems covering the entire range of TEGDMA contents at increments of 10%.
polymer is still transparent but not as clear as the pure PMMA and shows a significantly lower cure shrinkage: 10% vs. 13.5% for the slowly polymerized system with the same composition. In the third sample, which contains 20% TEGDMA the cure-shrinkage is decreased to ca. 4% and the cured polymer shows an interesting appearance with soybean-size, white, opaque domains formed in the transparent polymer matrix. Thin section transmission OM pictures of this cured system (Fig.V-1.(2-5.) at different magnifications (X100, X200, X500, X800) show that the soybean-size opaque regions are composed of clusters of much smaller, opaque microdomains that appear to precipitate from the transparent phase. In addition, the boundary areas between the opaque microdomains and the transparent phase are extremely tortuous.

There is a dramatic change in the consistency of the cured polymer when TEGDMA content reaches and exceeds 30 wt% (sample 4 thru 8); the entire sample becomes white and opaque upon polymerization and the acrylic system achieves zero shrinkage at compositions from 30 to 40% TEGDMA. At higher TEGDMA contents up to 70% the cured polymer is still white and opaque but starts to show cure shrinkage, which increases with TEGDMA content. At 80% TEGDMA the system again retains its single phase during rapid cure and shows the same cure shrinkage as the slowly-cured copolymer, which also retains its single phase.
Fig. V-1.2.2: Transmission OM picture of acrylic system with 20% TEGDMA. (x125)
Fig. V-1.2.3: Transmission OM picture of acrylic system with 20% TEGDMA. (X200)
Fig. V-1.2.4: Transmission OM picture of acrylic system with 20% TEGDMA. (X500)
Fig.V-1.2.5: Transmission OM picture of acrylic system with 20% TEGDMA. (X800)
Fig. V-1.2.6-8 are transmission optical microscopic pictures of thin sections (20 to 30 µ thickness) of the zero-shrinkage systems with 30%, 40% and 70% TEGDMA (fourth, fifth, and eighth sample from the left in Fig. V-1.2). It can be seen from the thin-section micrographs that the macroscopically opaque material of this system contains two types of microdomains: one is transparent, the other white and opaque (black under the microscope). The uniformly distributed tiny opaque microdomains block light from going through the specimen, therefore make those specimens with phase separation look opaque. The opaque microdomains we saw from microscope pictures could well have even further phase separated (sub-microdomains within them) which could not be picked up by the microscope due to the thickness of the sections and the limited resolution of the optical microscope.

Chemical composition has a strong impact on the morphology of the cured systems. The microdomain size, distribution and other aspects changed dramatically with the increasing TEGDMA content, 30 wt% to 70 wt%. Examination of samples with compositions outside the zero-shrinkage range of 30-40% TEGDMA shows further effects of composition on the morphology of the cured systems. As the TEGDMA content is increased the boundaries between the opaque and transparent microdomains (when viewed in thin sections under transmission OM) become less well defined: the transparency of
Fig.V-1.2.6: Transmission OM picture of acrylic system with 30% TEGDMA. (X800)
Fig.V-1.2.7: Transmission OM picture of acrylic system with 40% TEGDMA. (X500)
Fig. V-1.2.8: Transmission OM picture of acrylic system with 70% TEGDMA. (X500)
the clear microphase decreases and the opaque microdomains become less opaque. At 70% TEGDMA the difference in light transmission between the transparent and opaque phases becomes very faint. This indicates that in the range of 40 to 70% TEGDMA the two phases of the cured polymer become increasingly compatible until (at TEGDMA contents >70%) rapid polymerization no longer induces phase separation.

All the polymerizations discussed above were carried out in 10mm x 75mm glass test tubes at ambient temperature with BPO=0.8 wt% and DMPT=0.4 wt%. The peak exothermal temperatures ranged from 80 to 110°C and were attained within a few minutes once polymerization started. Phase separation occurred late in the polymerization: the system turned from clear liquid to cloudy within five to eight minutes, and subsequently became completely opaque (white) within 20 seconds.

In order to investigate the effect of incorporating PMMA into the raw resin on the phase separation containing a ratio of MMA/TEGDMA of 49/30 (which corresponds to a zero shrinkage system with 30% TEGDMA) was used and its curing behavior with different amounts of PMMA predissolved in the monomer was observed. Four samples were prepared, varying in PMMA content from 0 to 40%. A photograph of the rapidly cured polymers is shown in Fig.V-1.2.9, from left to right the PMMA
Fig.V-1.2.9: Rapidly polymerized systems with PMMA content from 0% to 40%.
contents are 0, 10, 20, 30, and 40%.

It can be observed that only the sample that contains 30% PMMA (second from right) shows zero cure shrinkage and microphase separation. Samples with higher (40%) and lower (20%) PMMA content show partial phase separation and increased cure shrinkage. At 10% PMMA the system shows no gross phase separation but has become translucent. At 0% PMMA the system retains the transparency of the single phase monomer mixture and show full cure shrinkage.

These data indicate that the amount of PMMA incorporated into the system prior to polymerization plays an important role in inducing phase separation and decreasing cure shrinkage. In general phase separation and cure-shrinkage depend very strongly on chemical composition. Within a certain chemical composition range, phase separation can be achieved. Whenever there is a phase separation, there is a reduction of cure shrinkage.

1.3 Effect of Polymerization Rate

Polymerization rate is another important factor which has a strong impact on phase separation and cure-shrinkage, as can be seen by comparing curves B and C in Fig. V-1.1. The systems forming Curve A were cured at low polymerization rates, (BPO=0.15% wt%, DMPT=0.05% wt%) and over night. The system
in Curve C were cured rapidly (BPO=1 wt%, DMPT=0.2 wt%) and polymerization was completed within 5 minutes. There are considerable differences in density between the same system cured at different rates, as it can be seen in Fig.V-1.1. Within the phase separation composition range, the density of the cured system at high polymerization rate is much lower than that of the same system cured at low polymerization rate.

1.4 Other Factors Affecting Phase Separation

To understand the mechanism of phase separation and the corresponding reduction in cure shrinkage it is necessary to consider certain other factors. These include: the miscibility between PMMA and poly(TEGDMA); the relative reactivity of MMA monomer and TEGDMA monomer; the crosslink density and chemical composition of the different phases; possible stresses and molecular chain orientation introduced by the precipitation of one polymer from the system during the liquid-gel-solid transition in the course of polymerization.

1.4.1 Miscibility Between PMMA and Poly (TEGDMA)

This was investigated by dissolving PMMA into TEGDMA and monitoring the phase behaviour of the system as the TEGDMA is rapidly polymerized.

15 g PMMA powder was poured into a beaker containing 85 g liquid TEGDMA. The beaker was then placed on a magnetic
stirring plate until PMMA dissolved completely into the TEGDMA. 1 wt% BPO, and 0.5 wt% DMPT were added and mixed for 60 seconds. The solution was then poured into a glass test tube and cured at ambient temperature. If PMMA and the polymer of TEGDMA are completely miscible, the system would retain its transparent single phase during the cure; if the two are not miscible or partially miscible, the cured copolymer sample would become opaque or partially opaque.

Before polymerization the TEGDMA solution with the dissolved PMMA is a clear liquid which means that PMMA was dissolved into TEGDMA completely. During polymerization the clear liquid turns into a semi-transparent solid with opaque spots on it which means PMMA has very limited solubility in poly(TEGDMA). PMMA forms its own domains (PMMA rich domains) the within poly (TEGDMA) matrix.

1.4.2. Relative Reactivity of MMA and TEGDMA

The insolubility (or very limited solubility) of the MMA and TEGDMA polymers in each other makes it possible to investigate how the two monomers copolymerize.

Liquid mixtures of Methyl Methacrylate (MMA) and TEGDMA were prepared at all proportions. The mixtures were poured into 75 x 8 mm glass test tubes and polymerized rapidly at room temperature with BPO and DMPT. Before polymerization all of these mixtures were clear single-phase liquids which means
MMA and TEGDMA monomers are soluble in each other in all proportions. These systems remained transparent during rapid polymerization and gave transparent single phase solids, which means that MMA and TEGDMA tend to copolymerize with each other instead of forming separate homopolymers. Since we know from 1.4.1 that PMMA is not miscible in Poly (TEGDMA), if MMA and TEGDMA tend to react with their own monomers then there would be PMMA domains and Poly(TEGDMA) domains after polymerization and the cured specimens would turn to be opaque instead of transparent.

1.4.3 Relative Crosslinking Density and Chemical Composition of the Different Phases

TEGDMA acts as crosslinking agent during copolymerization due to its dimethyacrylate moieties. Cured copolymerized specimens 20 mm long and 8.mm in diameter with partial phase separation (partially opaque) were soaked in chloroform to investigate their relative crosslinking density and chemical composition. Chloroform has a solubility parameter exactly the same as PMMA. Polymerized TEGDMA does not dissolve in chloroform due to the high crosslink density and its different solubility parameter. Therefore, phases that are rich in PMMA are expected to swell faster and to a greater extent when immersed in chloroform, compared to PMMA poor phases. Also, phases with lower crosslinking density (that is, phases that are poor in TEGDMA) will swell more than
highly crosslinked phases with (that is, phases rich in TEGDMA), since a high degree of crosslinking impedes penetration of the network by solvent molecules.

Fig.V-1.4.3.1 shows a photograph of a section of acrylic polymer showing distinct phase separation. Fig.V-1.4.3.2 shows the same section after immersion in chloroform for 20 minutes. The transparent phase of the cured specimen swelled and started peeling off, while the opaque part of the same specimen showed little change. From this simple experiment we can see that the transparent phase is rich in PMMA, less crosslinked, and thus poor in poly(TEGDMA). The opaque phase is rich in poly (TEGDMA), highly crosslinked, and poor in PMMA.

1.5 Phase Separation During Polymerization of (Nearly)
Two-Dimensional Specimens

In an effort to visualize the process of phase separation during rapid cure and observe in further detail the resulting morphology we constructed nearly two-dimentional specimens of the acrylic system. A droplet of uncured resin of the zero-shrinkage formulation was placed between two thin glass cover slides so as to form a layer several microns in thickness. Polymerization was carried on a hot stage in the polarized microscope at a temperature of 90 °C. This setup allowed us to observe directly the formation and aggregation of the opaque second phase during rapid polymerization.
Fig. V-1.4.3.1: Sample of acrylic system (TEGDMA=20%) with partial phase separation before immersion in chloroform.
Fig.V-1.4.3.2: Sample of acrylic system (TEGDMA=20%) with partial phase separation after immersion in chloroform for 20 minutes.
Fig. V-1.5.1-3 show pictures of a phase separation pattern at different magnifications. Nuclei of the opaque phase appeared about 90 seconds after the specimen reached the polymerization temperature and grew into characteristic dendritic structures within 10-20 seconds, at which point the polymerization was complete. The appearance of the second phase late in the polymerization and its subsequent rapid growth is consistent with observation of the curing process of the same system in bulk.

Since the thickness of the sample cured between glass slides is insignificant compared to the its radial dimension, the observed dendritic pattern can be considered as a near two-dimensional expression of the phase separation process of poly(TEGDMA) rich microdomains precipitating from the system. In bulk systems the radial growth pattern of the second phase proceed in three dimensions in a manner analogous to the formation of spherulites in the crystallization of bulk polymers.

Fig. V-1.5.1-3 are three pairs of pictures of the same dendritic pattern at different magnifications. In each pair of pictures, the top one was taken with the polarizer and analyzer parallel to each other, the bottom one under crossed polarizers. The pattern observed under crossed polarizers is exactly the
Fig. V-1.5.1: Phase separation of (nearly) two-dimensional specimen during rapid polymerization, the top one was taken with the polarizer and analyzer parallel to each other, the bottom one under crossed polarizer. (X40)
Fig.V-1.5.2: Phase separation of (nearly) two-dimensional specimen during rapid polymerization. (X150)
Fig.V-1.5.3: Phase separation of (nearl) two-dimensional specimen during rapid polymerization. (X375)
negative pattern of the one under non-polarized light, which indicates that the second phase polymer is not isotropic; there might be a certain degree of orientation or strains within the second phase. This birefringent effect is rather weak since the contrast of the dendritic pattern under crossed polarized light is very weak (the pictures taken under crossed polarized light in Fig.V-1.5.1~3 are ones after contrast enhancement).

The dendritic pattern which is characteristic of 2-d samples suggests that the aggregation of the second phase polymer started from a central nucleus and proceeded to grow in the radial direction. During polymerization, the system went from a liquid monomer to a gel mixture of polymer/monomer and then to solid polymer. The phase separation process was terminated when the viscosity of the system reached the solidification point after gelation.

Fig.V-1.5.4 and 1.5.5 were taken at the fringe of a fully grown dendrite, while Fig.V-1.5.6 was taken at the central part of the same dendrite. In Fig.V-1.5.6, the morphology and organization of the opaque domains is similar to morphology obtained from thin sections of bulk specimens, which is the cross section of a three dimensional structure (Fig.V-1.2.6~8). It is not hard to imagine from Fig.V-1.5.6 that the three-dimentional structure of this two-dimensional pattern
Fig.V-1.5.4: Phase separation of (nearly) two-dimensional specimen during rapid polymerization, picture was taken at the fringe of a fully grown dendrite. (X50)
Fig. V-1.5.5: Phase separation of (nearly) two-dimensional specimen during rapid polymerization, picture was taken at the fringe of a fully grown dendrite. (X200)
Fig. V-1.5.6: Phase separation of (nearly) two-dimensional specimen during rapid polymerization, picture was taken at the center of a fully grown dendrite. (X300)
would be the further details of the morphology which could not be picked up by the microscopic picture of the thin section samples (Fig V-1.2.6~8).

Fig.V-1.5.7 is a picture of a fully grown dendritic pattern of the aggregation of the second phase in another sample polymerized between glass slides. The growing process of the dendritic structures in these thin films is difficult to control; resin of same formulation cured on the same slide might well result in different aggregation patterns (Fig.V-1.5.8).

After immersion in chloroform for ten hours, the polymer film will separate from the glass slide. The dendritic aggregation pattern of the second phase disappears, and the film becomes translucent; it then reverse to white and opaque as soon as the chloroform evaporate from the film (Fig.V-1.5.9(a)). When the film is again solvated with several droplets of chloroform, it becomes again translucent (Fig.V1.5.9(b)) and goes back to white opaque as soon as the chloroform evaporates from the film.

1.6 X-ray Diffraction, IR

In an effort to ascertain whether the birefringence of the opaque dendritic structures observed in the thin film specimens is due to a specific orientation of their macromolecular chains we obtained X-ray diffraction patterns of a transparent, slowly
Fig.V-1.5.7: A fully grown dendritic pattern of the aggregation of the second phase polymer.
Fig.V-1.5.8: Different phase separation patterns of the same formulation cured at same condition.
Fig.V-1.5.9(a): Thin film after chloroform evaporated
Fig. V-1.5.9(b): Thin film solvated with chloroform.
cured film and a rapidly cured film of the same composition showing phase separation. The respective diffractometer scans are given in Fig.V-1.6.1-2.

IR scans of transparent film (slow cure, without phase separation) and opaque film (fast cure, with phase separation) of the same zero-shrinkage formulation are shown in Fig.V-1.6.3. No differences were observed for the scans between those two types of films, which indicates that in the second phase polymer there is no orientation at the scale which can be picked up by X-ray or IR.

1.7 Reflected Light Microscopy

Fig V-1.7 is the reflection optical microscopic picture (X400) of carefully polished smooth surface of a rapidly polymerized zero-shrinkage system. The final polish was done with 0.3 micron size of Al₂O₃. This picture is typical of several such preparations. No voids were observed.
Fig. V-1.6.1: X-ray diffraction of slowly cured film.
Fig.V-1.6.2: X-ray diffraction of rapidly cured film.
Fig. V-1.6.3: IR scans of slowly and rapidly cured film. Top line: slowly cured; Bottom line: rapidly cured.
Fig. V-1.7: Reflection OM picture of carefully polished surface of rapidly cured zero-shrinkage system. (X400)
2. PROPOSED MECHANISM FOR PHASE SEPARATION AND CURE SHRINKAGE REDUCTION

From the results in this Chapter we can see that the reduction in cure-shrinkage during rapid polymerization is closely associated with phase separation. To understand the mechanism of cure-shrinkage control, we have first to understand the mechanism of phase separation.

The phase separation mechanism we shall propose is based on the following experimental observations:

(A). PMMA has very limited solubility in Poly (TEGDMA ).

(B). MMA and TEGDMA monomers tend to copolymerize with each other instead of forming separate homopolymers.

(C). PMMA is much more soluble in its own monomer (MMA) than in TEGDMA.

I advance the following hypothesis, based on the distribution of the three components in the uncured system and their relative diffusion during polymerization. The acrylic systems investigated here were first prepared by dissolving PMMA into MMA and then adding TEGDMA. The mixture of these components formed a clear single phase solution. The uncured solution can be pictured as having numerous swollen macromolecular coils of dissolved PMMA, as well as MMA and TEGDMA monomers species. Since MMA is a much better solvent for PMMA than TEGDMA, the interactions between MMA
molecules and PMMA macromolecules are much stronger than those between TEGDMA molecules and PMMA macromolecules; therefore the local concentration of MMA is expected to be greater inside and in the immediate neighbourhood of the PMMA macromolecular coils. The reverse would occur with TEGDMA molecules, which would tend to concentrate more in regions free of PMMA. This means that we have micro domains relative rich in MMA and TEGDMA respectively, which are uniformly distributed in the solution before polymerization. The number of the MMA rich micro domains should be at the same level as the number of PMMA macromolecular coils, which is quite large. This micro-segregation concept is shown schematically in Fig. V-2.1.

The presence of the preexisting polymer chains in the MMA/PMMA-rich microdomains is expected to lower the local reactivity of these microdomains towards polymerization, since the preexisting PMMA is inert and its presence dilutes the local concentration of polymerizable double bonds. Consequently, when the initiator starts releasing free radicals at the onset of cure a (relatively) greater number of copolymer chains will be forming in the PMMA-poor (and TEGDMA-rich) microdomains.

At low polymerization rates the MMA/TEGDMA copolymer chains are formed at a sufficiently low rate for molecules of
Fig. V-2.1: Microsegregation concept of acrylic system before polymerization.
both MMA and TEGDMA monomers to diffuse into the polymerization sites and maintain a balanced concentration of both monomers so that both MMA and TEGDMA units enter the copolymer chains as they form. The resulting copolymer network contains a sufficient amount of MMA units to maintain the preexisting PMMA chains in solution. Consequently the single phase is maintained during polymerization and the cured system remains transparent.

At high polymerization rates, the clear uncured resin mixture gels within five to eight minutes and then turns from a semi-transparent gel into white opaque solid polymer in a matter of seconds. During this short period of time, MMA monomer molecules can not diffuse fast enough to move away from PMMA rich microdomains and replenish the local concentration of MMA in the TEGDMA rich regions, where the copolymer is formed fastest. This causes segregation in the composition of the forming chains: polymer formed in the TEGDMA-rich (MMA poor) regions becomes richer in TEGDMA. Polymer formed in the MMA & PMMA rich microdomains becomes poor in TEGDMA. Eventually we have the two near-homopolymers, of MMA and TEGDMA growing separately in their respective microdomains.

As polymerization proceeds, the concentration of the two different near-homopolymers in their respective microdomains
reaches a level which is high enough to cause phase separation. The microdomains rich in poly(TEGDMA) separate from PMMA-rich matrix forming the dendritic pattern. The two different types of microdomains are very well distributed among each other.

At this stage of cure, the polymerization system has reached peak exotherm temperature of 80-100°C; the PMMA rich micro domains and poly(TEGDMA) rich microdomains tend to repel each other due to their solubility parameter difference, while microdomains with similar composition tend to stick together. When two or more poly(TEGDMA) rich micro domains contact each other, they tend to coalesce, thus forming nucleus of a second phase; the formation and growth of dendritic pattern starts from there on.

The emerging second phase prefers to grow along the radial direction, because its formation consumes the TEGDMA rich microdomains from its immediate neibourhood along the aggregation path. Optical photographs of dendrites taken under intensified light (Fig.V-2.2) and high magnification (x1000) (Fig.V-2.3) show details of the dendrites growing process. At the forefront of the dendrites, the basic unit (the smallest unit that can be picked up by optical microscope, which is about 1 μ) can be seen aggregating to form the dendrite (Fig.V-2.3, x1000). Since the dendritic development is a difffusion-limited
Fig. V-2.2: Phase separation of (nearly) two-dimensional specimen, picture was taken under intensified light. (X375)
Fig.V-2.3: Phase separation of (nearly) two-dimensional specimen, picture was taken under intensified light. (X1000)
aggregation, the dendritic patterns can be considered as a frozen picture of phase separation process, which is terminated when the system solidifies.

The pronounced cure shrinkage of the PMMA-rich matrix may also help the aggregating second phase to grow radially and form a dendritic pattern. The constrains imposed on cure shrinkage in the rapidly solidifying system give rise to tensile stresses in the PMMA-rich matrix. When the second phase nucleates and segregates out it forms a discontinuity in the PMMA-rich matrix which tends to propagate rapidly. This facilitates aggregation of the second phase along radical pathways i.e. formation of dendrites as opposed to nondirectional clusters. Cure shrinkage of the polymer chains causes strains oriented in the tangential direction in the second phase, which may account for the observed birefringence of the dendritic material (Fig.V-1.5.1~3). The observed birefringence is very weak due to the low level of tangential stress and the limited extent of chain orientation in the crosslinked network.

During polymerization, the system goes through a transition from liquid monomer to a gel (mixture of monomer and polymer) to solid polymer. Dendrites start to grow only when the polymer concentration in each type of micro domain becomes high enough to cause phase separation. At that point,
the viscosity of the system is high due to the high concentration of polymer. The aggregation of second phase microdomains forming the dendrites is slowed down by the increasing viscosity. The growing of dendrites terminates when the system solidifies completely. In our experiments with thin specimens we observed that the formation of the dendritic second phase was triggered and terminated only during the gel-solid transition, within a matter of seconds in the rapidly polymerizing systems. Likewise the bulk specimens cured in a test tube appeared cloudy at the later stages of polymerization and became completely white and opaque within 10-20 seconds from the end of polymerization.

In all of these multiphase systems the decrease in cure shrinkage is closely associated with an increase in the ratio of interphase boundaries to specimen volume and the molecular chain packing at the interfacial area. From Fig.V-1.2.6~8 it can clearly be seen that the interfacial area is enormous due to the small size of the micro domains. In the interfacial boundary regions between the two types of micro domains, the macromolecular chain packing is less efficient than it is inside the microdomains, due to the lack of miscibility between the two polymers; i.e. the distances between neighboring macromolecular segments across an interface are greater than the corresponding intermolecular distances within a single phase. Consequently we attribute the reduction in cure
shrinkage to the cumulative local increase in volume at the boundaries between microphase domains.

With high enough polymerization rates and within certain composition ranges (TEGDMA=30-40 wt%), zero-shrinkage and slightly expanding systems were obtained. The separated microdomains boundaries were very well defined (Fig.V-1.2.6), which indicates that the two different types of microdomains were highly immiscible in this composition range and under this polymerization rate.

As it can be seen from Fig.V-1.1, with increasing of TEGDMA concentration from 30% to 70 %, the density increased considerably. This density increase is due to the higher miscibility between the two types of microdomains. With the increasing TEGDMA concentration, there would be decreasing of PMMA and MMA concentration before polymerization, that is, less PMMA "macromolecular coils" distributed in the solution and less MMA-rich regions before cure, which means after polymerization there would be less PMMA rich regions (therefore, less interfacial regions) and also the PMMA rich microdomains would not be that rich in PMMA (or, not that poor in poly(TEGDMA)), this would result in better miscibility between the PMMA-rich microdomains and Poly (TEGDMA) rich domains. This better miscibility can be observed under the optical microscope: TEGDMA rich microdomains are much finer
in Fig.V-1.2.7 (TEGDMA = 40 %) and Fig.V-1.2.8 (TEGDMA = 70 %) and
not quite well defined compared to those in Fig.V-1.2.6
(TEGDMA = 30 %). The color of the poly(TEGDMA) rich regions at
high TEGDMA content (70%) is deep orange or semi-transparent
instead of complete opaque as those of low TEGDMA
concentration. Better miscibility between the two types of
microdomains means better and tighter packing of
macromolecular chains in the interfacial regions, that is,
higher local density in those interficial regions, therefore
overall we have less cure-shrinkage reduction with the
increasing TEGDMA concentration from 30 % to 70 %.

Fig.V-2.4 is a two dimensional computer simulation pattern
of Diffusion Limited Aggregation (DLA) (Meakin, 1987). There is
quite a striking similarity between this two dimensional
simulation pattern and the two dimensional phase separation
pattern (Fig.V-1.5.1) shown by our acrylic systems: they all
have the multi-branch fractal structure, aggregations start
from the central seeding point and growth occurs along the
radial direction.

The physical model of this 2-dimensional simulation, the
Witten-Sander model, might help us understand the aggregation
and growth of the second phase in our polymer system. In this
model, particles are added one after another to a single growing
cluster. Aggregation starts from an immobile seed particle and
grows iteratively. At each iteration, a moving particle is released from a point chosen at random on a large circle centered on the seed, and undergoes a pure random walk until it touches the aggregates. After the first collision, the particle is considered as rigidly attached to the aggregate at its sticking position and another particle is released on the circle.

The two-dimensional aggregation pattern of the second phase polymer (Fig.V-1.5.1) is a perfect experimental example for two-dimensional Diffusion Limited Aggregation (DLA). Computer image analysis opens the potential of better understanding of the formation of the mechanism of 2-dimensional and 3-dimensional structures of the aggregating second phase.

From the proposed mechanism we postulate that the phase separation method cure-shrinkage control need not be limited to the acrylic systems studied here. The method is based on the occurrence of phase separation during polymerization and could be applied to other resin systems, provided that:

(A) The uncured system is multicomponent with differences in solubility parameter between the homopolymers of the different components so that they become immiscible during polymerization. One monomer should be crosslinkable. The larger the difference between the solubility parameters of the two polymers, the better
Fig.V-2.4: Witten-Sander aggregate grown on a square lattice, containing four million particles. (From Meakin)
chance the system will achieve cure shrinkage control.

(B) The system studied to date require a linear polymer fully dissolved in the above monomer solution. This linear polymer should have a solubility parameter that is very close to one of the monomers and quite different from the that of the other monomer. The solution of the three should be clear single phase. The linear polymer should be non-miscible with the polymer of the crosslinkable monomer. The function of the linear polymer here is to form "molecular coils" in the solution before polymerization and create micro regions that are rich in one monomer and poor in the other monomer, due to the difference of the interactions between the polymer and monomers.

(C) Relatively high polymerization rate. The aggregation of the second phase polymer is a diffusion controled process. High polymerization rate will force the gel--solid transition to complete in a short time and make diffusion the control factor of the aggregation process.

(D) The proper proportion of monomers and linear polymer in the system is used.
3. EXPLORATION OF OTHER ACRYLIC SYSTEMS: EFFECT OF DIMER ETHYLENE OXIDE CONTENT ON PHASE SEPARATION AND CURE SHRINKAGE CONTROL

In the acrylic system studied here the polyfunctional dimer is triethylene glycol dimethyacrylate (TEGDMA), which contains three ethylene oxide groups in between the two methyacrylate groups.

To study the effect of dimer composition on phase separation during rapid polymerization we replaced TEGDMA with each of following dimers: ethylene glycol dimethyacrylate (Sartomer 206), diethylene glycol dimethacrylate (Sartomer 231), and tetraethylene glycol dimethyacrylate (Sartomer 209). Together with the previously used triethylene glycol dimethyacrylate, we now have four acrylic dimers in which the ethylene oxide number between the methyacrylate groups varies from one to four.

All of these systems formulated with dimer contents ranging from 10 to 90% in increments of 10%. They were polymerized rapidly in bulk (in 8x75 mm test tubes) at ambient temperature. Fig.V-3.1, V-3.2 and V-3.3 show photographs of the cured sample with each different dimer content, while Fig.V-3.4, V-3.5, & V-3.6 show the density of the cured samples vs dimer content. The dendrits of the perviously discussed
Fig.V-3.1: Rapidly polymerized systems covering the range of EGDMA content from 10% to 90% at increments of 10%. 
Fig. V-3.2: Rapidly polymerized systems covering the range of DEGMDA content from 10% to 100% at increments of 10%.
Fig.V-3.3: Rapidly polymerized systems covering the range of Tetra-EGDMA content from 20% to 90% at increments of 10%.
systems with TEGDMA are also shown in dashed lines for comparison purposes.

For systems formulated with ethylene glycol dimethacrylate, with only one ethylene oxide in between the two methacrylate groups, the phase separation range is quite wide. All of the cured systems were white and opaque within the range from 10 wt% to 90 wt% EGDMA content, which means that phase separation started at 10 wt% or less EGDMA content, and did not end until 90 wt% or more EGDMA content. There is a broad range of low density polymers (from 20 to 60% EDGMA). However, Zero-shrinkage was not achieved by any of these formulations.

In systems with diethylene glycol dimethacrylate, (with two ethylene oxide in the dimethacrylates), the phase separation range is narrower compared to the systems with EGDMA. As it can be seen from Fig.V-3.2, the system shows only a few opaque domains at 10 wt% DEGDMA but turns complete white and opaque in DEGDMA range from 20 to 80%. The lowest density point is 35 wt% DEGDMA content, at which point zero-shrinkage was achieved.

For acrylic systems with tetraethylene glycol dimethacrylate, none of the polymerized systems turned to complete white and opaque (Fig.V-3.3), partial phase separation
Fig. V-3.4: Density of systems with EGDMA (Sartomer 206), compared with systems with TEGDMA.
Fig.V-3.5: Density of systems with DEGDMA (Sartomer 231), compared with systems with TEGDMA.
Fig.V-3.6: Density of systems with Trtra-EGDMA (Sartomer 209), compared with systems with TEGDMA.
happened at 20 wt% dimethacrylate content and ended at 50 wt%. The lowest density point is at 20 wt%. Zero-shrinkage was not achieved at this point.

For acrylic systems with poly ethylene glycol dimethacrylate, no phase separation was observed at any composition. Polymerized systems were all transparent single phase polymers.

Comparison of the above four types of acrylic systems, indicates the following effect of ethylene oxide content between the two methacrylate groups in the dimer:

(A) The phase separation range becomes narrower.
(B) The lowest density point moves towards lower dimethacrylate contents.
(C) At the given polymerization condition, zero-shrinkage was achieve only with TEGDMA and DEGDMA.

Changing the number of ethylene oxide groups in the dimer affects several factors in the polymerization systems:

(A) Solubility parameter of the dimethacrylate.
(B) Relative reactivity (while polymerizing in the presence of MMA).
(C) Polymerization rate, that is, the rate of increase in molecular weight. The larger the monomer molecular weight, the faster the molecular weight and viscosity
increase

(D) Crosslinking density of the polymerization systems.

(E) The size of the dimethacrylate therefore the diffusion coefficient of the dimethacrylate molecule.

A combination of one or more of the above factors may contribute to the sensitive response of the polymerization systems to the chemical changes in the dimer.
CHAPTER VI. SUMMARY AND CONCLUSIONS

(1) Control of cure shrinkage in ambient temperature polymerizations was achieved by utilizing the dilatation of specially modified mineral particles dispersed into the resin to counteract polymerization shrinkage. The most successful of these methods involves partial replacement of the hydration water in MMT with NH$_3$.

(2) The optimum conditions for dehydration/NH$_3$ addition to natural MMT is 50°C and a vacuum of 0.5 MPa. At too high dehydration temperature (such as 100°C), the crystal interlayer structure within the MMT particles collapses thus hindering the penetration of ammonia. The restored C-spacings are at the same level compared to that of natural MMT, probably due to the similarity in molecular size and polarity between water and ammonia molecule.

(3) Examination of the zero-shrinkage acrylic cement obtained by the use of NH$_3$/MMT additive under scanning electron microscope showed no voids. This confirmed that ammonia did not leave MMT particles during the polymerization process and that the cure-shrinkage control mechanism of ammonia-MMT is similar to that of the natural, hydrated mineral involving dilatation of MMT.
particles.

(4) This method of cure-shrinkage control also counteracts setting stresses in highly filled resin systems such as polymer concrete thus increasing the strength of the cured composite by 20 to 40%.

(5) Mixtures of MMA/PMMA/TEGDMA form a single-phase clear solution before polymerization. At relatively high polymerization rates growing chains rich in TEGDMA become insoluble in the MMA-rich system and start to precipitate during the later stage of the polymerization. The aggregation of the second phase is a diffusion-controlled process; it starts at the gel point and terminates during the gel-solid transition as the viscosity of the polymerization system approaches infinity. The aggregation process is completed within 20 to 30 seconds. The second phase, contains TEGDMA-rich polymer, is opaque, and non-isotropic.

(6) Generation of the interdispersed micro phases is associated with a volume increase which compensate for cure shrinkage. This results in zero-shrinkage (or slightly expanded) polymer. The polymerization process was carried out at room temperature and one
(7) A cure-shrinkage control mechanism based on microphase separation is proposed. Since PMMA and the polymer of TEGDMA are highly immiscible, the molecular chain packing at the interfacial area of the two different microdomains is not as tight as that inside the domains, thus creating internal areas of low local density. The accumulation of those low local density areas counteracts cure-shrinkage.

(8) In the acrylic systems studied, two key factors affect phase separation behavior: polymerization rate and chemical composition. At low polymerization rates no phase separation was observed with any acrylic resin systems. At relatively high polymerization rates, phase separation was observed only within certain composition ranges.

(9) The PMMA dissolved in the solution before the cure plays a very important role in the creation of phase separation and therefore is crucial to the cure-shrinkage control. No phase separation can be achieved in the developed acrylic system without the presence of dissolved PMMA in the uncured system. The PMMA chains are fully extended in the solution and form macromolecular coils.
Micro domains rich in MMA form in the immediate neighbourhood of PMMA macromolecular coils due to the better interaction between MMA and PMMA; so do MMA poor (that is, TEGDMA rich) microdomains away from the dissolved PMMA. The existence of those two types of microdomains (one rich in MMA, the other rich in TEGDMA) before polymerization is essential for phase separation during polymerization and therefore essential for cure-shrinkage control.

(10) Aggregation of the second phase polymer is a diffusion controlled process; it starts in the later stage of polymerization and terminates when the polymer solidifies. The aggregation starts from a central nucleus and tends to grow in the radial direction forming dendritic patterns.

(11) The second phase polymer shows weak birefringence, indicating the possible presence of a limited degree of chain orientation. However, IR and X-ray diffraction tests could not pick up the difference between the opaque and the transparent phase.

(12) The phase separation behavior is very sensitive to changes of the amount of ethylene oxide in the dimethacrylate component. The composition range of
phase separation, the lowest density point, and the cure-shrinkage reduction change dramatically with ethylene oxide content in the dimer.

(13) Our proposed mechanism of cure shrinkage control by phase separation implies that this cure-shrinkage control method is not limited to acrylic systems and can be applied to other systems that meet certain requirements with regard to: the chemical structure of the monomers, differences in monomer-monomer and polymer-monomer solubility parameter, crosslinking ability of one of the monomers, and polymerization rate.

(14) No voids or microcracks were found in the phase separated acrylic systems under both Scanning Electron Microscope and the reflection Optical Microscope (for the carefully polished surface).
CHAPTER VII. APPLICATIONS OF THE ZERO-SHRINKAGE METHODS

Both NH3/MMT and the phase separation methods successfully achieved zero-shrinkage or slight expansion in the cure of certain polymer systems. With those two methods, zero shrinkage can be effected at ambient temperature and atmospheric pressure. In addition, in the case of systems with MMT the strength of the cured polymer is considerably enhanced. This unique combination of properties is not offered by conventional shrinkage control methods. This enables our two methods to be utilized in certain industrial and medical applications in which conventional cure-shrinkage control methods are not applicable.

One of those applications is the use of polymer concrete or mortars in large, field erected structures cured at ambient temperature. In the previous cure-shrinkage control methods for conventional polymer concrete systems, natural MMT was used as the cure-shrinkage control additive (Haque, 1986). The expansion of natural MMT particle was realized by the release of interlayer hydration water, therefore an peak exotherm of over 100°C is required. PC systems usually contain only 12-14 wt% of resin. The heat of polymerization generated by such small resin content would not be enough for large structures even to reach temperatures over 100°C. Therefore external
heating (such as polymerization inside an oven) must be applied. This requirement of the natural MMT zero-shrinkage systems makes them totally impractical for outdoor and field applications. With ammonia modified MMT, zero-shrinkage can be achieved at ambient temperature and thus broadening considerably their application for polymer concretes and mortars.

Our cure-shrinkage control methods can also be used in molded polymer systems in which dimensional stability is required. The predominant method for cure-shrinkage control in the Plastic Industry is the Low Profile method, which requires molding conditions of 300°F and 400 psi and was mostly developed for the cure-shrinkage control of unsaturated polyester systems. The cure-shrinkage control methods developed in our laboratory offer several advantages:

1. Zero-shrinkage of acrylic systems can be achieved by both of these methods. Therefore our method provides an alternative resin system for polymer composite moldings to the unsaturated polyester resins currently used with LPA method. Our two shrinkage control methods can probably be generalized to other resin systems and therefore provide more options in the future.

2. Acrylic resins generally have very low viscosity
compared to other resins, thus making it possible to use the extremely high filler loading.

(3) Zero-shrinkage can be achieved at room temperature cure and one atmosphere instead of under conditions of high temperature, and high pressure, which will potentially make the processing easier and more economical.

The modified MMT and phase separation cure-shrinkage control method can also be applied to some other situations in which dimensional stability is required such as polymer dental composite restorations cured in patient's mouth, and the preservation and restoration of internally damaged artifacts by injection of low viscosity resins.

Acrylic resin is the most commonly resin used for dental restorative polymer composite. Cure-shrinkage is the main reason that causes the failures of the dental restorative composites. Cure-shrinkage develops while the filling is polymerized inside the cavity, this shrinkage will open a gap between the cavity wall and the filling matrix and make the penetrations of bacteria possible. Both modified MMT and phase separation cure-shrinkage control methods can be utilized for cure-shrinkage control for dental restorative polymer composites.
Antique wood structures such as buildings, bridges, and sculptures are often damaged internally. These internal tunnels are most of the times interconnected. They can be filled up by the injection of low viscosity resins and polymerized inside the structure (Fig.VII). The zero-shrinkage acrylic systems are the best candidate for this type of applications due their zero cure-shrinkage property and low viscosity, which facilitates the penetration of the resin into structures with tiny pores.
Fig.VII: Crosssection of internally damaged wood structure filled with resin of zero-shrinkage formulation polymerized inside the structure.
CHAPTER VIII. RECOMMENDATIONS FOR FUTURE WORK

This work accomplished the goal of achieving zero-shrinkage in ambient temperature polymerizations. It also proposed mechanisms for the different cure-shrinkage control process. At the same time, it also opened questions, directions and new challenges for further investigation.

(1) An program should be designed to investigate the state of ammonia in the MMT interlayer before, during and after the polymerization, and possible interactions between the ammonia molecule and MMT structure, ammonia and the organic resin, and the impact of these interactions on the mechanism for cure-shrinkage control. Experimental methods which can reveal the interactions at molecular level such as Infra-red Spectroscopy, Nuclear Magnetic Resonance (NMR) and Electron Spin Resonance (ESR) should be used for the study of those interactions.

(2) The phase separation cure-shrinkage control mechanism is based on the assumption that there are two types of micro regions existing in the resin systems before polymerization, one rich in MMA, the other rich in TEGDMA. An experimental program should be designed to verify this assumption. NMR, Light scattering, or IR are recommended for this work. Different systems should be scanned, such as MMA/PMMA,
TEGDMA/PMMA, MMA/TEGDMA, and MMA/TEGDMA/PMMA. The difference in the spectra should give some information on the interactions between MMA and PMMA with and without the presence of TEGDMA.

(3) The mechanical strength of the cured systems with phase separation is about 15% lower than their single phase counterpart. This is probably due to the loose molecular chain packing at the interfacial areas. There is a quite large potential for enhancing the strength of these systems. One obvious way to do it is to combine strong monomer such as BIS-GMA in the formulation. Other alternatives involve dissolving a block copolymer of the two polymers into the system: one section of this copolymer will dissolve in one microdomain and the other section will dissolve in the other type microdomain, as it can be seen from Fig.VIII, therefore forming chain connections which connect the two types of domains by covalent bonding instead of Van del Waal's bonding and enhance the overall mechanical strength.

(4) The possibility of calculating the interfacial area of the three dimensional phase separation structure should be explored. The starting point here is the two dimensional pattern of the phase separation process. Using computer image technology, we should be able to obtain the fractal dimension of the two dimensional aggregation patterns. With the aid of
Fig. VIII: Ideal location of block-and-graft copolymers at the interface between polymer phase A and B.
percolation theory, it should be possible to correlate the two dimensional patterns with the three dimensional structure. This would allow us to predict or calculate quantitatively the three dimensional interfacial area in a phase-separated polymer system.

(5) An experimental program should be designed to verify the assumption that interfacial molecular chain packing is not as tight as that inside the micro domains, that is, the local density difference between the interfacial area and inside domain matrix.

(6) More work needs to be carried out to investigate the effect of the chemical structure of the different components in the polymerizing system: relative reactivity of the two double bonds in the dimer, separation of reactive groups, etc.

(7) Generalization of the cure-shrinkage control method to other resin systems following the requirements mentioned in V-2. The generalization process itself is a way to verify the proposed cure-shrinkage control mechanism experimentally.
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the mineral crystal) then dispersed into the resin. During cure at ambient temperatures the polymerization exotherm raises the temperature to 60-80°C, breaking the SiO₂-NH₃ bonds; however the liberated gaseous ammonia cannot escape outside the resin-embedded MMT particles and forces them to dilate to more than twice their original size. By controlling the amount of ammonia-modified MMT added to the resin (in amounts of 6-10%) we obtain cured systems that show zero shrinkage and have no setting stresses. This can increase their strength by ca. 20-40%.

The second method achieves cure shrinkage control by microphase separation. Certain multicomponent acrylic systems, when polymerized rapidly, separate into microdomains of different phases with a corresponding reduction in cure shrinkage. We attribute this phenomenon to lower efficiency in molecular chain packing at the interphase boundaries; the phase separation itself is attributed to local, diffusion-controlled composition changes during rapid cure. Accumulation of the local volume increase at the microphase boundaries gives rise to the observed reduction in cure shrinkage.
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