

[E005]

# Investigation of the Effect of Different Hydroperoxides and Peroxides on Curing Rate of Methyl Methacrylate as an Anaerobic Adhesive

Vahaj B., Naimi-Jamal M. R.,\* Hassanshahi, M.

Organic Chemistry Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846, Iran

Email: [naimi@iust.ac.ir](mailto:naimi@iust.ac.ir)

## Abstract

In this paper we wish to report our results on investigation of the kind and the concentration of the hydroperoxides initiators on the polymerization rate. Four kinds of peroxides with different concentration have been examined such as), *tert*-butyl hydroperoxide (TBHP), cumene hydroperoxide (CHP), methyl ethyl ketone hydroperoxide (MEKP) and benzoyl peroxide (BP). Results show that the rate of the reaction depends on the type and percentage of initiators.

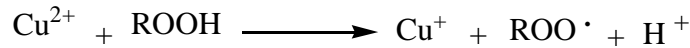
## Introduction

The anaerobic adhesive for the first time had been examined back in 1945; at the time that "Nordlander" and "Burret" discovered that dimetacrylate will be hard and will cause the joint of metal sheet to each other in the absence of oxygen and in high temperatures<sup>1,2</sup>. This adhesive is one of the one-part adhesives, which polymerize very fast without any oxygen.<sup>3</sup> Anaerobic adhesives are widely used in different industries, therefore different researchers have examined their adhesiveness. Although much attention has been paid on the polymerization rate of acrylates, but no report was found about the influence of the kind of the initiators on it. Main parts of these adhesives are usually:

- 1- A methacrylic monomer because of their diversity, transparency, and their resistance in different situations
- 2- Initiators such as peroxides
- 3- Accelerators such as *N,N*-dimethyl-*p*-toluidine (DMPT), benzoic sulfimide (saccharin).<sup>4</sup>
- 4- Other additives such as viscosity controller, colorants.<sup>5</sup>

These adhesives can cure via a redox radical mechanism at room temperature as soon as oxygen is removed. they cure very quickly when confined between the materials to be bonded (commonly metals). Copper and iron are well known to increase kinetics of reaction whereas cadmium or zinc are inactive and require the use of a primer.<sup>5</sup> Saccharin is able to dissolve metals by forming metal salts, that can easily decompose the hydroperoxide. The *N,N*-dimethyl-*p*-toluidine complexes only ions, for example for Cu<sup>+</sup>

two ligands may be accommodated around one cuprous ion. The complex is much more reactive than uncomplexed cuprous ions.<sup>6,7</sup> In the case of Cu ions, both oxidation states are able to induce the decomposition of hydroperoxide but because RO· is much more reactive with methacrylic monomers than ROO·, Cu<sup>+</sup> should be more reactive than Cu<sup>2+</sup>.

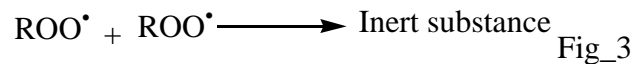
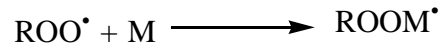
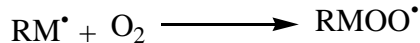
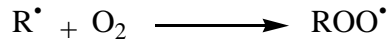


(Inactive)

Fig.1

DMPT appears to be necessary to give acceptable gelation times under anaerobic cure conditions. It appears to be responsible for causing a slow decomposition of hydroperoxide during storage.<sup>4</sup>

In the presence of oxygen, the following reactions are anticipated.



Fig\_3

M: monomer, R·: initial radical, RM·: monomer radical,  
ROO· and RMOO·: peroxide radical (of lower activity)<sup>2</sup>

## Results and Discussions

With the increase of initiator concentration and because of creation of active radical and its attack to doubled parts in monomers, we expected to see increase of temperature and rate of the reaction with time. With 30% commercial solution of TBHP in water, the increase of concentration of initiator resulted in decrease of the reaction rate. It seems that most of heat of the reaction was absorbed by water, because of its high specific heat capacity. So increasing the concentration of the initiator (and consequently water) causes in decrease of temperature (figure 4).

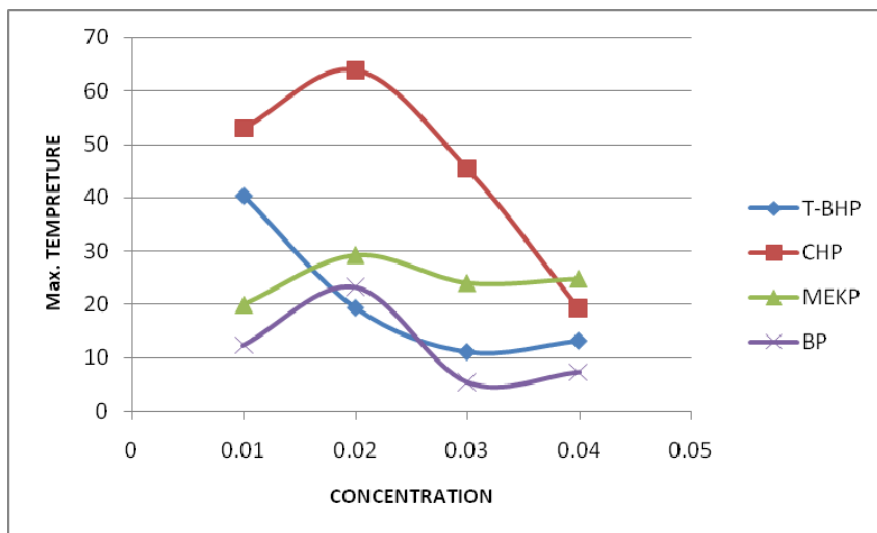


Fig. 4. Maximum temperature in different concentration of peroxides

Increasing the concentration of other peroxides like CHP, MEKP, and BP results in increase in free radicals concentration and increase in the rate of polymerization. On the other hand, increase of the concentration of the initiator more than 2% w/w will increase the rate of final undesirable reactions and decrease the rate of polymerization (Fig. 4).

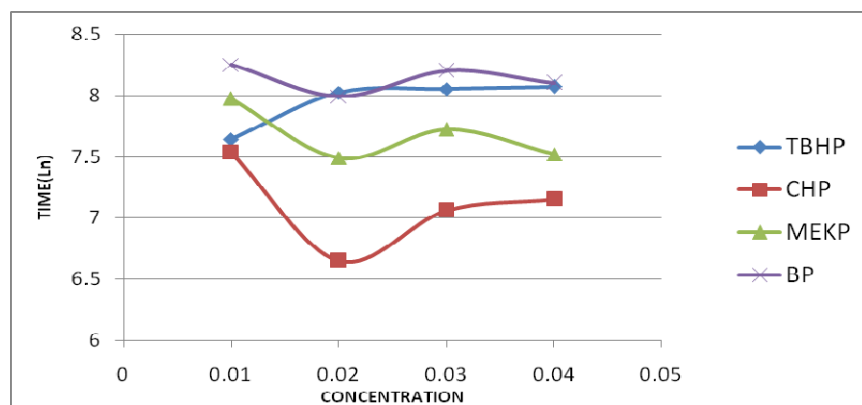


Fig. 5. Comparison of the time of polymerization in different concentrations of peroxides

## Conclusion

In this paper we concluded that 0.02% w/w of the most of the initiators will increase the rate of the reaction. CHP was found to be the best initiator. We are working on finding the reaction rate law for this polymerization reaction.

## Acknowledgment

We acknowledge Iran University of Science and Technology (IUST) for partial financial support of this work.

## Experimental Section

The reactions were tested in a three-necked 50 mL flask equipped with vacuum line and a digital temperature sensing probe. The temperature was recorded every 5 seconds. The results are shown in Fig. 6-9.

Monomer (1 g, 1.06 mL) with 0.01 g of saccharin and 0.01  $\mu$ l of DMPT mix was added to the flask. Then 0.002 g copper saccharinate<sup>7</sup> was added and the mixture was stirred vigorously. The solution turned to purple,<sup>6</sup> because of in situ prepared DMPT radicals. The flask was evacuated for 5 min. Then 1 to 4% w/w peroxides were added to the reaction mixture at room temperature. The temperature of the reaction mixture was monitored by the digital probe.

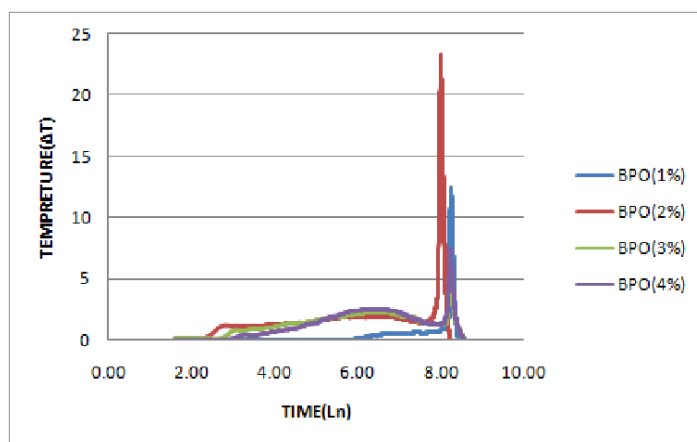


Fig. 6. Temperature of polymerization process with different concentrations of BPO

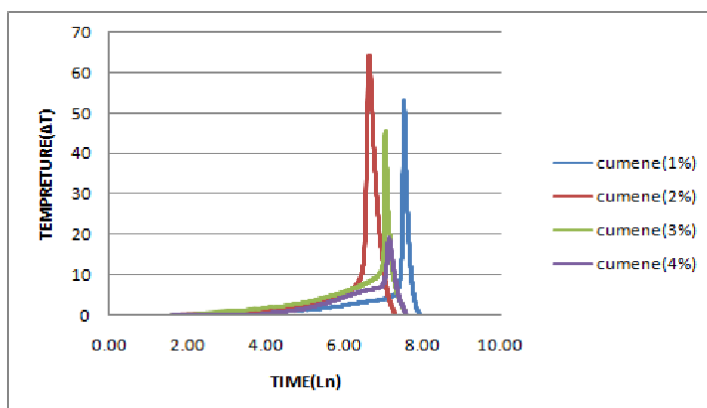


Fig. 7 Temperature of polymerization process with different concentrations of CHP

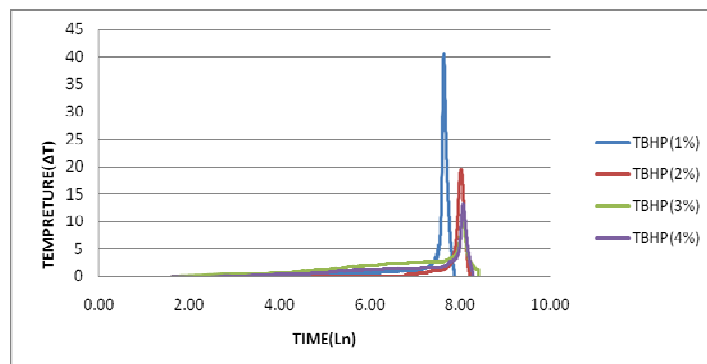


Fig. 8 Temperature of polymerization process with different concentrations of TBHP

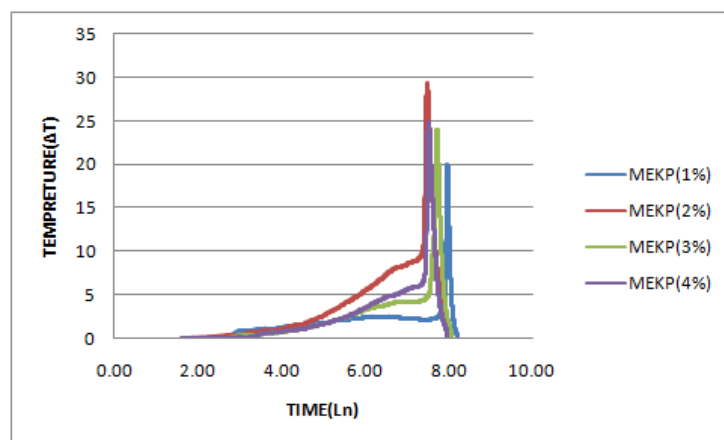


Fig. 9 Temperature of polymerization process with different concentrations of MEKP

## Reference

1. Chemistry of Free Radicals, Tokyo Kagaku Dojin, Tokyo, **1968**.
2. Masaoka, T.; Moshizuki, S.; Haruna, K. Three Bond Technical News, Issue April 1, **1986**.
3. George, B.; Touyeras, F.; Grohens, Y.; Vebrel, j. *INT. J. Adhesion and Adhesives*. **1997**, *17*, 2.
4. Smith, J. D. B. ; *Journal of Applied Polymer Science*, **1992**, *45*, 1-15.
5. Aronovich, D. A. Murokh, A. F. Khamidulova, Z. S. Sineokov, A. P. *Polymer Science, Series D. Glues and Sealing Materials*, **2009**. 2. 82-87.
6. Wellmann, St. Brockmann, H. *INT. J. Adhesion and Adhesives*. **1994**, *14*, 47-55.
7. Beaunez, P.; Helary G.; Sauvet, G. *Journal of Polymer Science, Part A. Polymer Chemistry*. **1994**, *32*, 1459-1469.