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Low temperature cure-on-command polymerization induced via free radical initiator in an oscillating magnetic field

K.R. Miller, M.D. Soucek*

Department of Polymer Engineering, University of Akron, Akron, OH 44325, United States

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ABSTRACT

Three magnetic nanoparticles (Fe_3O_4, FeCo, Co) were prepared and modified with azo-based free radical initiators via grafting. The resulting magnetic particles underwent a free radical initiation process in an oscillating magnetic field. Three acrylated oligomers, a urethane, epoxide, and polyphosphazene, were used to investigate the curing potential of the magnetic initiators (MI). The curing temperature, Tg, and conversion of the three MI based systems were compared. All three of the MI systems underwent initiation with only a modest temperature increase. The overall conversion and Tg for the MI initiated systems were lower than expected, but with some optimization an ~80% conversion could be obtained.

1. Introduction

Arguably, the most important part in free radical polymerization is initiation. Initiation is most commonly induced thermally with either peroxide or azo initiators [1]. For solution polymerization, thermally induced initiation is not problematic. However, when polymerization is induced on a substrate as in the case of coatings, thermal initiation is not always an option [2]. Radiation curing has the advantage of a close to ambient temperature cure which is an advantage for heat sensitive substrates [3]. The most prominent radiation curing is ultraviolet (UV) and electron beam (EB) [4].

In UV-curing, photoinitiators are decomposed into free radicals which initiate the polymerization process, while in EB curing, monomers are directly excited by the high energy beam. Both UV and EB curing can be used on a much broader selection of substrates as opposed to thermal curing. However, these are not without their drawbacks. UV curing cannot be performed on heavily pigmented films because pigments contained within the film can absorb or scatter the incoming radiation, causing the intensity of the UV rays propagating through the film to continually decease with depth [5]. However, the decrease in radiation intensity due to pigment is not experienced with EB curing. Even so, this advantage comes with a higher safety concern which requires extensive safety equipment [6]. Although UV and EB curing may have different radical producing mechanisms, each shares one major flaw: in order for proper and uniform

curing to take place, radiation needs to be distributed evenly throughout material. Consequently, these methods are usually limited to parts that can be easily manipulated around a radiation source allowing for uniform coverage [6].

Previous work on magnetically cured systems have all focused on the generation of thermal heat throughout the bulk of an adhesive or composite *via* vibration of magnetic particles contained within the system from an alternating current magnetic field (AC MF). Vibrations of the magnetic particles allow heat to be built up using a high frequency [7]. The downside of this curing method is that heat sensitive substrates cannot be used.

This study is focused on the initiation of free radical polymerization via the vibration of magnetic initiators (MIs) (Fe_3O_4, FeCo, Co) without the generation of deleterious heat. The synthesis and characterization of the three magnetic MIs has recently been reported [8]. Three acrylated systems, a urethane, epoxide, and polyphosphazene, will be used to investigate the curing potential of this first generation of MIs. The final conversion and Tg will be compared for all three of MI systems.

2. Experimental

2.1. Materials

Iron(II) sulfate heptahydrate, iron(III) chloride hexahydrate, ammonim hydroxide solution 28% (w/w), cobalt(II) chloride hexahydrate, Sodium borohydride, (3-aminopropyl)triethoxysilane

* Corresponding authorat: The University of Akron, Akron, OH 44325, United States.
E-mail address: msoucek@uakron.edu (M.D. Soucek).

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(APTS), citric acid monohydrate, ethanol (200 proof), potassium phosphate monobasic ≥98%, sodium chloride, hydrochloric acid, *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride ≥98.0%, 4,4′Azobis(4-cyanovaleric acid) ≥98.0% (ACV), phosphate buffered saline (PBS), methylene chloride, lithium bis(trimethylsilyl)amide 97%, diethyl ether, phosphorus trichloride 99%, sulfuryl chloride 97%, Celite® S, phosphorus pentachloride ≥98.0%, dichloromethane, L-phenylalanine ethyl ester hydrochloride 99%, tetrahydrofuran anhydrous ≥99.9%, triethylamine ≥99%, 2-aminoethyl methacrylate hydrochloride 90%, *N,N*-dimethylformamide anhydrous 99.8%, methyl methacrylate ≥98.5%, styrene, phosphate buffered saline (PBS), and Real Crystal® IR sample Cards with cover slips were purchased from Sigma. Aliphatic urethane diacrylate oligomer (CN981) and difunctional bisphenol A epoxy acrylate oligomer (CN120Z) were obtained from Sartomer.

2.1.1. Synthesis of magnetic Fe nanoparticles and APTS grafting

Magnetite nanoparticles were synthesized by a co-precipitation method. In a 100 mL three neck flask equipped with a mechanical stirrer were taken 0.675 mmol $FeSO_4{\cdot}7H_2O$ and 1.35 mmol $FeCl_3{\cdot}6H_2O$ in 40 mL of deionized water. The mixture was stirred under nitrogen gas for 30 min. Magnetite nanoparticles were obtained by adding 12 mL 28% (w/w) NH_4OH to the solution, immediately following addition of NH_4OH a black precipitate formed. Solution vigorously stirred under nitrogen for an additional 30 min. Next 0.9 mL APTS was added over a 10 min time period, followed by further stirring under nitrogen for 30 min. Particles were washed 5 times with deionized water by using magnetic separation.

2.1.2. Synthesis of FeCo nanoparticles and APTS grafting

FeCo nanoparticles were prepared by co-precipitation, method. To a 500 mL three necked flask equipped with a magnetic stirrer, 1.0 mmol $FeCl_3{\cdot}6H_2O$ and 1 mmol $CoCl_2{\cdot}6H_2O$ were added with 150 mL deionized water. Mixture stirred for 30 min under nitrogen. 1 mmol $NaBH_4$ dissolved in 50 mL deionized water was added to the solution followed by stirring under nitrogen for 4 h. Next 2 mL of APTS was added and the mixture was stirred for 1 h under nitrogen. The particles were washed with deionized water 5 times to remove residual Na and Cl ions using magnetic separation.

2.1.3. Synthesis of cobalt nanoparticles and APTS grafting

Cobalt nanoparticles were synthesized by the reduction of Co^{2+}. To a 1 L three neck round bottom flask equipped with a magnetic stirrer and containing 100 mL deionized water were added 10 mmol $NaBH_4$ and 0.005 mmol citric acid monohydrate. Solution was stirred under nitrogen for 30 min. Next, 1 mmol $CoCl_2{\cdot}6H_2O$ dissolved in 0.2 mL deionized water was added to the mixture; black precipitate immediately formed upon addition of the cobalt solution. Following 1 min of stirring, 500 mL of an ethanolic solution containing 350 μL APTS was added. After 15 min of stirring under nitrogen the particles were washed 5 times with ethanol by using magnetic separation.

2.1.4. Synthesis of magnetic macro-initiators

Magnetic macro-initiators were synthesized by a coupling reaction with 4,4′ azobis(canyoleric acid) (ACV). The APTS coated MNs (Fe_3O_4, FeCo, or Co) were activated by sonication for 30 min in 20 mL of coupling buffer. Coupling buffer was a 0.01 M potassium phosphate, 0.15 M sodium chloride solution adjusted to pH 5.6 with hydrochloric acid. The MNs were then magnetically separated and resuspended in 4 mL of the coupling buffer. Next, 10 mL of a solution containing 8.6 mmol of *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride and 8.6 mmol of ACV in deionized water was added to the MNs suspension. Reaction mixture was shaken for 24 h at room temperature in the absence of light. Magnetic macro-initiators were then magnetic separated and washed 3 times with distilled H_2O using magnetic separation.

2.1.5. Synthesis of biocompatible acrylic polyphosphazene

Biocompatible, acrylic functional polyphosphazene was synthesized by reacting poly(dichlorophosphazene) with phenylalanine and aminoethyl methacrylate. All manipulations were carried out using standard Schlenk techniques under nitrogen atmosphere. For the preparation of poly(dichlorphospahzene), the precursor, $Cl_3P{=}NSiMe_3$, was first synthesized. A suspension of $LiN(SiMe_3)_2$ (0.033 mol) in 100 mL of Et_2O (diethyl ether) was cooled to 0 °C. Fresh distilled PCl_3 (2.88 mL, 0.033 mol) was then added dropwise over 30 min while the solution was continuously stirred. The solution was then allowed to warm to room temperature and stirred for an additional 1 h. Next, the solution was cooled to 0 °C followed by the drop wise addition of fresh distilled SO_2Cl_2 (2.68 mL, 0.033 mol) over 30 min. The solution was stirred for 1 h at 0 °C, followed by 30 min of stirring at room temperature. The solution was then filtered through a 1 cm layer of Celite followed by concentration of $Cl_3P{=}NSiMe_3$ through the removal of volatiles by vacuum distillation. To a stirred solution of the $Cl_3P{=}NSiMe_3$ (1.0 g, 4.4 mol) in 35 mL CH_2Cl_2, a solution of PCl_5 (8 mmol) in 10 mL CH_2Cl_2 was added. The reaction mixture was stirred at room temperature for 24 h followed by the removal of volatiles by vacuum distillation. Yield of poly(dichlorophosphazene) was 83%. ^{31}P NMR: δ = −17.5 ppm (−N = $P(Cl_2)$−).

The biocompatible, acrylic functionalized polyphosphazene was synthesized as follows: phenylalanine ethyl ester hydrochloride (2.76 g, 12.01 mmol) was suspended in dry THF (60 mL) containing triethylamine (1.84 g, 18.15 mmol) and was added slowly to a solution containing poly(dichlorophosphazene) (1.0 g, 8.62 mmol) and dry THF (50 mL). The reaction mixture was stirred for 8 h at −60 °C followed by stirring for an additional 48 h at room temperature. Next, a solution of 2-aminoethyl methacrylate hydrochloride (1.71 g, 10.34 mmol), anhydrous DMF (10 mL), and triethylamine (2.01 g, 20.68 mmol) was added to the reaction mixture. The mixture was stirred for 24 h at room temperature followed by 24 h at 40 °C. The reaction mixture was filtered and concentrated by vacuum distillation. Yield of the biocompatible, acrylic functionalized polyphosphazene was 68%. M_n from GPC: 3140 with PDI 2.7. ^{31}P NMR (CDCl3, *δ*, ppm) 1.3. ^{1}H NMR (CDCl3, *δ*, ppm): 1.1 (3H, P−NH−CH(CH_2−Ar) −COO−$CH_2C\boldsymbol{H_3}$), 1.9 (3H, $CH_2{=}C(\boldsymbol{CH_3})$−of AEMA), 3.1 (2H, −NH−$\boldsymbol{CH_2}$−$CH_2$− of AEMA), 4.0 (2H, P−NH−CH($\boldsymbol{CH_2}$−Ar)− COO−CH_2CH_3), 4.4 (2H, P−NH−CH(CH_2−Ar) −COO−$\boldsymbol{CH_2}CH_3$ and −NH−CH_2−$\boldsymbol{CH_2}$− of AEMA), 4.8 (1H, P−NH−C$\boldsymbol{H}$(CH_2−Ar) −COO−CH_2CH_3), 6.5 (1H, $CH_2{=}C(CH_3)$−of AEMA), 6.7 (1H, $CH_2{=}C(CH_3)$−of AEMA), and 7.7 (5H, P−NH−CH(CH_2−$\boldsymbol{Ar}$) −COO−CH_2CH_3).

2.1.6. Magnetically induced free radical polymerization

Magnetically induced free radical polymerization was investigated by mixing various acrylic systems with magnetic MI and placing the sample in an AC MF. During exposure to the AC MF, polymerization was monitored by recording the FTIR spectrum of the sample every 5 s. In addition, the temperature of the system was continuously monitored with an IR temperature sensor. The conversion as a function of time was then calculated by use of Eq. (1),

$$Conversion\% = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where A_0 is the peak area at time zero and A_t is the peak area at time t. For polymerization of all the acrylic samples, the change in peak area of the C=C stretch, 1640–1660 cm^{-1}, was used to calculate the conversion. In addition to magnetic initiation, conversion as a

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