

Selective Adsorption of Polymer on Freshly Ground Solid Surfaces in Soapless Emulsion Polymerization

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Synopsis

Soapless emulsion polymerization of methyl methacrylate initiated by a redox system of sodium bisulfite and oxygen in water in the presence of limestone was carried out by grinding the limestone in a vibrating ball mill reactor. The effect of a fresh solid surface produced on the adhesion between the solid and polymer formed was investigated. Examination of the resulting composite powder by scanning electron microscope indicated that the polymer selectively adsorbed on sites of the simultaneously ground limestone, whereas nonselective adsorption was observed on the previously ground limestone. The selectivity can be explained by the heterogeneities on the solid surfaces and is attributed to the existence of active centers such as defects and disturbances in the crystal lattice. Using the new method, strength of the adhesion between polymer particles and the solid surface was improved over other composite powders.

INTRODUCTION

Soapless emulsion polymerization in water in the presence of inorganic powder seems to be one of the most promising processes for the production of composite materials of inorganic substance and organic polymer. In this process, the surface of powder can be partially or totally covered with the polymer formed when the reaction condition is appropriately selected.¹⁻³ The resulting composite powder may be molded without further processing or utilized as fillers in plastics.

The mechanical strength of these composites depends greatly on the interfacial interaction between the continuous and dispersed phases.^{4,5} The existence of a chemical bond between polymer molecules and the filler surface promotes strong adhesion between the two phases. It is well known that the solid surface has considerable reactivity the moment after grinding because of the existence of radical or ion-type active centers and is capable of initiating polymerization of a number of monomers under appropriate conditions.⁶⁻¹² However, the presence of moisture has a great inhibiting effect on this type of polymerization.^{9,10} We also carried out grinding of limestone suspended in water in the presence of methyl methacrylate by a vibrating ball mill, but no polymer formed. On the other hand, Morohashi et al.^{13,14} have studied the adsorption properties of Soma sand ($\text{SiO}_2 > 97.6\%$) ground in water by a ball mill. They found that the amount of methylene blue adsorbed on Soma sand was at a maximum immediately after grinding and decreased with time. Consequently, it may be considered that although the fresh solid

surfaces produced in water do not have active centers or free radicals capable of initiating polymerization, they have some capacity to participate in adsorption the moment after grinding. Therefore, if soapless emulsion polymerization is carried out in the presence of a freshly ground solid surface, stronger adhesion between the surface of the solid and polymer formed may be expected compared to the case of solid exposed to the atmosphere for a long period after grinding. In this work, the polymerization of methyl methacrylate (MMA) in water medium and the wet grinding of limestone were performed simultaneously in a vibrating ball mill.

EXPERIMENTAL

A cylindrical porcelain pot with an internal volume of 900 cm³ was employed as the polymerization reactor, in which porcelain balls, nominally 12 mm in diameter, were charged as grinding media. Grinding was conducted at a working frequency of 24 Hz and an amplitude of 8 mm.

Limestone of density 2.7 g/cm³ was crushed previously with a stamp mill to a particle size range of 149 μ m to 210 μ m. The particles were then fully washed and dried. Analytical-grade sodium bisulfite was used as a redox initiator, since its initiation condition was convenient for ordinary grinding operations at atmospheric conditions and room temperature. For comparison, another polymerization experiment was also performed in a two-neck flask at a stirring rate of 600 rpm, using limestone which was further ground in water up to an average size 2.6 μ m by the vibrating ball mill, dried, and permitted to stand in air for a few weeks. All experiments in this work were conducted in batchwise closed systems at 21 \pm 1°C. Table I shows the experimental conditions for both experiments. The net internal volume of each reactor was adjusted so that the amount of oxygen in each reactor was roughly equivalent.

TABLE I
Experimental Conditions

	Polymerization with grinding	Polymerization without grinding
Reactor	Porcelain pot	Two neck flask
Internal volume	900 cm ³	660 cm ³
Volume of charged balls	260 cm ³	—
Net internal volume	640 cm ³	645 cm ³
Stirring rate	Frequency 24 Hz ^a Amplitude 8 mm	600 rpm
MMA	1.0 mol/l H ₂ O	1.0 mol/l H ₂ O
NaHSO ₃	0.01–0.4 mol/l H ₂ O	0.01–0.4 mol/l H ₂ O
Limestone ^b	60 g/l H ₂ O ^c	60 g/l H ₂ O ^d
Water	200 ml	200 ml
Reaction temperature	21 \pm 1 °C	21 \pm 1 °C

^aVibrating ball mill (Yokoyama Kogyo Co.).

^bChemical analysis of limestone used; CaO 54.8%, MgO 0.28%, ignition loss 43.29%, and SiO₂, Al₂O₃, Na₂O, etc. 1.63%.

^cParticle size range of 149–210 μ m.

^dAverage particle size of 2.6 μ m (measured by photometric method).

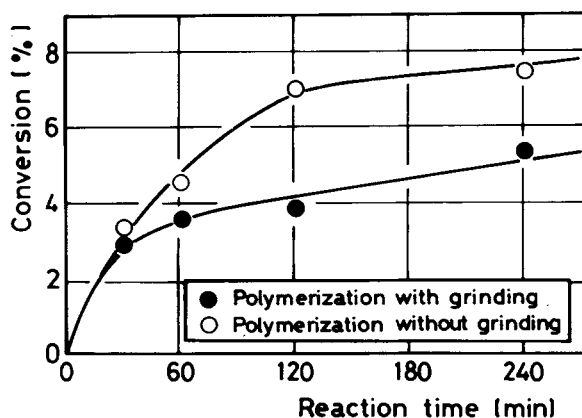


Fig. 1. Time conversion curves for two types of polymerizations. MMA 1.0 mol/l H₂O, NaHSO₃ 0.4 mol/l H₂O, limestone 60 g/l H₂O.

The reaction was stopped by the addition of hydroquinone to the reaction mixture and simultaneous ice cooling. After filtration and drying, the composite powders were observed by means of an electron microscope. The amount of polymer was determined by thermal analysis. Soxhlet extraction of the composite powders with benzene were also carried out to characterize the adhesion force between the solid and the polymer formed.

TABLE II
Experimental Results for Polymerization of MMA

	Initiator concentration NaHSO ₃ (mol/l H ₂ O)	Reaction time (min)	Conversion (%)	Polymer ^a content (%)
Polymerization with grinding	0.01	60	0	0
	0.01	120	0	0
	0.05	30	4.0	6.3
	0.05	60	6.1	9.3
	0.05	120	8.8	12.8
	0.1	60	5.6	8.5
	0.4	30	3.0	4.8
	0.4	60	3.6	5.6
	0.4	120	3.7	5.8
	0.4	240	5.6	8.5
Polymerization without grinding	0.4	60	2.3 ^b	—
	0.01	60	0.1	0.2
	0.05	60	4.0	6.3
	0.4	30	3.5	5.5
	0.4	60	4.4	6.8
	0.4	120	7.2	10.7
	0.4	240	7.4	10.9

$$^a \text{Polymer content} = \frac{\text{amount of polymer formed [g]}}{\text{amount of composite powder [g]}} \times 100.$$

^bPolymerization in the absence of limestone powder.

RESULTS AND DISCUSSION

Effect of Grinding on the Rate of Polymerization

No latex polymer in the reaction mixtures was found during any experimental run, and all polymer formed adhered to the surface of the limestone powder.

Principal results on polymerization are shown in Figure 1 and Table II. Figure 1 shows the time-conversion curves for two types of experiments. In

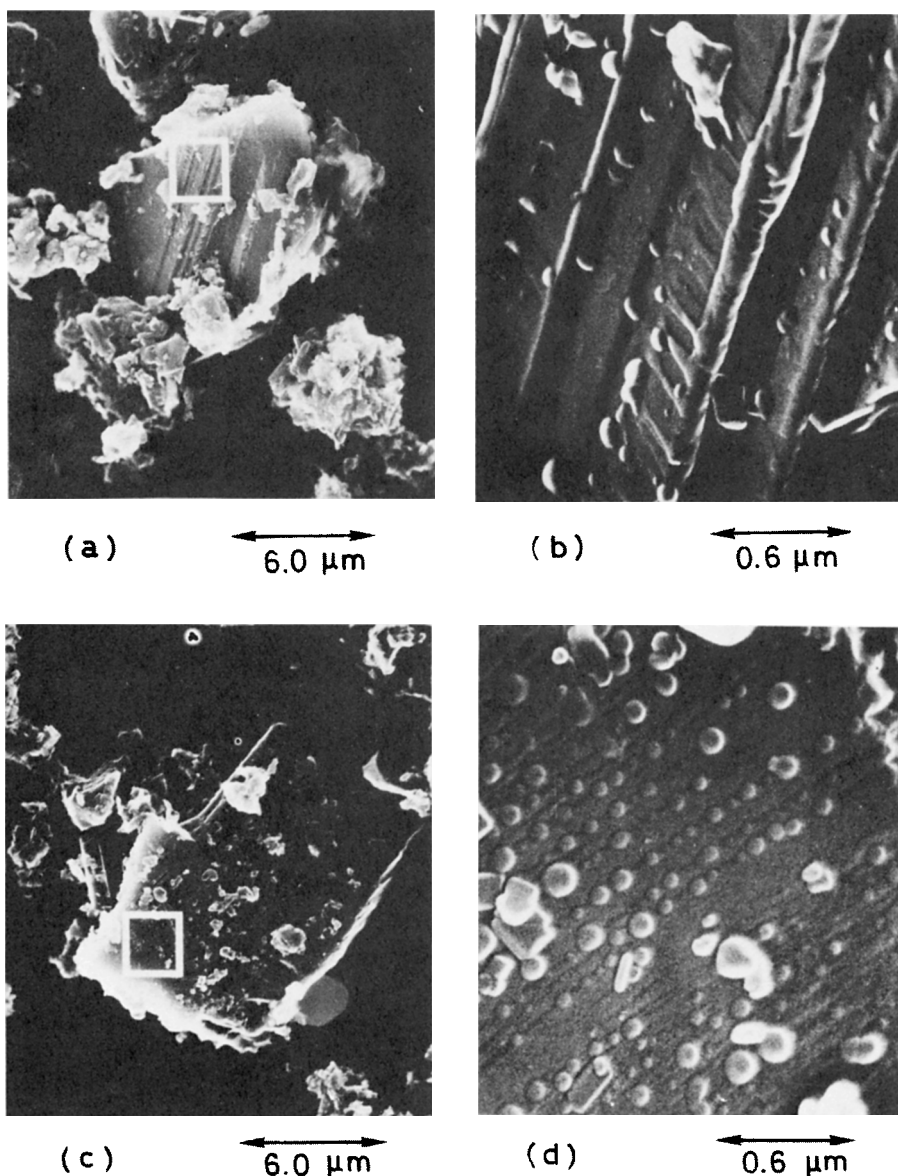


Fig. 2. Scanning electron micrographs of composite powder obtained by polymerization with grinding. MMA 1.0 mol/l H_2O , $NaHSO_3$ 0.4 mol/l H_2O , limestone 60 g/l H_2O .

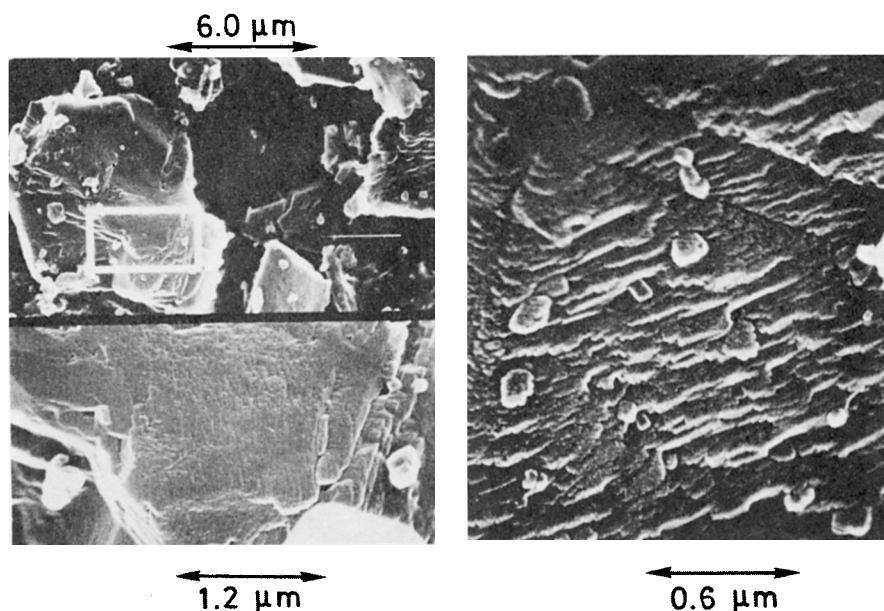


Fig. 3. Scanning electron micrographs of original limestone.

each case, the rate of polymerization decreases with time. This may be attributed to the consumption of oxygen for the initiation reaction in the closed reactor, since polymerization proceeds further when air is introduced into the system. It is also found that after about 30 minutes the conversion of MMA in the polymerization without grinding becomes greater than that with grinding. The difference is due to agitation and surface area of powder.

The vibration of the ball mill vigorously agitates the reactants and oxygen in the mill is more rapidly consumed. On the other hand, the rate of soapless emulsion polymerization in the presence of powder increases with an increase of the surface area of powder. From these two effects, the rate of polymerization with grinding initially shows almost the same rate as that without grinding and decreases more rapidly. From Table II, it is revealed that there is a certain initiator concentration to give the maximum rate of polymerization. Yamazaki et al.^{15,16} carried out the polymerization of MMA in water in the absence of powder using the same initiator. They explained the existence of optimum initiator concentration to maximize the initial rate of polymerization by showing the mechanism of the initiation process.

Observation of Composite Powders by Electron Microscope

Figure 2 shows the scanning electron micrographs of composite powder obtained by simultaneous operation of grinding and polymerization. For comparison Figure 3 shows micrographs of the original limestone. Micrographs (b) and (d) in Figure 2 are magnifications ($\times 10$) of a square part in micrographs (a) and (c), respectively. From micrograph (b), it was found that polymer preferentially covered the edge of the limestone surface. The edge produced by grinding seems to be the locus of polymerization in preference to

other places. Thiessen¹⁷ also observed preferential adsorption of gold colloid particles on the edge of kaolinite crystal. Micrograph (d) also shows an interesting phenomenon that polymer particles regularly existed along the stripes which appeared to be cracks or cleavages on the limestone surface.

These phenomena may be attributed to the heterogeneities of the solid surface, that is, the existence of active centers such as defects and disturbances in the crystal lattice.

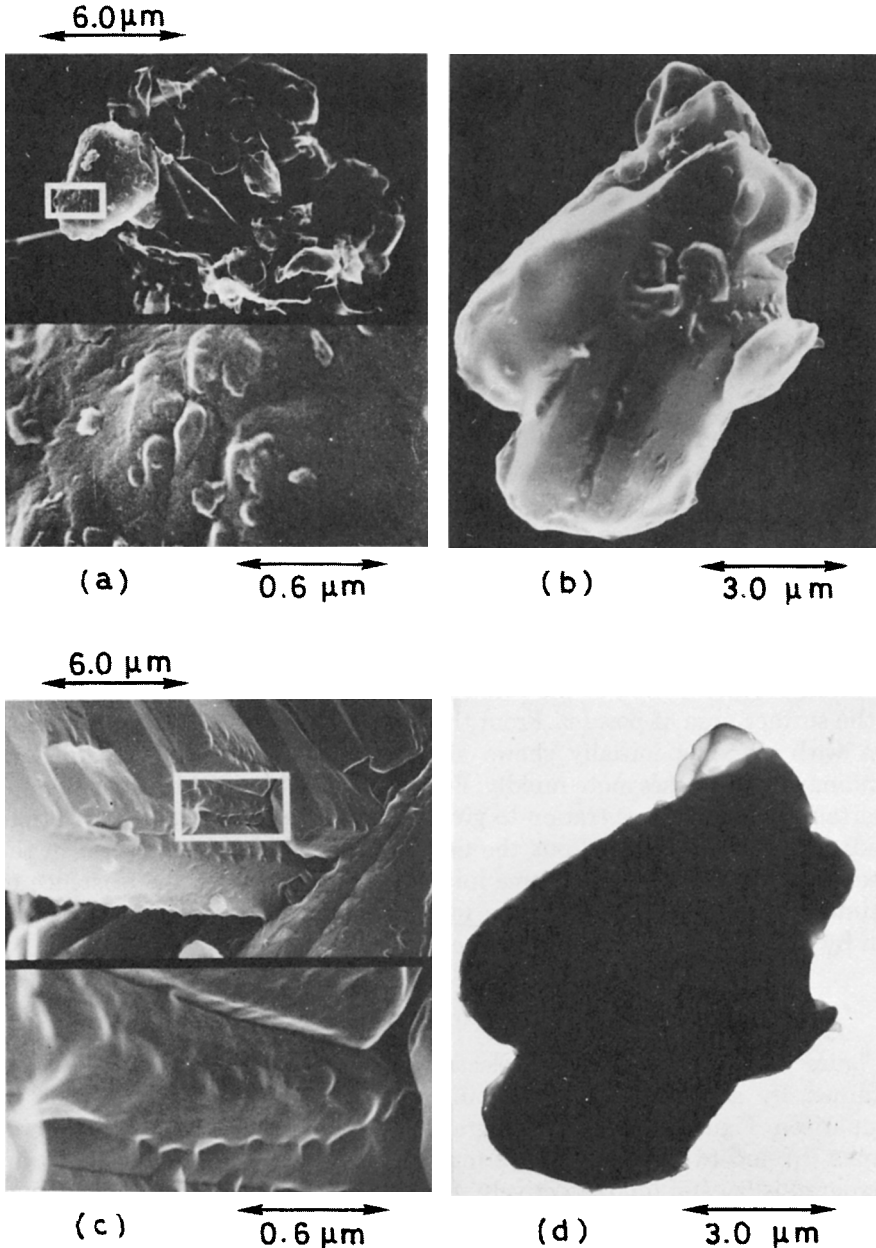


Fig. 4. Electron micrographs of composite powder obtained by polymerization without grinding. MMA 1.0 mol/l H_2O , $NaHSO_3$ 0.4 mol/l H_2O , limestone 60 g/l H_2O .

TABLE III
The Results of Soxhlet Extraction for Composite Powders with Heated Benzene

	Polymerization with grinding				Polymerization without grinding			
	30	60	120	240	30	60	120	240
Reaction time (min)	30	60	120	240	30	60	120	240
Polymer content before extraction (%)	4.8	5.7	5.8	8.5	5.5	6.8	10.7	10.9
Polymer content after extraction (%)	2.4	4.3	3.0	6.2	1.0	2.9	1.7	2.5
Extracted polymer (%) ^a	50	25	48	27	82	57	84	77

$$^a \text{Extracted polymer} = \frac{\text{amount of extracted polymer [g]}}{\text{amount of polymer before extraction [g]}} \times 100.$$

The micrographs in the case of polymerization without grinding are shown in Figure 4. Micrographs (a), (b), and (c) are obtained by scanning method and (d) is transmission electron micrograph of the same particle shown in micrograph (b). Any regular arrangement of polymer particles on the limestone surface was hardly observed and the surface appeared to be covered with polymer. As shown in a transmission micrograph (d), the existence of filmy polymer is revealed clearly. In micrograph (c), a byproduct of rhombic crystal covered with a film of polymer was recognized. This crystal is thought to be calcium sulfite produced by the reaction between calcium carbonate and bisulfite ion.

Characterization of Composite Powders

The surface of inorganic powders such as limestone in general is hydrophilic. However, all composite powders obtained by two types of experiments were found to have a hydrophobic surface because they have better wettability for benzene than for water. Polymer in the composite powders was extracted for 8 hours by Soxhlet extraction with benzene to characterize the adhesion force between the solid surface and the polymer formed. Table III shows the polymer content in the composite powders before and after extraction. It was found that polymer in the composite powders obtained by the polymerization with grinding was more difficult to extract than that without grinding.

CONCLUSION

In soapless emulsion polymerization of methyl methacrylate in water in the presence of limestone conducted by grinding the limestone in a vibrating ball mill reactor, all polymer formed adhered to the surface of the limestone. Observation of the resulting composite powder by scanning electron microscope revealed that the polymer selectively adsorbed on sites of the simultaneously ground limestone. The selectivity can be explained by the heterogeneities on the solid surfaces and is attributed to the existence of active centers such as defects and disturbances in the crystal lattice. The freshly ground surface formed in water medium does not have the capability of initiating polymerization, but has some capacity to promote stronger adhesion between

polymer and solid surfaces. Therefore, the simultaneous operation of polymerization and grinding in water medium is considered to be a useful process for producing some composite materials.

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