Reaction Catalyzed by Montmorillonite: Polymerization of Methyl Methacrylate

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ABSTRACT: The polymerization of methyl methacrylate (MMA) was carried out in aqueous media having various concentrations of potassium persulfate as initiator in the presence or the absence of montmorillonite (Texas) at various temperatures. The rate of polymerization increased with increasing initiator concentration. Thermal stabilities of the resulting composite materials were studied and the activation energies of polymerization and degradation were determined. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 367–372, 1997

Key words: montmorillonite; methyl methacrylate; catalyst

INTRODUCTION

Clays have been used for a variety of purposes since prehistoric times. During this century, use has extended to the chemical industry, e.g., paint, paper, and rubber.[1] In the early 1930s, acid-treated natural clays were the preeminent solid catalysts used in petroluem refining, as they had the ability to induce vapor phase cracking of long chain molecules in crude oil to provide useful fuels for petrol engines.[2,3]

The organic chemist's interest in the use of clays was also kindled by the burst of activity started in the 1970s when the potential of clay for solid acid catalysis and the utility of clay-supported reagents were described. Since that time, there have been numerous reports of the catalytic activity of clay-based materials involving a tremendous variety of organic reactions.[4–6]

The aim of this work is a study of the catalytic polymerization of methyl methacrylate (MMA) in the presence of montmorillonite (Texas). The rate of polymerization using different concentrations of ($K_2S_2O_8$) initiator with or without the catalyst has been determined. The activation energies of polymerization and degradation of poly MMA were determined.

EXPERIMENTAL

MMA (BDH Chemicals, Ltd., U.K.) stabilized with 0.1% hydroquinone was washed with sodium hydroxide solution to remove inhibitor. The crude MMA monomer was degassed and twice distilled on a vacuum line, dried over anhydrous Na_2SO_4 and stored below $-18°C$. Montmorillonite (English China Clay Ltd.) and Al^{3+}-exchanged montmorillonite were prepared[7,8] by standard ion-exchange method using solutions of $Al(SO_4)_3 . 16H_2O$. The exchanged clay was repeatedly washed and centrifuged before drying in a vacuum oven at 60°C for 12 h. It was then ground and sieved at 140 mesh (ASTM). The material was then stored in a dry-

Table I   Effect of Weight of Catalyst in Polymerization of Methyl Methacrylate

Catalyst (g)	Yield (g)	Yield (%)
0.00	1.485	31.6
0.25	2.131	45.3
0.50	3.091	65.8
1.00	3.821	81.3
1.50	3.880	82.6
2.00	4.235	90.1

Figure 1   Effect of weight of catalyst on the yield of PMMA of 4.7 g MMA with 0.02 mol/L $K_2S_2O_8$, 3 h at 55°C.

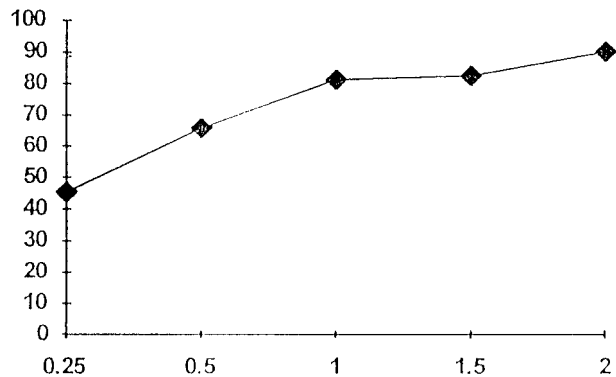air container. Potassium persulfate ($K_2S_2O_8$) was a product of BDH Chemicals Ltd.

The reactions were carried out by dissolving the required amount of initiator in distilled water (45 mL) in a 250 mL conical flask into which MMA (4.7 g) was introduced. The montmorillonite was added, and then the flask was well stoppered and put in a thermostated water bath for the reaction time. The polymerization was stopped by addition of hydroquinone (0.2 w/v % monomer). The reaction product was then filtered off. It was washed thoroughly with distilled water and finally dried at 80°C for several days, the conversion was calculated from the relation

$$\text{Conversion } (\%) = (\text{Cp} - \text{C}) \times 100/\text{M}$$

where Cp, C, and M are the weight of clay–polymer composite, clay, and monomer, respectively.

Thermogravimetry (TG)

Thermogravimetry (TG) measurements were made with a Mettler 3000TA thermobalance. The

sample (about 10 mg) was heated from 50° to 700°C under dynamic N_2 flow (60 mL/min) at a rate of 10°C/min. TG also was used isothermally at the initial degradation temperature to various times. The activation energy of degradation was determined using the Arrhenius relationship.

Mechanical Properties

Hardness

Brinel hardness tester (HPO 250) (WPM) with a ball 2.5 nm and a load of 31.25 kg and 62.50 kg was used for the determination of the hardness of PMMA and MMA–clay polymer composite. The PMMA homopolymer and MMA–montmorillonite polymer composite materials (~5 gm) were milled and sieved, and the powder having particle size

(a)   **(b)**
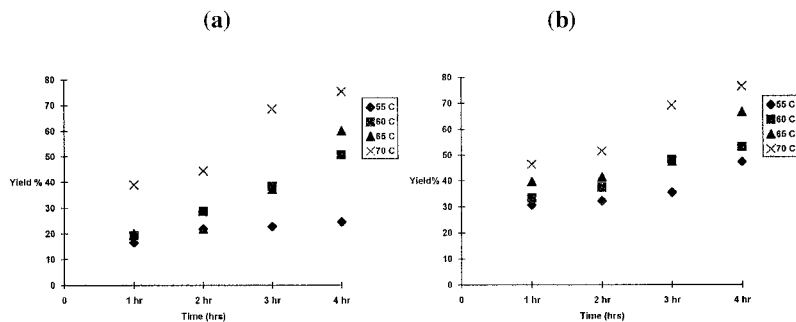
Figure 2   Polymerization of MMA with 0.02 mol/L $K_2S_2O_8$: (a) MMA alone, (b) MMA with clay (106 μm) at different temperatures.

(a)   **(b)**
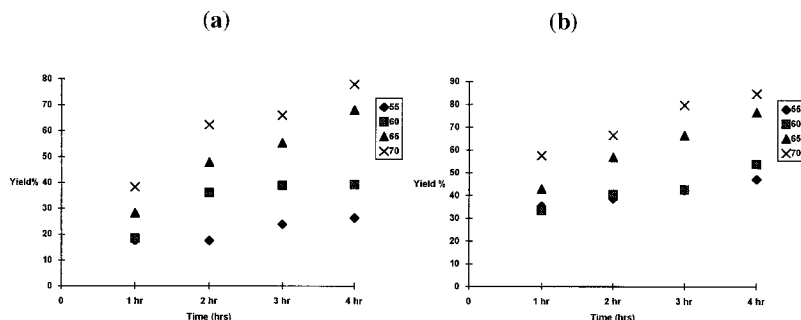
Figure 3 Polymerization of MMA with 0.03 mol/L $K_2S_2O_8$: (a) MMA alone; (b) MMA with clay (106 μm) at different temperatures.

<200 mesh was molded by applying a pressure of 50 kg/cm^2 for 5 min at 180°C.

Compression Strength

Compression strength measurements were made with a Universal Testing Machine No. 15376, Losen-Housenwerk, of 40 tons capacity.

RESULTS AND DISCUSSION

### Effect of Weight of Catalyst

Table I represents the conversion of MMA at different weights of clay. Figure 1 indicates that the conversion reaches a limiting level using 1 g of catalyst. Therefore, all the further experiments were carried out using 1 g of clay.

Effect of Initiator

Figures 2 through 5 show the conversion of MMA in the absence and in the presence of clay at various temperatures by using 0.02, 0.03, 0.04, and 0.05 mol/L of $K_2S_2O_8$, respectively. It was found that the rate of polymerization of MMA is greater in the presence of the clay than in its absence. The percentage also increases by increasing the temperature and initiator concentrations. It seems that the catalytic effect of clay can be attributed to the formation of an addition product with potassium persulfate which must be active enough to increase the rate of polymerization of methyl methacrylate. The activity of this addition product was found to increase with decreasing particle size of montmorillonite, due to the opening of the framework of the montmorillonite and consequently to the increase of active centers. Therefore, the catalytic effect of clay is attributed

(a)   **(b)**
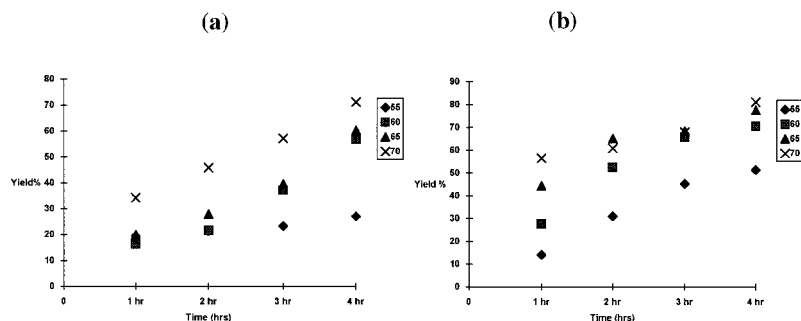
Figure 4 Polymerization of MMA with 0.04 mol/L $K_2S_2O_8$: (a) MMA alone; (b) MMA with clay (106 μm) at different temperatures.

(a)   (b)
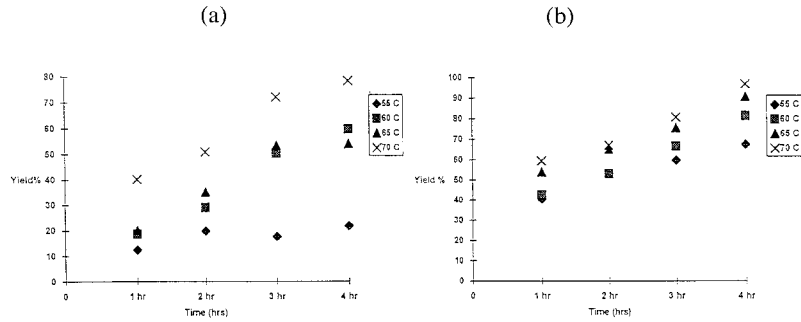
Figure 5   Polymerization of MMA with 0.05 mol/L $K_2S_2O_8$: (a) MMA alone; (b) MMA with clay (106 μm) at different temperatures.

Table II   Activation Energies of Polymerization of MMA With and Without Clay

$K_2S_2O_8$ Concentration (mol/L)	Activation Energy, E_a (kJ/mol)	
	MMA Alone	MMA + Clay Composite
0.02	56.9	43.0
0.03	50.5	37.8
0.04	24.7	—
0.05	16.7	10.5

to formation of an active complex with the initiator, which increases the rate of polymerization more than for $K_2S_2O_8$ alone. This explanation was found to be in agreement with that suggested for the polymerization of MMA in the presence of soda lime glass,[9] using sodium bisulfite as initiator. It was found that the formation of an addition product between the glass powder and the initia-

tor increases the rate of polymerization of methyl methacrylate.

Activation Energy of Polymerization

Apparent activation energy, E_a, was determined from initial rate of polymerization of MMA with and without clay, at 55°, 60°, 65°, and 70°C. Plots of ln K versus $1/T$ were made so that the activation energies could be determined by using the Arrhenius relationship. Table II shows that the activation energies of polymerization of MMA/E_a are higher in the absence of clay than in its presence, and at a higher concentration of initiator, E_a decreases.

Thermal Stability of Composite Materials

TG thermograms of PMMA and composite materials of MMA−clay are shown in Figure 6. It is clear that the composite has higher stability than

(a)   (b)
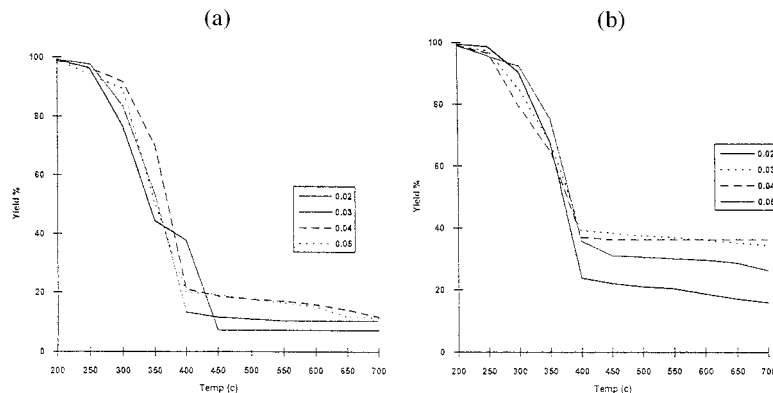
Figure 6   TGA: (a) PMMA alone; (b) MMA−clay composite.

Table III   TGA of the PMMA and MMA–Clay Composite

$K_2S_2O_8$ (mol/L)	PMMA				MMA + Clay Composite			
	0.02	0.03	0.04	0.05	0.02	0.03	0.04	0.05
Peak (1) T_{max} (°C)	273	280	284	286	278	287	288	290
Weight loss (%)	25.9	21.05	20.70	18.50	15.02	15.5	18.8	19.1
Peak (2) T_{max} (°C)	360	365	368	370	365	368	371	378
Weight loss (%)	62.3	61.8	60.9	60.2	50.1	47.32	39	36.89
Residue (%)	11.8	17.1	18.8	21.45	34.85	39.29	35.5	40.52

PMMA homopolymer. Table III presents the percentage weight losses for PMMA and MMA–clay composite and the maximum rate of weight loss shown by the derivative equipment associated with the TG apparatus.

Activation Energy of Degradation

Isothermal kinetics were studied by using TG to determine the rate of degradation from the initial temperature of degradation. Measurements were carried out at 210, 220, 230, and 240°C, and the activation energy of depolymerization was determined using the Arrhenius equation. Table IV summarizes the results for some PMMA and MMA-clay composite. It is clear that the activation energy of degradation is in the same order of polymerization and is in agreement with the thermal stability.

Hardness and Compression Strength

Hardness and compression strength of PMMA and MMA–clay were measured and are listed in Table V. The hardness and compression strengths of PMMA lie in the range 22–25 B.N. and 620 kg/cm^2, respectively, while increasing to the ranges of 30–38 B.N. and 890–963 kg/cm^2 in MMA clay composite.

It seems that the increasing yield percentage increases the hardness and the compression strength of the materials. This indicates that the polymer composites contain partly some polymer combined with montmorillonite. Therefore, increasing yield increases hardness and compressive strength due to the higher combination between MMA and montmorillonite in the polymer composite. This is supported by the part of polymer that was found to be insoluble in benzene even when subjected to sohxlet extraction for 24 h.

CONCLUSIONS

The rate of polymerization of MMA, using potassium persulfate as initiator, increased in the presence of montmorillonite clay. The catalytic effect of clay in the polymerization of methyl methacrylate is attributed to the formation of a clay/$K_2S_2O_8$ complex which accelerates the polymerization process. The increasing stabilities, hardness, and compression strength of the polymer composite are due to the combination between MMA and montmorillonite clay.

Table IV   Activation Energies of Degradation of the PMMA With and Without Clay

Initiator $K_2S_2O_8$ Concentration (mol/L)	PMMA	MMA + Clay Composite
0.02	64.1	50.4
0.03	61.6	47.7
0.04	51.3	—
0.05	43.2	30.8

Table V   Mechanical Properties

Polymer	Initiator (mol/L)	Brinell Hardness	Compression Strength (kg/cm^2)
PMMA	0.03	21–22	620
PMMA	0.04	22–27	670
MMA + Clay	0.03	31–33	940
MMA + Clay	0.04	35–38	963

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