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THERMAL POLYMERIZATION OF RADIATION
CONDITIONED MONOMERS FOR THE PRODUCTION
OF CONCRETE-POLYMER MATERIALS

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February 1972

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Abstract

For the purpose of reducing the hazard of handling excess monomer containing a chemical initiator in the production of polymer impregnated concrete and to reduce the radiation dose requirements for the polymerization of monomer in concrete, a system is proposed to remove the inhibitor in the bulk monomer prior to impregnation by gamma radiation reactions. The radiation conditioned monomer is then allowed to impregnate the concrete after which the monomer is thermally polymerized in-situ with no further addition of chemical catalyst. Data are presented for the removal of inhibitor by Co^{60} gamma radiation from the bulk monomers, methyl methacrylate (MMA), styrene, t-butyl styrene and trimethylolpropane trimethacrylate (TMPTMA). The subsequent thermal polymerization of the radiation conditioned monomers are indicated. The in-situ polymerization of radiation conditioned styrene-TMPTMA comonomers and t-butylstyrene has been

shown and compressive strength of the polymer-concretes have been been measured. In the case of MMA further work is needed to determine the reason for incomplete polymerization of the monomer in the center part of the concrete. A process based on this system is discussed.

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Introduction

There are three common methods for initiating the in-situ free radical polymerization of vinyl monomers for the preparation of concrete-polymer materials. These are:

1. radiation initiation
2. chemical initiation
3. activator-chemical initiation

In its simplest form the process of free radical polymerization consists of three steps: initiation, propagation, and termination. Initiation in the presence of an initiator I, may be considered in two steps: first the decomposition of the initiator into free radicals, $R\cdot$,

and second the addition of a monomer unit to form a chain radical, $M_1\cdot$,

The general step of propagation is

The reaction rate constant k_p is assumed to be the same for each propagation step since it is assumed that the radical reactivity is independent of the chain length.

Bimolecular reaction between a pair of chain radicals accounts for annihilation of active centers or termination of the reaction.

In each of the three polymerization methods, the primary mechanism is the formation of free radicals. High energy radiation such as gamma energy from Co^{60} can initiate free radicals at most any temperature condition. Chemical initiators capable of generating free radicals have been shown to be potent accelerators for the polymerization of typical vinyl monomers such as styrene and methyl methacrylate. The most commonly employed initiators are organic peroxides such as benzoyl peroxide. These are known to decompose slowly at temperatures of 50° to $100^\circ C$ with the release of free radicals. In the activator-initiator method a reducing agent such as dimethyl aniline or a metallic salt of cobalt or manganese is added to the monomer. Then the initiator is added and the reducing agent activates the initiator at room temperature to form free radicals thus initiating monomer polymerization.

Certain monomers including styrene and methyl methacrylate which have been carefully purified to remove all traces of initiators still undergo polymerization at elevated temperatures. In these cases the initiation is presumably due to thermal decomposition of the monomer to radicals. This decomposition takes place by a mechanism as yet unknown but presumably its rate is proportional to monomer concentration. Initiation rates are many times smaller than those for polymerization in the presence of an initiator.⁽¹⁾ Because of this phenomenon chemical inhibitors such as hydroquinone and t-butyl pyrocatechol are added to monomers so that they can be handled, shipped, and stored conveniently and safely. The inhibitors act as scavengers for free radicals and remove them by rapid reaction so that they are unable to react with monomer molecules to initiate polymer chain reactions. Uninhibited monomer has a short storage or "shelf-life" before polymerization. The inhibitor in effect extends the shelf-life of the monomer. Monomer manufacturers publish data on the shelf life of various monomers as a function of inhibitor concentration.⁽²⁾ The inhibitors are very effective scavengers and are generally used in concentrations of 10 ppm - 200 ppm depending on the type of inhibitor and the monomer in which it is being used. Table 1 gives several examples of monomers, inhibitor types and concentrations for the monomers used in this study.

During the conversion of monomer to polymer the inhibitor must be consumed by free radicals through chemical reaction before the initiation of polymerization can take place. The period in which the inhibitor is being consumed is called the induction period. In the case of radiation as much as 50% of the total radiation energy used for polym-

erization is required to remove the inhibitor. In the case of chemical initiators a significant portion is consumed by the inhibitor before the excess initiator can supply a sufficient amount of free radicals for the conversion of monomer to polymer. The addition of initiator to monomer makes the handling and storage of such a monomer a safety problem. Monomers with initiators added to them are hazardous and cannot be stored since polymerization can occur at any time.

In processes where large quantities of initiated monomers are used hazardous conditions exist. The disposal of excess monomer in such processes is uneconomical in addition to being very hazardous. The impregnation of concrete with monomers to form concrete-polymer composites is one of the processes where excess monomer is required to insure full impregnation of the specimen. ⁽³⁾ The amount of excess monomer can be significant, depending on the design of the impregnator and the shape of the specimen. In most cases, the monomer cannot be treated as a waste product since the cost of the monomer is a substantial part of the overall cost of the finished product.

In an effort to find a safe economical method of handling excess monomer for the concrete impregnation process experimental work was initiated to investigate a novel method of in-situ polymerization.

The radiation requirements of monomer impregnated concrete are high since only the radiation absorbed in the relatively small mass of monomer (6% by weight of concrete) is effective for polymerization purposes. The remaining gamma radiation is dissipated in the inert concrete mass. Of this approximately one half of the dose is usually used to decompose the inhibitor prior to initiation of polymerization. Thus only approximately 3% of the total radiation is effectual for in-situ monomer polymerization.

In this work we propose to essentially remove all the inhibitor by radiation treatment prior to the use of the monomer for impregnation. The uninhibited monomer is then used to impregnate the concrete specimens. It is further proposed to thermally polymerize the monomer in-situ by heating the specimen. The excess inhibitor-free monomer is returned to the inhibited monomer storage vessel. The cycle is then repeated when additional specimens are to be impregnated.

The removal of inhibitor can be accomplished in several ways as discussed in the following.

1. Inhibitor can be removed by distillation. Vacuum distillation is recommended, however, it is an extremely hazardous operation since the distilled monomer can spontaneously polymerize or it can form explosive mixtures with air.

2. Most inhibitors can be removed by multiple washings with aqueous caustic solutions. The caustic is then washed out with distilled water and the water removed by drying the monomer over silica gel or anhydrous sodium sulfate until clear. The inhibitor free monomer is then filtered prior to use. The procedure is lengthy and requires the disposal of large quantities of caustic solution.

3. Ion exchange can be used to remove inhibitor from monomers. Periodic regeneration of the resin is accomplished with methanol. The method however, is not effective for all types of inhibitors and is also limited due to the capacity of the ion exchanger.

4. High energy gamma radiation from Co^{60} or Cs^{137} can be used to remove inhibitors from monomer systems. The radiation provides free radicals in the monomer which are scavenged by the inhibitor thus becoming eventually consumed.

The monomer is irradiated until the polymerization reaction just begins which can be noted by checking for a precipitate when a few drops of the irradiated monomer are added to methanol.

Of all the methods outlined it appears that high energy gamma radiation is ideally suited to remove inhibitors from monomers and condition the monomer for subsequent polymerization because:

- a. There will be no waste products to dispose of.
- b. The method is suited to a bulk or continuous process.
- c. The method is simple and can be continually monitored.

Experimental Work

To test the radiation conditioning of monomers followed by in-situ thermal polymerization in concrete, the following experimental program was conducted.

1. Bulk Polymerization

Experiments were first undertaken to establish the principle of radiation conditioning followed by thermal polymerization in bulk polymer.

Test tube quantities, 10 gms, of various inhibitor containing monomers were irradiated and tested for polymer conversion by precipitation with methanol, and weighing the dried precipitate. The data are listed in Table 1.

Polymerization takes place after the inhibitor has been decomposed. The formation of a precipitate when a few drops of the monomer is dropped into methanol indicates the initiation of polymerization. The conversion at this point is about 1%. Table 1 indicates the dose required to remove the inhibitor in 10 gm samples. When larger quantities of

monomer are irradiated the total dose is decreased. This was noted when irradiating 1 liter quantities for the impregnation studies. The simplest control for the onset of polymerization is to measure the viscosity and to limit it to 2.5 cps. A monomer having this value of viscosity can impregnate most concrete specimens. The actual inhibitor content can also be measured by the iodine or spectrophotometric method both of which are more time consuming.

Methyl methacrylate monomer containing inhibitor was placed in a radiation field at room temperature until the inhibitor was destroyed as indicated by the polymer conversion test. The total dose required was 4.95×10^5 rads. The dose requirement will vary with inhibitor concentration. After treatment, monomer samples were exposed to temperatures of 80°, 85° and 90°C. Polymerization at 90°C was completed in less than 24 hrs while at 80° it took some 48 hrs. Thermal polymerizations are very much temperature dependent. With 60% styrene-40% TMPTMA at 90°C, complete conversion of monomer to polymer is obtained in 2 hours when the monomer is sensitized by radiation to a dose of $\approx 300,000$ rads. Without sensitizing the monomer complete conversion of monomer to polymer takes about 4 hrs.

In bulk monomers what the radiation conditioning does is remove the inhibitor by decomposing it or inducing its reaction chemically with other species in the monomer and allow complete thermal polymerization of monomer in a shorter period of time and at a lower temperature than is possible with inhibited monomer. Table I gives data on the complete thermal polymerization of monomers used in this study.

2. Polymer Impregnated Concrete

A series of tests were undertaken to thermally polymerize concrete specimens impregnated with radiation conditioned monomers.

One liter of monomer was placed in a glass container and irradiated at an intensity of 160,000 rad/hr until the inhibitor was destroyed as indicated by periodic monomer-polymer conversion tests. The viscosity of the irradiated monomer at this point was less than 2.5 cps @ 25°C. Specimens of 5000 psi compressive strength concrete which were dried to constant weight at 150°C were used for the impregnation test. The radiation sensitized monomer was introduced into the previously evacuated impregnation vessel containing the concrete specimen. The vessel was then pressurized with nitrogen to about 25 psig. The concrete specimen is soaked in the monomer in time periods varying from 2 to 24 hrs. After the desired soaking period the pressure was relieved and the concrete specimen was placed in a glass container with a slight excess of monomer. The container is then placed in an air circulating oven for various lengths of time until the polymerization appears to be complete. In most cases, the samples were allowed to cure over extended periods to insure maximum polymerization. The sample was then removed from the containment vessel used during polymerization and the ends were ground flat for strength measurements. Compressive strengths were measured on a standard testing machine. The strength results indicate how well the samples were impregnated with polymer. The data for the impregnated concrete specimens are given in Table 2.

Complete polymerization with several monomer systems was obtained and suitably high strengths comparable to those obtained with radiation initiated or chemical initiated polymer impregnated concrete resulted.

Concrete specimens impregnated with radiation conditioned methyl methacrylate monomer did not fully cure. A center core of 1 to 2 inch in diameter of a 3 inch diameter specimen was always uncured. It is our opinion that the alkalinity of the concrete is causing inhibition. The addition of 5% methacrylic acid to the MMA in an attempt for neutralization and used a two stage curing cycle. The strength improved, however, complete curing was still not achieved. When the samples were broken during compression testing strong monomer odors were noted and weight losses due to evaporation could be recorded. The anomalous effects with MMA in concrete must be further investigated.

It is interesting to note that styrene impregnated concrete could be completely thermally polymerized in-situ at temperatures of 125°C to 150°C even though the radiation conditioned styrene could not be polymerized at temperatures of 85 to 90°C.

Process Description

The application for the thermal polymerization of radiation conditioned monomers for the production of concrete-polymer materials can be followed in the process flow sheet shown in Figure 1. In the concrete batch plant, standard mixes of concrete are cast and either fog or steam cured. For maximum strength results, the concrete is then dried and placed in a closed vessel for impregnation. After evacuation the radiation conditioned monomer is introduced and the concrete specimen is allowed to soak for a period of time.

The inhibited monomer is delivered to the plant and placed in storage tanks. It is then fed to a monomer make-up tank where it is mixed with excess uninhibited monomer from the impregnator. The mixed recycled monomer is fed to a Co^{60} gamma irradiator. This could be a continuous stirred type flow irradiator, with monomer either in a coil or a vessel with Co^{60} sources located internally or external to the monomer vessel with the necessary shielding. The irradiation of the monomer can be controlled by controlling the residence time of the monomer in the gamma field. Flow rate or time in source can be controlled by means of analysis of the effluent from the irradiator. The analysis of the inhibitor can be made by the peak exotherm method, spectrophotometrically or by titration. The polymer conversion can be measured by precipitation with methanol or by viscosity measurements.

After impregnation, the excess monomer is drained and recycled to the make-up tank. The concrete specimens are put into an oven and the thermal polymerization can take place overnight.

The method of radiation conditioning followed by thermal polymerization should be applicable to the process of impregnating any porous body for the formation of a polymer aggregate composites.

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CONCRETE POLYMER PLANT FLOW SHEET
THERMAL POLYMERIZATION OF RADIATION CONDITIONED MONOMERS

FIGURE 1

CONCRETE POLYMER PLANT FLOW SHEET
THERMAL POLYMERIZATION OF RADIATION CONDITIONED MONOMERS

FIGURE 1

TABLE 1
THERMAL POLYMERIZATION OF RADIATION CONDITIONED MONOMERS IN BULK⁽¹⁾

Inhibitor			Radiation Conditioning			Thermal Polymerization		
Monomer	Type	Conc., ppm	Dose Rate rads/hr	Dose, rads	% conv.	Temp., °C	Time, hrs	% Conversion
MMA (2)	HQ (4)	30-40	165,000	495,000	1-3	80	48	100
MMA	HQ	30-40	0	0	0	80	48	0
MMA	HQ	30-40	165,000	495,000	1-3	85	24	100
MMA	HQ	30-40	165,000	495,000	1-3	90	<24	100
Styrene	t-BPC (5)	45-55	160,000	805,000	1-3	95	~72	100
60% styrene	t-BPC	30	160,000	480,000	1-3	95	30	100
40% TMPTMA (3)	MEHQ (4)	80						
60% styrene	t-BPC	30	300,000	275,000	1-3	90	2	100
40% TMPTMA	MEHQ	80						
60% styrene	t-BPC	30	0	0	0	90	2	0
40% TMPTMA	MEHQ	80						
60% styrene	t-BPC	30	300,000	275,000	1-3	90	4	100
40% TMPTMA	MEHQ	80						
60% styrene	t-BPC	30	0	0	0	90	4	100
40% TMPTMA	MEHQ	80						
t-butyl styrene	t-BC	10	160,000	506,000	1-3	95	48	100
t-butyl styrene	t-BC	10	300,000	525,000	1-3	90	13	<100
t-butyl styrene	t-BC	10	0	0	0	90	13	0
t-butyl styrene	t-BC	10	300,000	525,000	1-3	150	4	100
t-butyl styrene	t-BC	10	0	0	1-3	150	4	100

(1) Sample sizes, 10 gms

(2) MMA - methyl methacrylate

(3) TMPTMA - trimethylolpropane trimethacrylate

(4) HQ - hydroquinone

(5) tBPC - t-butyl pyrocatechol

(6) MEHQ - monomethylether of hydroquinone

(7) t-BC - t-butyl cathechol

Table 2

THERMAL POLYMERIZATION OF MONOMER IMPREGNATED CONCRETE SPECIMENS

Sample No. (a)	Monomer System	Radiation treatment dose, rads	Loading wt. % Increase	Thermal Polym-erization		Compressive strength psi
				Temp. °C	Time, hrs	
CP-5B-11C	MMA (b)	330,000	6.8	95	48	6670 (d)
CP-5A015C	MMA + 1% TMPTMA (c)	330,000	4.3	90	18	7100 (d)
CP-5B-12C	MMA + 3% Methacrylic acid	240,000	-	85/145	20/20	11,420 (d)
CP-5A-Y	Styrene	805,000	6.5	95	72	4,780
72.T1-10	Styrene	-	6.0	125/200	24/8	14,300 (d)
CP-R-8	Styrene	-	5.3	150/200	24/24	14,285
CP-5B-14E	Styrene + 1% TMPTMA	805,000	6.6	95	72	8,310 (d)
CP-5B-14C	60% Styrene 40% TMPTMA	320,000	8.1	95	48	21,400
CP-4B-14C	60% Styrene 40% TMPTMA	160,000	6.5	90-95	6	15,850 (d)
CP-0-11A	60% Styrene 40% TMPTMA	-	6.6	90-95	6	14,250 (d)
CP-HB-15C	60% Styrene 40% TMPTMA	-	7.0	90-95	40	19,600
CP-2A-11B	90% Styrene 10% TMPTMA	-	5.4	90-95	72	16,550 (d)
CP-R-41	90% Styrene 20% TMPTMA	-	6.0	90-95	72	18,170
CP-4B-15E	70% Styrene 30% TMPTMA	-	6.2	90-95	72	18,342
CP-5B-13F	t-butyl styrene	506,000	5.7	90/150	20/20	17,630
CP-4B-Y	t-butyl styrene	506,000	5.7	90/150	20/20	17,550
CP-4B-15B	t-butyl styrene	506,000	6.1	150	7.5	15,750 (d)
CP-4B-13F	t-butyl styrene	-	6.1	150	7.5	8,400 (d)

(a) Specimen size, 3" diam x 6" long

(b) Methyl Methacrylate

(c) Trimethylolpropane Trimethacrylate

(d) Not fully polymerized; detected strong odor of monomer or found soft polymer.