

# Preparation and Characterization of Poly(methyl Methacrylate)–Lead Silicate Composites

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## Synopsis

Poly(methyl methacrylate)–lead silicate composites were prepared with different amounts of crystalline or amorphous PbO–SiO<sub>2</sub> binary composition (70 mole % PbO). The polymerization reaction was carried out in aqueous medium and in methanol–water mixture at 40°C using sodium bisulfite as initiator. The presence of lead silicate was found to increase the molecular weight of the poly(methyl methacrylate). The prepared composites were characterized by studying their shielding properties to  $\gamma$  radiation, mechanical hardness, dielectric constant, and thermal stability. It was found that lead silicate increases the absorbing power of the composites to  $\gamma$  radiation. This behavior was found to be dependent on the amount and the type of lead silicate (amorphous or crystalline). Gamma irradiation of the composites was found to cause chemical degradation of the poly(methyl methacrylate) leading to a decrease in mechanical hardness. Molecular weights of the poly(methyl methacrylate) for some of the composites were determined before and after irradiation viscosimetrically. Dielectric constants for some of the composites were determined at two different temperatures. The thermal stability of the composites was studied by means of an automatic thermogravimetric analyzer.

## INTRODUCTION

A study of the polymerization of methyl methacrylate (MMA) in aqueous media was carried out in the absence and presence of inorganic materials. It was reported that lead dioxide polymerizes the methyl methacrylate by a radical mechanism,<sup>1</sup> but it proved to be ineffective with respect to styrene and acrylonitrile. The rate of polymerization of methyl methacrylate was accelerated by the addition of dimethyl aniline to the reaction system.

It was found that the sodium bisulfite-initiated polymerization of methyl methacrylate in water was catalyzed by soda lime.<sup>2,3</sup> The iron oxide<sup>4</sup> present in the sand as impurity proved to have a catalytic effect on the aqueous polymerization of methyl methacrylate. It seems that the metal oxide–water interface plays an important role in the acceleration of the polymerization process.

It was also reported<sup>5</sup> that methyl methacrylate was polymerized in an aqueous solution of NaHSO<sub>3</sub> without stirring to obtain polymers of very high molecular weights. The polymerization took place not only in the aqueous phase, but also at the interphase between the water and monomer phases and also in the monomer phase.

Polymeric composites containing different amounts of inorganic additives were prepared by others<sup>6–8</sup> for the purpose of studying their shielding properties toward radiation energy such as  $\gamma$  radiation. It was found that lead sulfide, in

the form of galena concentrate dispersed in a solidified organic plastic matrix material, improved the energy shielding properties of the plastic material.<sup>6</sup> The plastic matrix may be a thermoplastic substance, an elastomeric substance, or an asphaltic composition. A flexible shield for ionizing radiation<sup>7</sup> is composed of a barrier layer of powdered lead, silicone rubber, and fiber black sandwiched between two fabric layers. This shield gives excellent x-ray absorption. Combination plates of plastics and metal powder with cadmium and boron additives were found to be suitable for screening against neutrons and gamma radiation.<sup>8</sup>

The purpose of this paper is to prepare some poly(methyl methacrylate) (PMMA)-lead silicate composites in aqueous medium using sodium bisulfite as initiator and to study the effect of lead silicate (amorphous and crystalline) on the chemical, physical, and mechanical properties of the produced composites. Characterization of the composites involving shielding properties (with respect to  $\gamma$  radiation), mechanical properties such as hardness and its relation to  $\gamma$  irradiation, electric properties, and measurements of dielectric constant, and finally the effect of lead silicate on the thermal stability of the prepared composites was performed.

## EXPERIMENTAL

### Materials

Methyl methacrylate was obtained by the thermal degradation of scrap polymer, washed with sodium hydroxide, dried by anhydrous sodium sulfate, and fractionated by means of a fractionating column of about 15 theoretical plates. The fraction boiling between 100.0 and 100.5°C was collected. Sodium bisulfite was laboratory-grade reagent. Chemical-grade lead oxide and high-purity quartz powder were used.

### Preparation of PbO-SiO<sub>2</sub> Binary System

A composition of 70 mole % PbO was prepared in the present investigation. The weighed amounts of PbO and SiO<sub>2</sub> were mixed in an agate mortar and the mixture was melted in a platinum crucible at about 200°C over the melting point of each composition. The melt was held at that temperature for 2 hr through which crucible was swirled about every 20 min to obtain a homogeneous melt. The melt was then quenched by being poured on an iron plate at room temperature. Some melts when cooled gave glassy material, and others gave crystalline material. The cooled material was ground into powder and two portions were prepared, the first above 200 mesh and the second less than 200 mesh.

### Preparation of Poly(methyl Methacrylate)-Lead Silicate Composites

The polymerization of methyl methacrylate (5.6 g) in water and in methanol-water mixture (400 ml) was carried out at 40°C for 6 hr using sodium bisulfite (0.1 g-mol/l.) as initiator in the presence and absence of different amounts of lead silicate (crystalline or amorphous). The reaction mixture was then left overnight at laboratory temperature. The obtained PMMA-lead silicate composites were

filtered, washed with water and methanol, and then dried in an oven at 70°C for a week. The choice of the PbO-SiO<sub>2</sub> binary system (70 mole % PbO) was based on its highest catalytic effect on the monomer conversion and the overall rate of polymerization of methyl methacrylate compared with the other PbO-SiO<sub>2</sub> binary compositions.<sup>9</sup> Monomer percent conversion for each composite is given in Table I. The composites were then ground in an agate mortar and thoroughly mixed and sieved to < 120 mesh. The mixture was then molded at 150°C by applying a pressure of 400 kg/cm<sup>2</sup> for 10 min into disks 2.53 cm in diameter and 0.39-0.42 cm thick.

### Characterization of Composites

**Gamma Radiation Shielding Properties.** The composites were subjected to  $\gamma$  radiation at room temperature in a <sup>60</sup>Co gamma cell (500 curies) at a dose rate  $4.2 \times 10^5$  rads/hr. The shielding properties were measured by the use of the thermo luminance dosimetric (TLD) technique.<sup>10</sup> The percentage of the transmitted dose was determined using a CaF<sub>2</sub> crystal. The transmitted dose during certain time (15 min) was estimated by placing the TLD crystal at a constant distance from the cone in order to obtain an absorbed dose of  $2 \times 10^4$  rads. The composite sample was maintained in contact with the crystal facing the source, and the transmitted dose was detected and measured. The difference between the two doses is the dose value absorbed (shielded) by the composite. The percentage of the absorbed dose was calculated according to the relation

$$\text{absorbed dose \%} = \frac{\text{dose absorbed by composite}}{\text{original dose}} \times 100$$

**Effect of Gamma Irradiation on Mechanical Properties of Composites.** The effect of  $\gamma$  irradiation on the mechanical hardness of the prepared composites was examined using the hardness tester Finmechanick Ralf Kögel, Leipzig, with load ranges from 5 to 98 kg of the ball type. The hardness measurements for each composite were carried out within 15 min after irradiation had ceased.

**Molecular Weight Determination.** Molecular weights of the PMMA present in the prepared composites were determined before and after irradiation by means of intrinsic viscosity measurements. Viscosity-average molecular weights ( $\bar{M}_v$ ) were calculated from the  $[\eta]$  values using the equation<sup>11</sup>

$$[\eta] = 0.74 \times 10^{-4} \bar{M}_v^{0.76}$$

All viscosity measurements were performed at 25°C.

TABLE I  
Effect of Lead Silicate on Monomer Conversion

Composite no.	PbO-SiO <sub>2</sub>		Monomer conversion, %
	Type	Amount, g	
1	crystalline	2.5	81.5
2	crystalline	3.0	76.8
3 <sup>a</sup>	crystalline	2.5	91.5
4	amorphous	2.5	84.8
5	—	—	91.6

<sup>a</sup> Preparation was carried out in methanol-water mixture (20% v/v).

**Determination of Dielectric Constant.** The dielectric constant ( $\epsilon$ ) of some of the composites was determined using the Multidekometer Type DK06.<sup>12</sup> The measurements were based on the superheterodyne principle. The frequency used was 2 MHz/sec and was indicated on a cathode ray tube. The tuning condenser, which had 4500 uniform divisions, permitted fine adjustment and allowed a sensitivity of the order of  $10^{-5}$ . A trial was carried out to measure the conductance of these composites by mounting the samples in a holder between opposite electrodes connected with an external circuit using a dc electrometer.

**Thermal Stability Measurements.** The thermal stability of some of the composites was determined by means of an automatic thermogravimetric analyzer in atmospheric oxygen. The loss in weight with increase in temperature was recorded.

## RESULTS AND DISCUSSION

PMMA-lead silicate composites were found to have shielding properties when subjected to  $\gamma$  irradiation. PMMA itself was also found to have the same property, but of much lesser extent than the PMMA composites. Data of the percent shielding to the applied  $\gamma$  radiation dose for the different composites are given in Table II. From the table it is seen that the presence of lead silicate has an obvious effect on the shielding properties of PMMA (compare sample 5 with the rest of the composites).

The change in the type of lead silicate has some effect on the  $\gamma$  radiation total absorbance and scattering (compare samples 1 and 4). This could be explained by the fact that amorphous lead silicate absorbs more radiation than its crystalline counterpart.

It is also shown that the medium of the polymerization process has a pronounced effect on the shielding property of the composite (compare samples 3 and 1). This could be attributed to the change in the tacticity<sup>13</sup> of the polymer molecules as composite 3 was prepared in methanol-water mixture.

It must be mentioned that the shielding values given in Table II are really undervalued as the slit (opening) of the <sup>60</sup>Co cell is a little larger than the diameter of the composite discs used.

Gamma irradiation of PMMA-lead silicate composites are known to cause some degradation of the polymer molecules. This was proved in this investigation by molecular weight determinations of the PMMA before and after irradiation. The average molecular weight values are given in Table III. The drop in the molecular weight of the PMMA by  $\gamma$  irradiation indicates that these composites could be regarded as temporary shielding material, in other words,

TABLE II  
Shielding Measurements of Poly(methyl Methacrylate)-Lead Silicate Composites

Sample No.	Type of PbO-SiO <sub>2</sub>	Composition of PbO-SiO <sub>2</sub> , %	Transmitted dose, $\times 10^{-4}$ rad	Shielded dose, %
1	crystalline	35.7	0.80	60
2	crystalline	41.1	0.18	91
3	crystalline	32.9	0.24	88
4	amorphous	34.7	0.70	65
5	—	—	1.00	50

TABLE III  
Effect of  $\gamma$  Irradiation on Molecular Weight

Sample No.	[ $\eta$ ]		$\bar{M}_v \times 10^{-5}$	
	Before irradiation	After irradiation	Before irradiation	After irradiation
2	0.83	0.38	2.133	0.763
4	0.93	0.41	2.477	0.843
5 <sup>a</sup>	0.70	0.39	1.704	0.789

<sup>a</sup> Sample 5 is pure poly(methyl methacrylate).

the shielding property will be time and dose dependent. It was also found that lead silicate accelerates the degradation process of PMMA by  $\gamma$  irradiation (compare samples 2 and 5).

On the basis of these results, one can say that PMMA might be used as dosimeter determining its molecular weight before and after irradiation. The same idea could be applied in case of lead silicate composites knowing the exact lead silicate composition which will correspond to the amount of dose shielded. In this respect, it must be taken into consideration that the type of the lead silicate as well as the conditions of the composite preparation affects to a great extent the amount of the absorbed  $\gamma$  radiation. Therefore, the possibility of using these composites as dosimeters is restricted by the above-mentioned conditions.

It has been found that the polymerization of methyl methacrylate in aqueous media in the presence of lead silicate resulted in the formation of PMMA of higher average molecular weights than in the absence of lead silicate. This may be attributed to the formation of coordination linkage between Pb ions and the bisulfite ions of the initiator leading to a decrease in the free bisulfite ions and consequently to less bisulfite radicals, thus leading to higher average molecular weights.

The effect of  $\gamma$  irradiation on the mechanical properties of the prepared composites was estimated using the hardness tester mentioned in the experimental part. Table IV shows the hardness values obtained by varying the radiation dose. The mechanical hardness depends to a great extent on the structure of the PMMA which in turn depends on the medium and conditions of the polymerization process. It also changes with the change in the amount and the type of lead silicate present in the composite. Figure 1 shows the relation between the applied dose and the mechanical hardness of the prepared composites. From the figure it is seen that the hardness decreases with increase in

TABLE IV  
Effect of  $\gamma$  Radiation on Hardness (HPK) of PMMA-Lead Silicate Composites

Sample No.	Composite composition, %		Hardness (HPK)					
	PMMA	PbO-SiO <sub>2</sub>	0 rads <sup>b</sup>	10 <sup>3</sup> rads	10 <sup>4</sup> rads	2 × 10 <sup>5</sup> rads	10 <sup>6</sup> rads	8 × 10 <sup>6</sup> rads
1	64.3	35.7	2390	1800	1500	1130	1000	900
2	58.9	41.1	3600	2700	2350	2000	1800	1700
3	67.1	32.9	3000	2100	1830	1250	1100	1090
4 <sup>a</sup>	65.3	34.7	3500	2600	2300	1900	1700	1600
5	100	—	3650	2800	2500	2050	1900	1800

<sup>a</sup> Amorphous PbO-SiO<sub>2</sub>.

<sup>b</sup> Radiation dose.

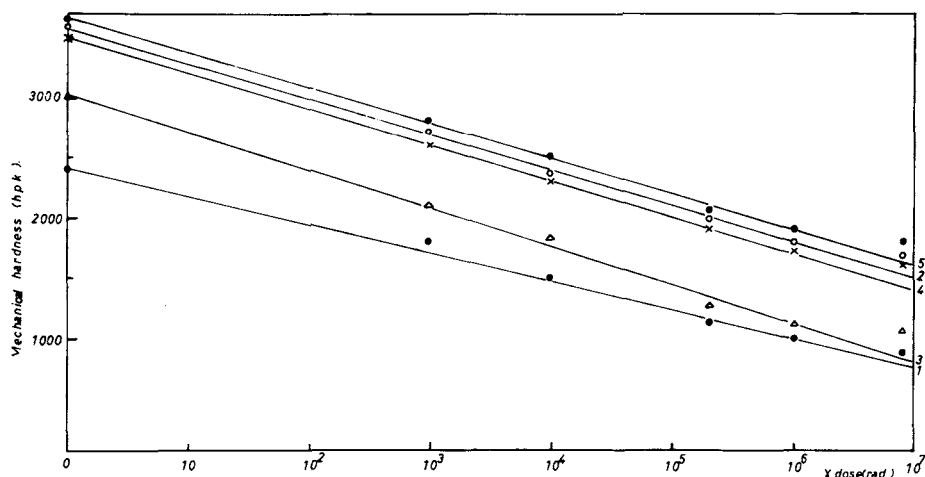


Fig. 1. Effect of  $\gamma$  radiation on mechanical hardness of poly(methyl methacrylate)-lead silicate composites.

the applied dose. The doses used were as high as  $\sim 10^7$  rads. The decrease in hardness with increasing dose was due to the degradation process of the PMMA molecules by  $\gamma$  irradiation. Pure PMMA (sample 5) was found to have the highest value of mechanical hardness at both low and high doses.

The electrical conductivity of the composites was found to be less than  $10^{-14}$   $\Omega^{-1}/\text{cm}$  even at a temperature of 100–120°C, which is beyond the limit of accurate measurement of the circuit used. The prepared composites seem to be good insulators. The dielectric constant of some of these composites was determined at temperature 25 and 60°C (Table V). From the table it is seen that the presence of lead silicate in the composite causes an increase in the dielectric constant value. This could be explained by the fact that lead silicate increases the polarity of the composite which in turn causes an increase in the dielectric constant, i.e., the lead silicate charged ion pairs act as effective dipoles. An increase in the temperature leads to a corresponding increase in the dielectric constant values, which could be attributed to a decrease in the energy of activation of the vibrational motion of the polar groups within the polymer molecules. This behavior is more pronounced in the composite case rather than the pure PMMA and could be explained by an additional increase in the dipole effect (being heated) of the lead silicate ion pairs.

Figure 2 shows the thermal stability of PMMA-lead silicate composite as well as pure PMMA. The pure polymer and the composite start to degrade at  $\sim 310^\circ\text{C}$ . From the figure it is seen that PMMA decomposes completely, while PMMA-lead silicate (41.1% lead silicate) reaches 55% decomposition. This

TABLE V  
Effect of Composite Composition and Temperature on Dielectric Constant  $\epsilon$

Sample No.	Sample composition	$\epsilon$	
		25°C	60°C
3	PMMA-lead silicate (crystalline)	3.89	4.07
5	PMMA	3.52	3.57

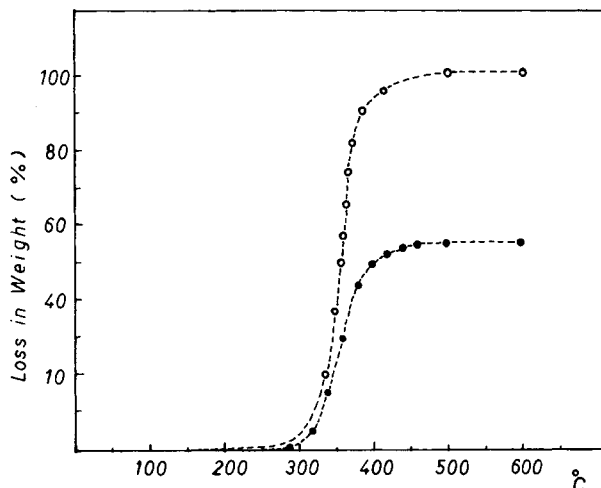


Fig. 2. Thermal decomposition curves: (●) PMMA-(PbO-SiO<sub>2</sub>) Composite 2; (○) PMMA 5.

confirms the inorganic percent composition of the composite which remains undegraded. The degradation curves show that the catalytic decomposition effect of the lead silicate on the poly(methyl methacrylate) is hard to observe.

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### References

1. L. Munum and M. Yuji, *Kogyo Kagaku Zasshi*, **73**(1), 125 (1970).
2. A. B. Moustafa and M. A. Diab, *Angew. Makromol. Chem.*, **45**, 41 (1975).
3. A. B. Moustafa and M. A. Diab, *J. Appl. Polym. Sci.*, **19**, 1585 (1975).
4. A. B. Moustafa, *Angew. Makromol. Chem.*, **39**, 1 (1974).
5. M. Hamashima and S. Yamajaki, *Hokoku*, **59**(4), 180 (1964).
6. Br. Pat. 988,414 (April 7, 1965).
7. J. V. Weinberger, U.S. Pat. 3,239,669 (Mar. 8, 1966).
8. H. Wilski (to Farbwerke Hoechst AG., vormals Meister Lucins and Bruening, Frankfurt am Main), *Atomwirtschaft*, **10**: 70 (Feb. 1965).
9. A. B. Moustafa and A. S. Badran, *J. Polym. Sci.*, in press.
10. K. Becker, *Solid State Dosimetry*, CRC, Cleveland, Ohio (1973).
11. A. I. Goldberg, W. G. Hohenstein, and H. J. Mark, *J. Polym. Sci.*, **2**, 502 (1947).
12. K. Slevogt, Wissenschaftlich-Technische Werkstätten Gmb, H. Weilheim, Oberbayern, West Germany (Scientific workshop).
13. A. B. Moustafa, M. H. Nosseir, and N. E. Nashed, *Angew. Makromol. Chem.*, **52**, 71 (1976).

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