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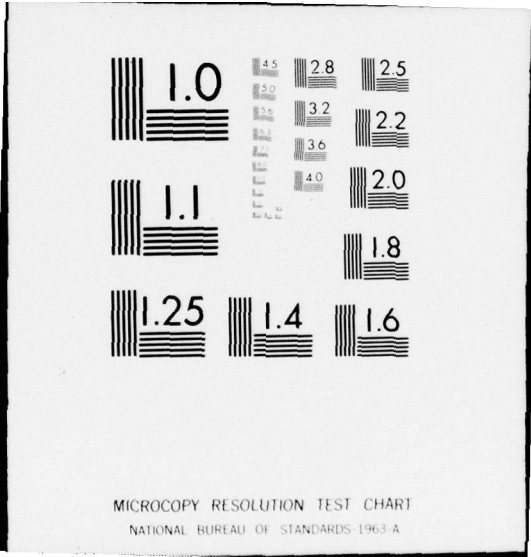
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LOW-TEMPERATURE POLYMERIZATION
OF METHYL METHACRYLATE II

JEROME RUBIN

APRIL 1977



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER
WEAPON SYSTEMS LABORATORY
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20. ABSTRACT (Continued)

In either case, the exotherm can be kept below 100°C. The temperature generated during the reaction is dependent upon both the concentration of peroxide added, and the time needed to solidify. A partially polymerized inhibited methyl methacrylate monomer containing an excess of amine is stable to further spontaneous polymerization.

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INTRODUCTION

The polymerization of methyl methacrylate using a thermodynamically activated peroxide initiator-activator system as a source of free radicals has been shown to develop a high exotherm as a result of polymer formation (Ref 1). The ratio of initiator to activator as well as the concentrations involved was found to influence the speed of polymerization.

The polymer could be formed in one to four hours, depending upon the percent peroxide used initially. In cases where the polymerization yielded molecular weights over 100,000, the reaction temperature generated was in excess of 100°C in the system investigated.

The emphasis was placed on developing a system that would cure at temperatures below 100°C, and have potential application in the presence of some energetic materials. The polymerized acrylics had already been shown to be compatible with Comp B and selected propellants.

Work on the polymerization process was focused on keeping the reaction temperature as low as possible while polymerizing within a reasonable time period.

DISCUSSION AND RESULTS

Polymerization of distilled methyl methacrylate using benzoyl peroxide and dimethyl-p-toluidine in which the exotherm exceeded 100°C always resulted in the final polymer being in a foamed state. This came about because the temperature during polymerization exceeded the boiling point of the monomer, and resulted in simultaneous boiling of the monomer and polymerization.

It was found that not all ratios of initiator to activator led to a solid state at the completion of the reaction. When more activator than initiator was used, the final product resulted in a mixture of solid and viscous liquid or all viscous liquid.

Using distilled monomer and 0.5% peroxide and 1% amine the final product contained a layer of viscous liquid above hard polymer after 6 days. At 1% peroxide and 2% amine there was less liquid and more solid after 5 days. The results and polymer characteristics at the same levels of peroxide and amine are different depending on whether the commercial monomer containing an inhibitor is used directly or first distilled.

Inhibited Monomer

Commercial monomer samples when reacted with 1% peroxide plus 2% amine or 0.5% peroxide plus 1% amine remained viscous liquids after 30 days. The product from using 1% peroxide was less viscous, indicating a lower molecular weight than from 0.5% peroxide.

By using more amine than peroxide with the inhibited monomer, solutions of varying viscosities could be achieved that were stable to further spontaneous polymerization. With the distilled monomer the polymerization, once started, would continue until all the monomer was consumed under the conditions used.

Polymerizing Inhibited Viscous Liquid Polymer Solutions

The viscous solution obtained as described from inhibited monomer probably contained monomer, oligomer, polymer, unreacted and reacted amine inhibitor and decomposition products from the peroxide. It is believed that the stability of the solution to further spontaneous polymerization is a result of the excess unreacted amine acting as a free radical trap to prevent the radicals from causing polymerization.

Since some unreacted amine activator was still believed to be present in the viscous solution, it was felt that addition of peroxide alone to these solutions would once again initiate polymerization at lower temperatures.

Samples of a viscous solution made from 0.5% peroxide plus 1% amine and commercial monomer were reacted with 0.25%, 0.5% and 0.75% peroxide to determine what the effect of added peroxide would be. The results are summarized as follows:

0.25% peroxide	temperature reached 52°C at 45 minutes; after 24 hours top soft, bottom hard
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0.5% peroxide	temperature reached 76°C at 27 minutes; after 24 hours little viscous liquid on top, remainder solid
0.75% peroxide	temperature reached 80°C at 22 minutes; after 24 hours all solid

The polymerization reaction continued for each of these samples, and after seven days rubbery layers had become hard.

These results clearly show that a partially polymerized solution which still contains an excess of unreacted amine can be polymerized further by the addition of peroxide. The temperature generated during the reaction and the characteristics of the polymer produced are dependent upon the concentration of peroxide used.

The sample may contain some liquid polymer after 24 hours even though the solid had been formed initially. The reaction will continue until eventually all the liquid has solidified provided the unreacted amine is not too great.

Plasticizer Use

Another possibility to hold down the temperature rise during polymerization was thought to be the presence of an inert material that would absorb heat but actually not get involved in the reaction. Such a material could be considered a heat-sink.

The non-reactive plasticizer dioctyl phthalate (chosen as a heat-sink candidate) was added to distilled monomer at several concentrations to determine its effect on polymerization. The results were as follows:

<u>Monomer sample system</u>	<u>Resulting product</u>
1. 0.5% peroxide, 0.5% amine and 10% phthalate	after 2½ hours cloudy and hard
2. 0.5% peroxide, 0.5% amine and 20% phthalate	after 2 hours soft layer on top, remainder hard
3. 0.5% peroxide, 0.5% amine and 30% phthalate	after 2 hours some bubbles, all hard

<u>Monomer sample system</u>	<u>Resulting product</u>
4. 0.25% peroxide, 0.25% amine and 30% phthalate	after 3 hours top soft, remainder hard
5. 0.25% peroxide, 0.25% amine and 20% phthalate	after 3½ hours top soft, remainder hard
6. 0.125% peroxide, 0.125% amine and 40% phthalate	after 4 hours temperature reached 61°C, liquid on top, remainder cloudy and hard
7. 0.125% peroxide, 0.125% amine and 50% phthalate	after 3 hours, completely cloudy, top soft, remainder hard

These results show that monomer can be made to polymerize within a few hours with a low temperature rise when a non-reactive plasticizer is used as a heat sink. The resultant solid polymer in this case is different from the solid formed by polymerizing the inhibited viscous liquid mentioned previously. The solid products range from cloudy to completely opaque depending upon the amount of plasticizer added. Essentially the entire sample is hard after a few hours.

In the polymerization of the inhibited viscous solutions the product polymer solid was a transparent brown color, and the remaining liquid would eventually solidify. The use of plasticizer leads to solid polymer formation after a few hours. Polymerization of the inhibited viscous solution at a low exotherm takes much longer.

Molecular Weight

The molecular weights of selected samples were determined using the technique of solution viscosity (Ref 2). A number of different combinations of peroxide and amine concentrations in conjunction with commercial and distilled monomer were studied. The results are compiled in Table 1 and summarized as follows.

At a concentration of 3% peroxide using commercial monomer the molecular weight of the polymer produced increases as the amine concentration is reduced from 0.75% to 0.25%. A similar effect is seen with the distilled monomer. Comparing commercial to distilled monomer at like initiator-activator concentrations, the distilled monomer resulted in lower molecular weight. One would expect the reverse, since the distilled monomer should be easier to polymerize.

An explanation may be that the distilled monomer is, in fact, easier to polymerize. The free radicals originally produced are efficient in initiating polymerization. If this were the case, oligomer formation would be extensive and so would chain termination by combination of active sites. This would lead to a lower molecular weight than if there were fewer growing chains that added monomer continuously and remained active.

There is a slight gradation in molecular weight within the product polymer samples. When a sample of the product polymer was removed from the reaction test tube and segmented from top to bottom, the molecular weight was found to be highest at the bottom and lowest on top. This is not unexpected since air acts as an inhibitor toward the polymerization (Ref 3). It is also the probable cause of samples being liquid or tacky on the top while the interior is hard. The surface is exposed to air thereby interfering whereas the interior sees no such inhibiting effect.

EXPERIMENTAL DETAILS

Since many combinations of peroxide, amine and monomer were studied, a listing of the specific experiments with product observations would be useful. The experiments were done in a cork stoppered \approx 50 ml test tubes, one-third the volume of which contained the reacting liquid. A thermocouple was inserted approximately three-quarters of the way down into the sample being careful not to touch the inside surface of the tube. The thermocouple was connected to either a digital thermometer or a previously calibrated recording instrument.

The peroxide percent used was weight to volume and the amine and dioctyl phthalate were volume to volume. The volume of monomer liquid usually used was 20 ml. In the experiments with the inhibited viscous solutions, they were prepared at least 24 hours in advance of the second addition of peroxide. This procedure assured that they were stable.

The abbreviations used in the table are:

P	- benzoyl peroxide
A	- N,N-dimethyl-p-toluidine
DMMA	- distilled methyl methacrylate
SMMA	- commercial (inhibited) methyl methacrylate
phthalate	- dioctyl phthalate

Table 1

Viscosity average molecular weight

<u>Selected samples</u>	<u>Molecular weight</u>
3% P 0.75% A SMMA	
bottom of sample	90K
middle of sample	80K
top of sample	70K
3% P 0.5% A SMMA	110K
3% P 0.25% A SMMA	225K
2% P 0.5% A SMMA	108K
3% P 0.75% A DMMA	44K
3% P 0.5% A DMMA	37K
3% P 0.25% A DMMA	106K
2% P 0.5% A DMMA	49K
2% P 0.25% A DMMA	109K

P benzoyl peroxide
A dimethyl-p-toluidine
SMMA commercial stabilized methyl methacrylate
DMMA distilled methyl methacrylate

<u>Reactants</u>	<u>Product observations</u>
1. 1% P, 0.25% A and DMMA	after 5 days top layer tacky and rubbery, remainder hard
2. 1% P, 0.5% A and DMMA	after 5 days all hard
3. 1% P, 0.75% A and DMMA	after 5 days all hard
4. 1% P, 1% A and DMMA	after 5 days all hard
5. 1% P, 1.25% A and DMMA	after 5 days top 20% rubbery, remainder hard
6. 1% P, 1.5% A and DMMA	after 5 days top 1/3 viscous, remainder hard
7. 1% P, 1.75% A and DMMA	after 5 days top 2/3 viscous, remainder hard
8. 1% P, 2% A and DMMA	58°C at 11 minutes, after 24 hours top half flowed easily, after 4 days top liquid, bottom hard
9. 0.5% P, 0.25% A and DMMA	after 48 hours top 20% viscous, remainder hard
10. 0.5% P, 0.5% A and DMMA	after 48 hours top 20% rubbery, remainder hard
11. 0.5% P, 0.75% A and DMMA	after 48 hours top 20% rubbery, remainder hard
12. 0.5% P, 1% A and DMMA	39°C at 18 minutes, after 24 hours top half flowed easily, after 48 hours top 60% tacky, remainder hard
13. 0.5% P, 1.25% A and DMMA	after 48 hours top 80% viscous, remainder hard
14. 0.5% P, 1.5% A and DMMA	after 48 hours top 90% viscous, remainder hard
15. 0.75% P, 0.5% A and DMMA	after 3 hours all hard, some bubble formation

<u>Reactants</u>	<u>Product observations</u>
16. 0.25% P, 0.25% A and DMMA	after 3 hours all but top layer hard
17. 0.5% P, 0.5%A, 90% DMMA and 10% phthalate	after 2½ hours slightly cloudy, hard
18. 0.5% P, 0.5% A, 80% DMMA and 20% phthalate	after 2 hours soft layer on top, remainder hard
19. 0.5% P, 0.5% A, 70% DMMA and 30% phthalate	after 2 hours, cloudy, all hard, some bubbles
20. 0.25% P, 0.25% A, 70% DMMA and 30% phthalate	after 3 hours top soft, remainder hard
21. 0.25% P, 0.75% A, 80% DMMA and 20% phthalate	after 3½ hours, slightly cloudy, top soft, remainder hard
22. 0.125% P, 0.125% A, 50% DMMA and 50% phthalate	after 3 hours completely cloudy, top soft, remainder hard
23. 0.125% P, 0.125% A, 60% DMMA and 40% phthalate	61°C at 4 hours, liquid on top, remainder cloudy and hard
24. 1% P, 2% A and SMMA	58°C at 12 minutes, after 30 days thin liquid, film forming
25. 1% P, 1.5% A and SMMA	after 30 days all liquid
26. 1% P, 1% A and SMMA	after 30 days viscous solution
27. 0.5% P, 1% A and SMMA	after 30 days viscous solution
28. 0.5% P, 1% A and SMMA	41°C after 25 minutes

<u>Viscous solution</u>	<u>Product observations</u>
1. 0.5% P, 1% A, SMMA and 0.5% P	76°C at 27 minutes, after 24 hours layer of viscous liquid on top, remainder solid
2. 0.5% P, 1% A, SMMA and 0.25% P	52°C at 45 minutes, after 24 hours top half flowed, bottom hard

Viscous solution

Product observations

3. 0.5% P, 1% A, SMMA and 0.75% P	80°C at 22 minutes, after 24 hours all solid
4. 0.5% P, 1% A, SMMA, 0.1% and 5 ml SMMA	32°C after 2½ hours, after 48 hours top 3/4 rubbery bottom hard, after 5 days all hard
5. 0.5% P, 1% A, SMMA and 0.1% P	32°C at 1 hour, after 48 hours top half rubbery, bottom hard
6. 0.5% P, 1% A, SMMA, 20% SMMA and 0.1% P	43°C at 1½ hours, after 24 hours extremely viscous, after 5 days rubbery
7. 0.5% P, 1% A, SMMA, 20% SMMA and 0.2% P	53°C at 1 hours, after 5 days rubbery
8. 0.5% P, 1% A, SMMA, 20% SMMA and 0.4% P	57°C at 37 minutes, after 24 hours top half rubbery, bottom hard
9. 1% P, 1.38% A, SMMA and 0.1% P	35°C at 40 minutes, after 24 hours all hard
10. 1% P, 1.38% A, SMMA and 0.2% P	44°C at 35 minutes, after 24 hours all hard
11. 1% P, 1.38% A, SMMA, 35% SMMA and 0.1% P	29°C at 2 hours, after 3 days all hard
12. 1% P, 1.38% A, SMMA, 35% SMMA and 1% P	82°C at 30 minutes, after 3 hours all but extreme top hard

CONCLUSION

The polymerization of methyl methacrylate accompanied by a low exotherm can be accomplished by alternative methods; (1) use of a heat sink such as a non-reactive plasticizer with the monomer, (2) polymerizing further a partially polymerized viscous solution. In either method the exotherm developed can be kept below 100°C.

Polymerizing in the presence of a plasticizer may result in a completely opaque or cloudy solid product depending upon the amount of plasticizer used. Polymerization of a partially polymerized inhibited solution leads to a brown transparent solid. There is considerable variation in the exotherm developed in the case of the inhibited viscous solution, depending upon its original viscosity and amount of peroxide added. Generally, the lower the exotherm the longer the time needed to achieve the final solid state.

RECOMMENDATIONS

Based on these preliminary results which indicate that the technique developed for curing methyl methacrylate is feasible for use as a potting agent for thermally sensitive energetic materials, it is recommended that further effort be directed to optimizing the various parameters. In order of priority the following should be carried out:

1. Characterization of the viscosity resulting from partial polymerization of the monomer at several ratios of initiator-activator.
2. Characterization of the variation of peroxide concentration on furthering the polymerization of the partially polymerized monomer.
3. Characterization of the molecular weight of the final product.
4. Characterization of the physical properties of the final product.

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