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EFFECT OF THE POLY(METHYL METHACRYLATE) MOLECULAR WEIGHT ON THE MECHANICAL PROPERTIES BISGMA/TEGDMA SEMI-INTERPENETRATING POLYMER NETWORKS

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Key Words: Poly(methyl methacrylate), Molecular Weight of Polymer, Photopolymerization, Glass Transition Temperature, Compressive Strength, Knoop Hardness, Thermal Expansion Coefficient

ABSTRACT

The effect of poly(methyl methacrylate) [PMMA], with different molecular weights on the mechanical properties of a polymerized BisGMA/TEGDMA base monomer resin was investigated. With the aid of acetone solvent, PMMA could be readily dissolved in BisGMA/TEGDMA mixtures. The addition of PMMA can significantly improve the compressive strengths and decrease the Knoop hardness values of the BisGMA/TEGDMA/PMMA semi-IPNs. The thermal expansion coefficients rapidly increased before T_g, and decreased after T_g. The observed properties could be attributed to the effect of the molecular weight of the PMMA on the phase structures of the semi-IPNs .

INTRODUCTION

Semi-interpenetrating polymer networks (semi-IPNs) are polymeric materials in which one or more of the polymers are crosslinked and one of the polymers

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is linear [1]. Semi-IPNs tend to show better physical and mechanical properties than their individual component. Thus, their attractive applications in polymeric materials are more and more interesting to polymer workers in various fields [2-5]. The possible use of IPN or Semi-IPN is a well established area of study in our laboratory, specially for dental biomaterials [6-8]. Significant research on the synthesis, morphology, and structure-properties relationship of semi-IPNs has been successfully documented [1]. Since the molecular weight of the crosslinked polymer in semi-IPNs is infinite, few research studies have examined the molecular weight of the linear polymers in IPNs, looking at what is the role of the linear polymer and the effect of its molecular weight on properties.

The molecular weight of a polymer is one of the most important factors in its application. The interesting and useful mechanical properties, which are uniquely associated with polymeric materials, are a consequence of their high molecular weight. Most mechanical properties depend on, and vary considerably, with molecular weight of the polymer. The early works on the stress-strain behavior of polymers were designed to establish a simple relationship between properties and molecular weights [9-11]. Their results have shown that the molecular weight dependence of mechanical properties is more complex. The average molecular weight and molecular weight distribution are the important variables. In general, practical application of polymers require higher molecular weights to obtain higher strength. However, most properties show different quantitative dependencies on molecular weight.

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2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl] propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) blends are a principal base resin for dental composites or restorative formulations [12]. Since both BisGMA and TEGDMA are multi-functional monomers with capacity to blend with linear poly(methyl methacrylate) (PMMA), the mixtures of BisGMA/TEGDMA/PMMA are easy to form semi-IPNs with proper initiators. In this study, we report the effect of PMMA with different molecular weight on the mechanical properties of BisGMA/TEGDMA formulations.

EXPERIMENTAL

Materials

BisGMA was supplied by Cook Composites and Polymer Co. (±)-Camphoroquinone (CQ), 2-(dimethylamino)ethyl methacrylate (DMAEMA), TEGDMA, and PMMA, with different molecular weights were obtained from

Aldrich Chemical Co. The weight average molecular weights of PMMA are 101,000 (L-PMMA), 120,000 (M-PMMA) and 996,000 (H-PMMA) respectively. All chemicals were directly used as received.

Sample Preparations

BisGMA/TEGDMA (50/50, wt/wt) mixtures were combined with PMMA in clean vials, using acetone solvent. The solutions were stirred at room temperature until all the PMMA solid disappeared. Then the photopolymerization initiator CQ and accelerator DMAEMA were added. After initiator addition, the vials were transferred into a vacuum oven to remove the acetone solvent. The viscous photopolymerizable liquids were handled under orange light to prevent polymerization. All samples for mechanical test were made by photopolymerizing the liquids at room temperature, using a standard Elipar visible light curing apparatus.

Determination of Polymerization Shrinkage

The photopolymerization shrinkage was obtained by comparing the densities of the liquid mixtures and the semi-IPNs. Liquid mixture density was found by weighting the liquid contained in a calibrated syringe. The semi-IPN polymer samples, after visible light curing, were polished to be a cylinder for convenient determination of the volume which was used to calculate the materials density.

Mechanical Property Testing

The photopolymerized samples were polished to rectangular bars 2 x 2 x 25 mm for the fracture toughness (FT), cylinder bars with diameter 4 mm and height 10 mm for compressive strength (CS), and cylinder bars with diameter 4 mm and height 2 mm for diamentral tensile strength (DTS) testing. Instron testing equipment was used with the head speed set at 0.5 mm/min for the DTS and FT tests, at 1.0 mm/min for the CS test. All stress-strain curves were recorded.

Thermomechanical Analysis

Thermal behavior of the semi-IPNs were studied on a 2940 Thermomechanical Analyzer (TA Instruments). The sample size was the same as that for the DTS test. Scans were run at 10°C/min. heating under nitrogen gas atmosphere. Data were treated by the TA Thermal Analyst 2100 program.

Knoop Hardness Testing

Knoop Hardness Testing was performed on a LECO M-400 Hardness Tester, with a force of 50 g, objective lens set at 10X and testing time 20 seconds. At least 10 data sets were collected for each sample.

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TABLE 1. The Compatibilities of BisGMA/TEGDMA/PMMA Mixtures

Sample Number	0#	1#	2#	3#	4#	5#	6#	7#
BMS[a] g	5.00	4.75	4.50	4.00	4.75	4.50	4.75	4.50
L-PMMA, g	/	0.25	0.50	1.00	/	/	/	/
M-PMMA, g	/	/	/	/	0.25	0.50	/	/
H-PMMA, g	/	/	/	/	/	/	0.25	0.50
Appearance	clear	clear	clear	opaque	clear	opaque	opaque	two layers

a: BMS: BisGMA/TEGDMA (50 : 50 / wt.: wt.) monomer system

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RESULTS AND DISCUSSION

Compatibility of BisGMA/TEGDMA and PMMA

The three kinds of PMMA, in our experimental range studied, could not be readily dissolved in TEGDMA or BisGMA/TEGDMA solutions at room temperature. Since acetone is a good solvent for PMMA, TEGDMA and BisGMA, their combination were blended in acetone to form clear solutions. After acetone removal, the solutions of TEGDMA and PMMA 10% by wt. appeared clear, becoming more and more viscous with increasing PMMA molecular weight and content. With an increasing amount of M-PMMA, the viscosity of the TEGDMA/M-PMMA solutions became very high. As the content of PMMA approaches 25%, the solutions became opaque, indicating that TEGDMA and M-PMMA blends were not compatible at high content of M-PMMA.

The BisGMA/TEGDMA/PMMA were prepared in the same fashion as described for TEGDMA/PMMA. Their compatibilities are shown in Table 1.

The molecular weight of PMMA has an important effect on its miscibility with the BisGMA/TEGDMA base monomer mixture. BisGMA/TEGDMA solutions are compatible with 10% of L-PMMA, less than 10% of M-PMMA, or less than 5% of H-PMMA. With higher molecular weights or increasing content, the solubility of PMMA in BisGMA/TEGDMA mixture decreases rapidly. Compared with the solubility of PMMA in TEGDMA, PMMA showed much poorer compatibility with the BisGMA/TEGDMA blend. Higher molecular weight chains tend to entangle more tightly, affording small monomer molecules more difficulties to penetrate into it. For monomers such as BisGMA, the penetration of high

TABLE 2. The Polymerization Shrinkage of BisGMA/TEGDMA/PMMA System

Sample Number	0#	1#	2#	4#
BisGMA/TEGDMA, g	5.00	4.75	4.50	4.75
L-PMMA, g	/	0.25	0.50	/
M-PMMA, g	/	/	/	0.25
Shrinkage, %	12.47	11.70	10.59	11.36

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molecular weight PMMA is more difficult. After visible light-curing, the clear solutions became transparent solids with no observable phase separation. This demonstrated that the photopolymerization was readily achieved at room temperature. As the polymerization proceeded, the viscosity of the mixtures increased, inhibiting the self-aggregations of monomers and chain segments of PMMA. The polymerized semi-IPNs of the BisGMA/TEGDMA/PMMA blends kept the phase structure of a clear solution.

After polymerization, due to the stronger interaction among monomer molecules, the semi-IPNs system with high density were obtained, leading to polymerization shrinkage. The polymerization shrinkage of BisGMA/TEGDMA/PMMA systems are shown in Table 2. With the increase of the content or molecular weight of PMMA, the shrinkage decreased. But in the experimental range studied, changes are not very significant.

Mechanical Properties of TEGDMA/PMMA Semi-IPNs

During polymerization the TEGDMA and PMMA mixtures formed semi-IPNs, where TEGDMA was crosslinked, and PMMA interpenetrated into the networks of poly-TEGDMA. It has to be noted that there was little to no weight loss when the Poly-TEGDMA/PMMA semi-IPNs were extracted by boiling acetone for 72 hours. The latter result implies that the physical and/or chemical interactions between TEGDMA chains and PMMA chains are very strong and stable. Mechanical properties of the semi-IPNs are shown in Table 3.

The flexural bars of poly-TEGDMA/PMMA semi-IPNs were tested in three-point bending with a span to depth ratio of 10:1. According to our experimental procedure, flexural load-displacement traces showed a clear maximum load.

TABLE 3. The Mechanical Properties of Semi-IPNs Poly-TEGDMA/PMMA

Sample[a]	Flexural Strength MPa	Compressive Strength MPa	Compressive Modulus of Elasticity, MPa
TEGDMA/L-PMMA	93.2(2.4)	321(28)	1386
TEGDMA/M-PMMA	99.6(1.8)	425(37)	1330
TEGDMA/H-PMMA	86.4(4.8)	526(40)	738

a: For all samples, TEGDMA/PMMA is 90/10 (wt/wt)

Flexural strength for each sample was calculated from the maximum load on the trace. The semi-IPNs sample containing PMMA with medium molecular weight exhibited the highest flexural strength, but the effect of molecular weight of PMMA is not pronounced. As shown in Table 3, compressive strengths were rapidly improved with the use of higher molecular weight PMMA. The compressive modulus of elasticity changed reversibly. Compressive strength is the maximum stress that a material can sustain under crush loading. For polymer materials, debonding and shear failure are two major failure mechanisms. In semi-IPNs of poly-TEGDMA/PMMA, poly-TEGDMA is a crosslinked network, and PMMA interpenetrates into the networks, but not on a molecular scale. PMMA might form a finely divided phase. The distribution of the PMMA phase strongly affected the size of the poly-TEGDMA networks formed during polymerization. The phase domain sizes of PMMA with high molecular weight tend to be large, so in this semi-IPNs, the size of crosslinked poly-TEGDMA networks should be large too. In other words, the crosslinking density in this semi-IPNs is low, and the length of chain segment between crosslinking sites increase. Longer flexible TEGDMA chains can absorb more compressive energy, which was shown in the increase of compressive strength. The increased flexibility of molecular chains can result in the decrease of elastic modulus in polymer materials. In Table 3, the compressive modulus of elasticity in poly-TEGDMA/PMMA semi-IPNs decreased significantly with an increase of the molecular weight of PMMA. High molecular weight PMMA can improve the elastic modulus of this semi-IPN system, but its content was small (only 10%). So the structure of crosslinked TEGDMA is the main factor influencing the properties of the semi-IPNs.

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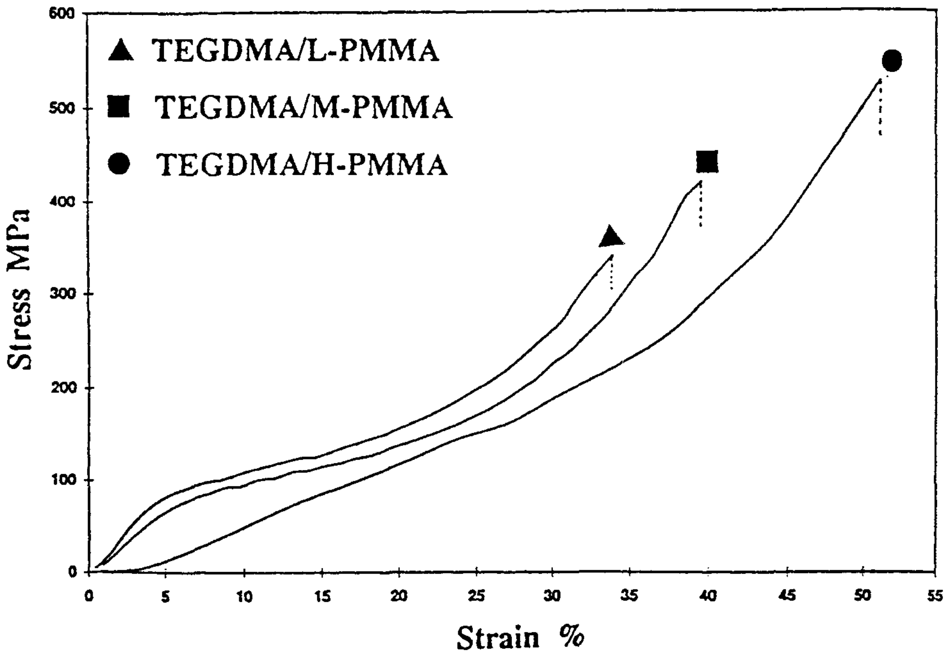

Figure 1. Compressive Stress-Strain Diagram of Poly-TEGDMA/PMMA Semi-IPNs.

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The compressive stress-strain curves of poly-TEGDMA/PMMA semi-IPNs are shown in Figure 1. The compressive strain increased with the molecular weight of PMMA. From the area under the stress-strain curve, the resilences of the semi-IPNs were improved with higher molecular weight of PMMA.

Mechanical Properties of BisGMA/TEGDMA/PMMA semi-IPNs

After the addition of BisGMA to the TEGDMA/PMMA mixtures, the polymerization of this mixture becomes more complex. Since BisGMA and TEGDMA are bifunctional monomers, they can copolymerize and/or homopolymerize to form crosslinked networks. Having large steric hindrance, with BisGMA having more difficulty to interpenetrate into the PMMA microphase. This means that PMMA assembles to form relatively large phase size, finally resulting in semi-IPNs of BisGMA/TEGDMA/PMMA with larger network size after polymerization. PMMA with small content performs in the BisGMA/TEGDGMA/PMMA mixtures by affecting the phase structures of the semi-IPNs. The mechanical

TABLE 4. The Mechanical Properties of BisGMA/TEGDMA/PMMA Semi-IPNs

Sample[a]	0#	1#	2#	4#
Compressive Strength, MPa	303(41)	326(38)	389(36)	380(13)
Flexural Strength, MPa	46.9(4.1)	43.5(1.2)	57.9(1.6)	32.9(2.9)

a: Sample numbers are the same as in Table 2

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properties of BisGMA/TEGDMA/PMMA semi-IPNs are listed in Table 4. All these samples appeared homogeneous.

With the addition of PMMA, the compressive strengths of BisGMA/TEGDMA/PMMA semi-IPNs, compared with BisGMA/TEGDMA base resin, have been rapidly improved. For the sample containing 10% of L-PMMA, its mechanical properties in Table 4 are much better than that of the sample containing 5% of L-PMMA. The flexural strength of the sample containing 5% of M-PMMA is much lower than that of the BisGMA/TEGDMA base resin. These results may be attributed to the effect of the molecular weight of PMMA on the phase structures of BisGMA/TEGDMA/PMMA semi-IPNs. Although all samples after polymerization were transparent, their microphase distribution could be somewhat different, due to the different content and molecular weight of PMMA. The compressive stress-strain diagram of BisGMA/TEGDMA/L-PMMA semi-IPNs are shown in Figure 2. The sample containing 10% of L-PMMA showed the maximum compressive strength and compressive breaking-strain.

Thermomechanical Properties of BisGMA/TEGDMA/PMMA Semi-IPNs

Thermal Mechanical Analysis (TMA) curves of BisGMA/TEGDMA/PMMA semi-IPNs are shown in Figure 3, With the results listed in Table 5. The glass transition temperature (T_g) of the samples containing L-PMM increased with the content of L-PMMA, but for the sample with 5% of M-PMMA, the T_g is lower than that of the BisGMA/TEGDMA base resin.

With an increase of the molecular weight and/or the content of PMMA in the mixture, the thermal expansion coefficient (TEC) of the semi-IPNs increased rapidly before the glass transition temperature, and the TEC after T_g changed reversibly. It is interesting that the TEC value of the BisGMA/TEGDMA base resin after T_g is larger than that before. With the addition of PMMA, all samples showed

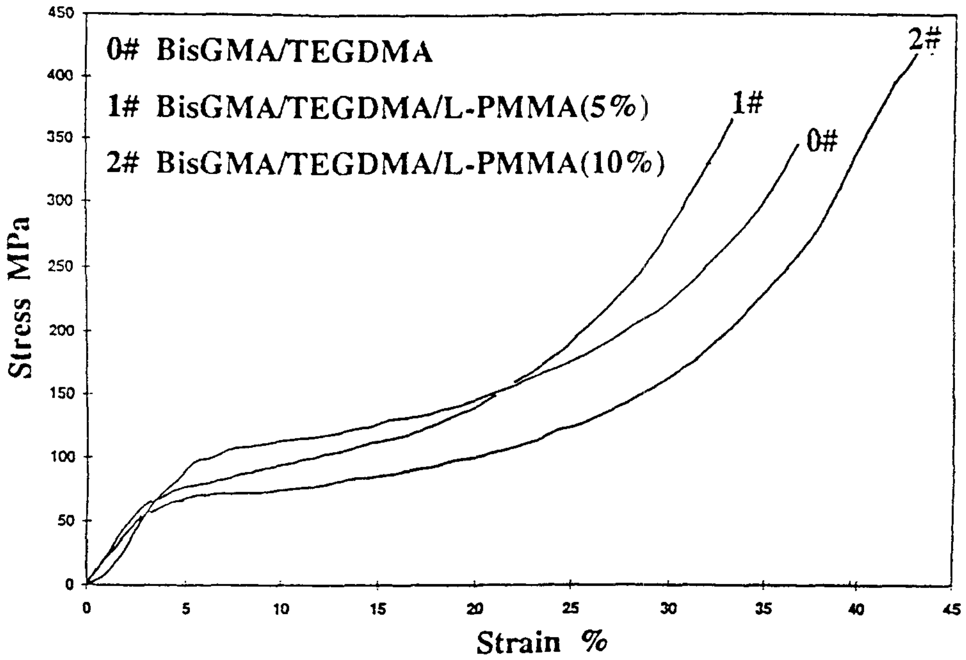

Figure 2. Compressive Stress-Strain Diagram of BisGMA/TEGDMA/PMMA Semi-IPNs.

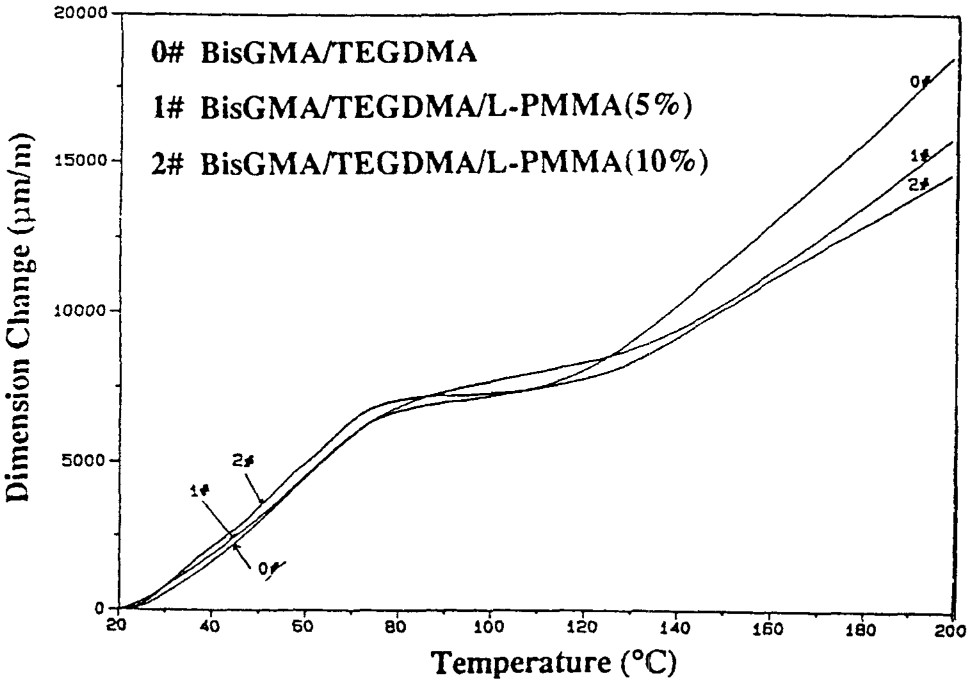

Figure 3. Thermal Mechanical Analysis Curves of the BisGMA/TEGDMA/PMMA semi-IPNs.

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TABLE 5. TMA and Hardness Testing Results of BisGMA/TEGDMA/PMMA Semi-IPNs

Sample	$\alpha_1{}^a$	T_g	$\alpha_2{}^b$	$\Delta\alpha^c$	Knoop Hardness
	µm/m•°C	°C	µm/m•°C	µm/m•°C	Kg/mm^2
0#	124	74.1	138	14	18.9(0.3)
1#	131	77.7	111	-20	17.9(0.4)
2#	139	79.5	95	-44	15.9(0.2)
4#	154	72.6	87	-67	13.8(0.1)

a: TEC before T_g, b: TEC after T_g, c: $\Delta\alpha = \alpha_2 - \alpha_1$

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higher TEC before T_g than after T_g, and the difference increased with the molecular weight and/or content of PMMA in the semi-IPNs. Before T_g, TEC is strongly dependent on the free volume in the system. After T_g, the chain flexibility is the main factor affecting the TEC. Due to the change of phase structure, the addition of PMMA could lead to an increase of free volume in the system. The hardness testing results are also listed in Table 5. Knoop hardness values of BisGMA/TEGDMA/PMMA semi-IPNs decreased with the molecular weight and/or content of PMMA. The sample containing 5% of M-PMMA exhibited the least Knoop hardness value. Also, the addition of PMMA could decrease the mobility of molecular chains in the semi-IPNs due to the chain entanglement, which could result in the decrease of TEC after T_g.

CONCLUSION

PMMA can be miscible with the BisGMA/TEGDMA monomer base resin. With increasing molecular weight and/or content of PMMA, the compatibility decreases. The compatibility between PMMA and TEGDMA is much better.

With an increase of the PMMA molecular weight, the compressive strengths of poly-TEGDMA/PMMA semi-IPNs maybe rapidly improved. The compressive modulus of elasticity changed reversibly.

With the addition of PMMA, the compressive strengths of BisGMA/TEGDMA/PMMA semi-IPNs increased. The semi-IPNs containing 10% of L-PMMA showed the maximum compressive strength and compressive breaking-strain.

With the increase of the molecular weight and/or content of PMMA in the BisGMA/TEGDMA/PMMA semi-IPNs, the thermal expansion coefficient rapidly increased before T_g, and decreased after T_g. The Knoop hardness values also decreased.

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