

Transmittance and Mechanical Properties of PMMA-Fumed Silica Composites

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SYNOPSIS

The transmittance, flexure strength, Young's modulus, and Vickers hardness of poly(methyl methacrylate) (PMMA), filled with fumed silica, was measured. Transmittance decreased with increasing content of filler. At 2 vol % filler content, composites had a higher transmittance with a lower surface area of fumed silica (larger primary particle size) because the lower surface area filler was better dispersed. At 4 vol % filler content, composites had a higher transmittance with a higher surface area fumed silica (smaller primary particle size). Flexure strength and Young's modulus of the composites was measured using three point bending. Addition of fumed silica led to a decrease of strength. Also, addition of fumed silica led to an increase of Young's modulus and Vickers hardness. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, a variety of highly transparent oxide/polymer composite materials have been investigated. One class of these transparent composites has received names such as ormocers (organically modified ceramics) and ormosils (organically modified silicates).^{1,2} A second class of transparent oxide/polymer composite materials is poly(methyl methacrylate) (PMMA) impregnated silica gels.^{3,4} These composites often possess high transparency because the scale of the individual phases is on the molecular or nanometer level.

Transparent oxide/polymer composite materials often combine useful attributes of both the oxide and polymer constituents. For example, ormosils are both transparent and hard. Ormosil coatings, applied on polycarbonate lenses, have been shown to provide abrasion resistance.¹ Another possible application of these composites is as a host for an organic dye molecule. Like polymers, these composites can be processed at or near room temperature, allowing incorporation of organic dye molecules. Yet these composites have improved thermal properties with

respect to polymers due to the ceramic phase. When used as hosts for organic dyes, transparent oxide/polymer composite materials often improve the photostability and thermal stability of the dye molecules, in comparison to polymer hosts. For example, organic laser dyes incorporated in ormosils showed improved photostability.⁵ Also, an electro-optically active aniline dye showed improved thermal stability when incorporated in PMMA-silica gel composites.⁶

Over the years, a number of polymers have been filled with submicron fumed or precipitated silica to yield transparent composites. Filled polymers are typically not nearly as transparent as the new classes of transparent composites described above. Nevertheless, one outstanding advantage of filled polymers is that they can easily be prepared in very large size. Like ormosils and PMMA-silica gel composites, filled polymers show improvement in thermal properties over bulk polymers. For instance, acrylic-fumed silica composites show an increase in the glass transition temperature.⁷ This effect has been attributed to a boundary layer surrounding the filler particle, in which the mobility of the polymer is restricted.⁸ The degree of interaction at the boundary layer can be increased by use of a crosslinking agent⁹ or by grafting the polymer onto the filler particle.¹⁰

It may be possible to prepare a filled polymer of very high transparency. Transparency of composite

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materials is limited primarily by light scattering. Light is scattered by the filler particles because the refractive index of the particles differs from the refractive index of the matrix. Ideally, if the two refractive indices were equal, the scattering would then become null and the particles would be invisible.

The concept of preparing a filled polymer of high transparency by matching the refractive indices could be realized in different ways. First, a polymer could be chosen that has a refractive index, n , well matched to a filler particle, such as fumed silica ($n = 1.46$). Most polymers have a refractive index considerably greater than 1.46, but a few polymers, most of which are elastomers, have a value of n close to 1.46.¹¹ Along the same lines, a polymer matrix could be chosen with a refractive index adjusted to that of the filler particle. For instance, the refractive index of silicone can be adjusted to a value between 1.35 and 1.70 by chemical modification.¹² The converse approach would be to use a filler particle, whose refractive index is adjusted to that of the matrix. For instance, with the addition of about 10 wt % titania,¹³ or 20 wt % alumina,¹⁴ the refractive index of silica is raised from 1.46 to the value for PMMA, 1.49. It is possible to prepare amorphous fumed silica with a dopant, such as alumina.¹⁵ It is also possible to prepare submicron silica particles with a dopant, such as titania by sol-gel processing.¹⁶

It should be possible to match the refractive index of a polymer to the refractive index of a silicate filler quite closely over a wide range of wavelength. However, several factors prevent the ability to match exactly the refractive indices. For instance, batch to batch variation in the refractive index of PMMA is as great as 0.001.¹⁷ Likewise, there would be uncertainties in the refractive index of a silicate filler. A polymer matrix and a silicate filler have differences in the temperature and wavelength dependence of refractive index. This also would place a very small but finite limit on the ability to match the refractive indices.

The main purpose of this study is to analyze the transmittance of poly(methyl methacrylate) (PMMA) filled with fumed silica. There has been one study of the transmittance of a fumed silica filled polymer. Transmittance of fumed silica filled silicone has been measured at a wavelength of 500 nm as a function of increasing surface area (smaller primary particle size). Silicone has a refractive of 1.43, which is slightly below the refractive index of silica. Transmittance of the fumed silica filled silicone increased as the surface area of the fumed silica increased to 200 m²/g. At higher surface area (smaller primary particle size), 400 m²/g, there was no fur-

ther increase of transmittance and this result was attributed to incomplete dispersion of these finer particles. Transmittance of silicone, filled with about 7 vol % (14 wt %) fumed silica of 0.20 cm thickness, was on the order of 60% at 500 nm.¹⁸

Dispersion of fumed silica in various solvents has also been investigated. Transmittance is dependent on dispersion. At low concentrations of filling, fumed silica is well dispersed. At higher concentrations, the silica particles form a gel network, due to hydrogen bonding between the silanol groups of the silica surfaces.¹⁹

Mechanical behavior of filled elastomers and acrylics has been observed in the past. A motivation for the addition of fumed silica to elastomers, such as silicone, is reinforcement. Addition of fumed silica increases the tensile strength of silicone to about 2 MPa.¹⁸ Studies of the mechanical behavior of silica filled acrylics have been limited primarily to viscoelastic properties, such as the dynamic storage modulus (G') and the tangent of the loss angle ($\tan \delta$).^{7,8} In this study, flexure strength, Young's modulus, and Vickers hardness of PMMA-fumed silica composites are reported.

EXPERIMENTAL

Materials and Sample Preparation

PMMA-fumed silica composites were prepared from methyl methacrylate (MMA, 99% with inhibitor, Aldrich), benzoyl peroxide (97%, Aldrich), and fumed silica. Two grades of Cabosil (Cabot Corporation) fumed silica were used: Cabosil L90 and Cabosil EH5. Cabosil L90 is a (low thickening efficiency) relatively coarse grade, with a specified surface area of 100 ± 15 m²/g and a specified primary particle diameter of 27 nm, as calculated from BET surface area. Cabosil EH5 is a (extra high thickening efficiency) fine grade, with a specified surface area of 380 ± 30 m²/g and a specified primary particle diameter of 7 nm, as calculated from BET surface area.¹⁹ All materials were used as received. Relative humidity was on the order of 20% during processing.

A monomer solution of 1 g benzoyl peroxide catalyst per 100 mL MMA was prepared. Fumed silica was added to the monomer solution, stirred for 5 min, and was then treated with ultrasound for 15 min. The suspensions were cast in glass vials and cured at 30°C in a mechanical convection oven for one week.

PMMA-fumed silica composites and unfilled PMMA were prepared in a disc shape for transmit-

tance measurement. The discs were 2.4 cm in diameter and were cut to a thickness of 1.0 ± 0.3 cm. The discs were polished with 1μ diamond and then with 0.05μ ceria. Discs for transmittance measurement were prepared with 2, 4, 6, and 8 vol % L90 fumed silica and with 2, 3, and 4 vol % EH5 fumed silica.

PMMA-fumed silica composites and unfilled PMMA were prepared in a rod shape for mechanical testing. The rods measured 1.3 cm diameter by 10 cm length. Rods for mechanical testing were prepared with 2, 4, and 6 vol % L90 fumed silica. Prior to testing, rods were annealed at 90°C for 4 h and were slowly cooled (less than $15^\circ\text{C}/\text{h}$) to room temperature.²⁰

Characterization

Transmittance was measured between 300–800 nm at a spectral bandwidth of 1 nm and with a scan speed of 2 nm/sec on a Cary model 2390 spectrophotometer (Varian).

The flexure strength and Young's modulus were measured using three point bending.²¹ The fixture had a support span of 7.0 cm. Rods were fractured at a crosshead speed of 12.7 cm/min (5.0 in./min), which corresponds to a strain rate of about 3×10^{-2} /sec. The strain rate was high enough to insure brittle failure. The number of samples per test was 10. Rods were fractured on a gear driven, universal materials tester (Instron model 1125).

Vickers hardness was measured with a load of 1

kg and an indent time of 15 sec. A factor of 0.99 was used to correct for the curvature of the test surface. Ten indentations were made on a sample at each concentration of filler. Tests were made on a Leco hardness tester, model DM-400.

RESULTS AND DISCUSSION

Transmittance

The transmittance data may be compared to the most general predictions of light scattering theories. For instance, it is expected that transmittance should decrease with increasing content of filler. It is also expected that transmittance should decrease with increasing particle size.²² However, a comparison of the transmittance data to a quantitative prediction is beyond the scope of this article. A prediction would be complicated by the fact that the particles are irregularly shaped. According to the manufacturer, fumed silica is made of spherical primary particles with a narrow size distribution. The primary particles are fused together in short aggregate chains. The aggregates may, in turn, be hydrogen bonded as a gel network and also as agglomerates if they are not well dispersed.¹⁹ A prediction would also be complicated by the fact that multiple scattering occurs. That is, the incident light is scattered a large number of times as it transverses a sample of 1 cm thickness with 2 vol % or more of filler.

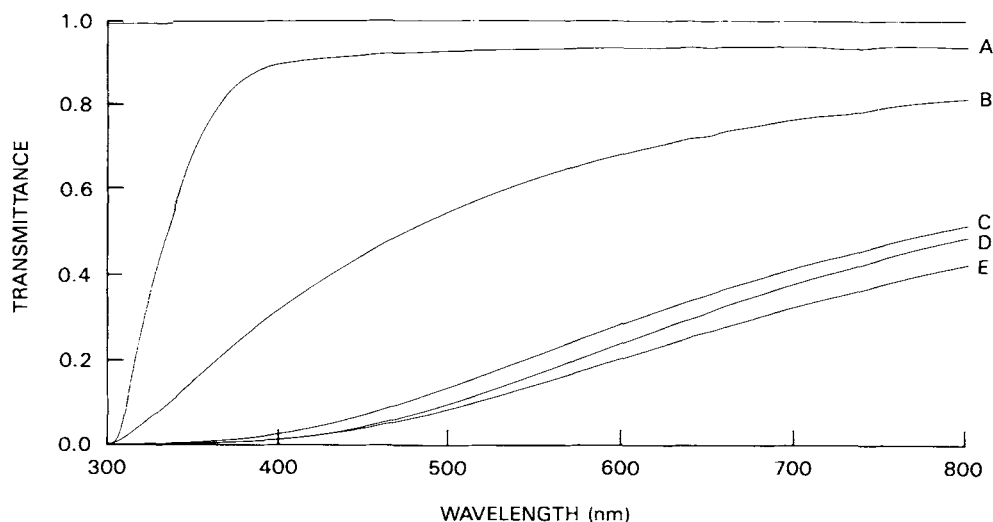


Figure 1 Transmittance of composites with Cabosil L90 fumed silica and of bulk PMMA: (A) unfilled PMMA; (B) PMMA with 2 vol % L90; (C) PMMA with 4 vol % L90; (D) PMMA with 6 vol % L90; (E) PMMA with 8 vol % L90.

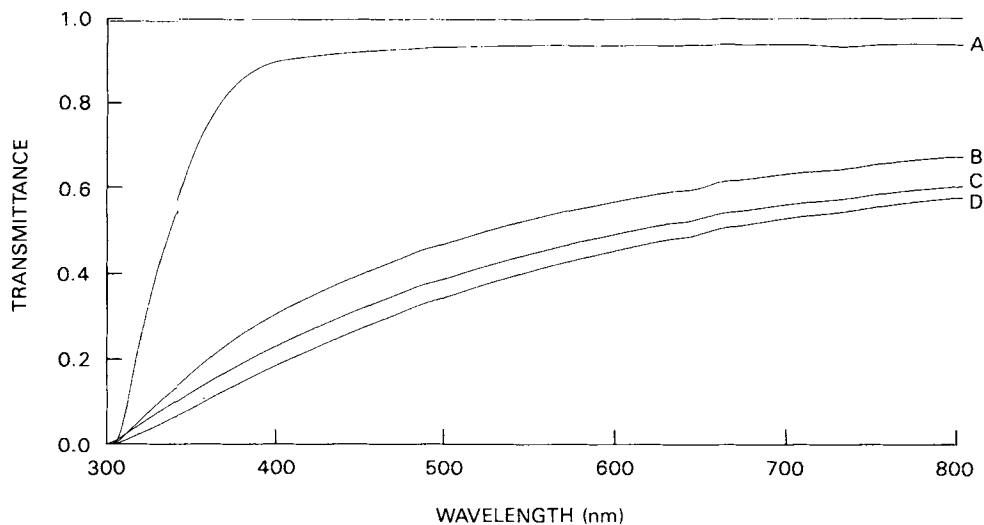


Figure 2 Transmittance: (A) unfilled PMMA; (B) PMMA with 2 vol % EH5; (C) PMMA with 3 vol % EH5; (D) PMMA with 4 vol % EH5.

The transmittance curves of composites with 2, 4, 6, and 8 vol % coarse grade Cabosil L90 grade fumed silica (primary particle diameter of 27 nm) are shown in Figure 1. The transmittance of unfilled PMMA is also shown for comparison. Transmittance of the composites dropped sharply as the filler content was increased from 2 to 4 vol % and then decreased more gradually as filler content increased to 8 vol %. For composites with L90 fumed silica, the observed trends in transmittance suggest the following about the dispersion of fumed silica in the composite. At low filler content, 2 vol %, fumed silica is well dispersed. At higher filler content, 4 vol % or more, the L90 fumed silica particles are arranged into a gel network.

The transmittance curves of composites with 2, 3, and 4 vol % of fine grade Cabosil EH5 fumed silica (primary particle diameter of 7 nm) are shown in Figure 2. The transmittance of unfilled PMMA is also shown for comparison. It was expected that transmittance would increase when using a filler particle with a smaller primary particle size. That is, composites with fine grade EH5 were expected to be more transparent than composites with an equal content of the relatively coarse grade L90. However, composites with 2 vol % EH5 were actually less transparent than composites with the same content of L90 fumed silica. At higher filler content, 4 vol %, composites with EH5 were more transparent than composites with the same content of L90 fumed silica, as expected. Accordingly, the data suggests that the EH5 fumed particles were arranged into a gel network even at low filler content, 2 vol %.

Mechanical Properties

Table I lists the flexure strength distributions of composites with L90 fumed silica, as represented by the two parameter Weibull analysis.²³ For each set, the Weibull modulus (m), and the correlation coefficient of the Weibull fit (R^2) is given. Figure 3 illustrates the strength distributions. Strength decreased with the addition of Cabosil L90 fumed silica. Strength distributions of the composites were wider than the strength distribution of unfilled PMMA. Loss of strength, due to the addition of fumed silica, may have been caused by the weak hydrogen bonding between the fumed silica surface and the PMMA. Widening of the distribution may have been due to increased sensitivity to flaws or introduction of flaws. Since unfilled PMMA has excellent strength, it is not surprising that the addition of fumed silica led to a decrease of strength, rather than a reinforcement, especially since no attempt was made to dehydrate the silica surface or to strengthen the interaction between the silica and the PMMA.

Table I Flexure Strength Distributions of Composites With L90 Fumed Silica

Material	σ (MPa)	m	R^2
Unfilled PMMA	149	21	0.95
PMMA with 2 vol % L90	126	9	0.95
PMMA with 4 vol % L90	115	6	0.84
PMMA with 6 vol % L90	102	7	0.98

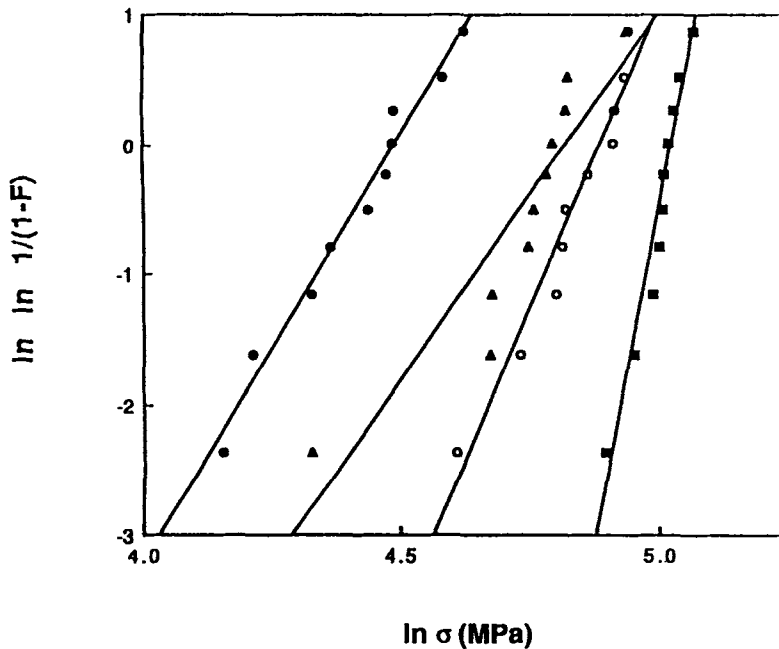


Figure 3 Strength distributions: (■) unfilled PMMA; (○) PMMA with 2 vol % L90; (▲) PMMA with 4 vol % L90; (●) PMMA with 6 vol % L90.

The Young's modulus of composites with L90 fumed silica is shown in Figure 4. Young's modulus increased with addition of fumed silica. In view of the fact that the Young's modulus of silica is about 70 GPa, the observed values of Young's modulus for the composites are within the lower and upper

bounds predicted by the Reuss and Voight models, respectively.²⁴

Vickers hardness of composites with L90 fumed silica is shown in Figure 5. Vickers hardness increased modestly with the addition of fumed silica. Composites, such as ormosils and PMMA impreg-

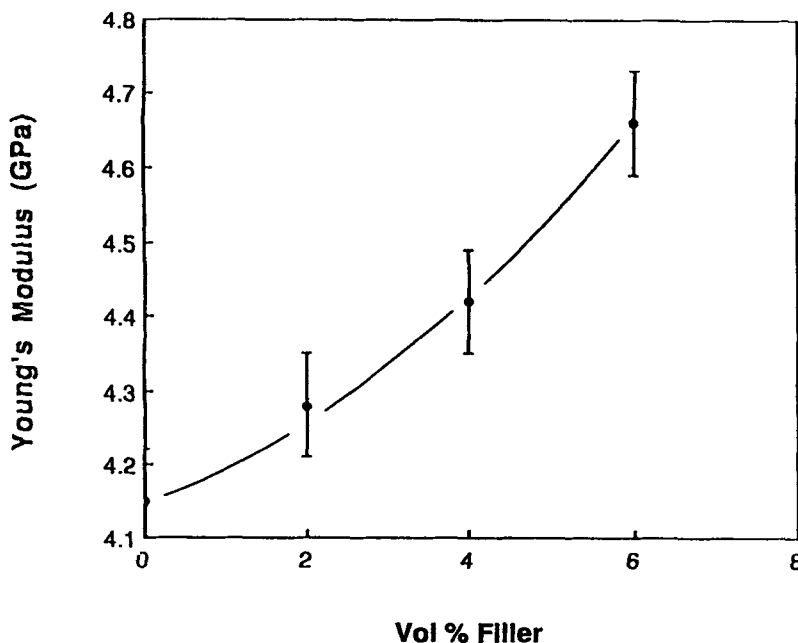


Figure 4 Young's modulus of unfilled PMMA and PMMA with L90.

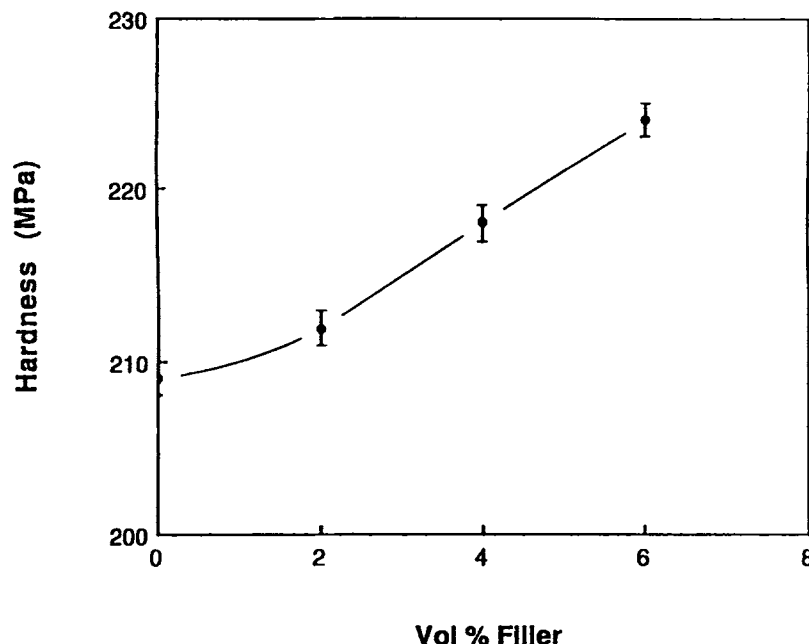


Figure 5 Vickers hardness of unfilled PMMA and PMMA with L90.

nated silica gels, often show hardness much greater than the hardness of PMMA because they contain a covalently bonded oxide network. The hardness of the PMMA-fumed silica composite did not increase dramatically with the addition of fumed silica, because the particles did not form into a covalently bonded network.

CONCLUSIONS

Transmittance of PMMA-fumed silica composites decreased with increasing content of filler. At 2 vol % filler content, composites had a higher transmittance with a lower surface area fumed silica (larger primary particle size) because the lower surface area filler was better dispersed. At 4 vol % filler content, composites had a higher transmittance with a higher surface area fumed silica (smaller primary particle size).

The addition of fumed silica led to a decrease of strength of PMMA. Also, the addition of fumed silica led to an increase of Young's modulus and Vickers hardness.

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