

The characteristic of the secondary thiol compounds and its application.

Katsumi Murofushi

Corporate R&D Center, Showa Denko K.K., Kawasaki, Japan

1. Introduction

UV curing technology attracts attention as a productive process that it can harden quickly, and is used for various uses. On the other hand, radical polymerization system, especially an acrylic polymerization system is used with UV curing technology. The thiol compounds introduced by this presentation used conventionally as a curing accelerator of a radical polymerization system.

The thiol compounds react thermal addition reaction, radical addition reaction, etc. to double bond competitively. With this characteristic, it can be used as a chain transfer agent at UV curing system and as a monomer at a thiol-en reaction. However, such biggest problem of a thiol compound is the instability (short pot life) in the Michael addition reaction of a thiol group and double bond.

2. The secondary thiol compounds

Although the characteristic of a thiol-en curing reaction is a radical reaction, it is the point of being hard to receive the polymerization inhibition by oxygen. In addition, adhesion strength, a mechanical property (tensile strength and elongation rate), etc. show the useful characteristic. However, as for the thiol compounds, the heat addition reaction of a thiol group and double bond occurs, and a thiol-en composite is instability and is gelled.

In order to solve such a problem, we developed multi-functional secondary thiols as shown in Figure.1 as what can satisfy other performances, maintaining preservation stability.

The design is the following two points.

1. In order to improve instability (short pot life) of this composite, steric hindrance around of the thiol group was enlarged. As a result, the addition reaction (Michael addition reaction) to double bond was able to be inhibited.
2. In order to improve UV curing performance, the multi-functional thiol is used for raising crosslinking.

This multi-functional secondary thiols can give the following characteristics by adding to UV curing system.

1. The preservation stability of a composite is good.
2. UV curability improves (a double bond reaction rate increases).
3. Adhesion strength improves.
4. Flexibility improves.

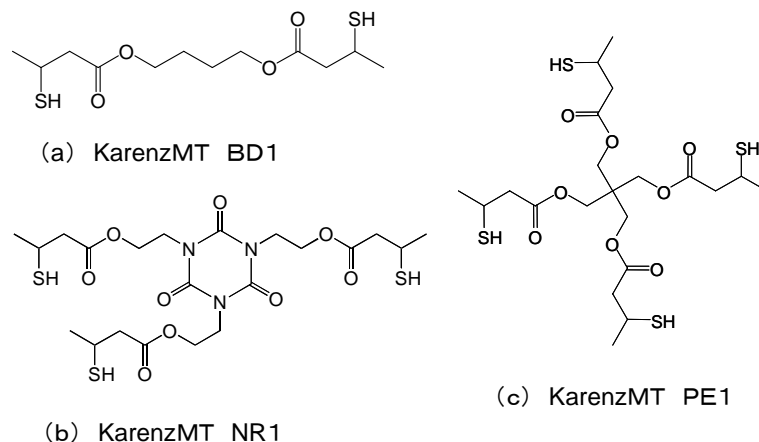


Figure.1 The multi-functional secondary thiol compounds

3. UV Curable Properties

The multi-functional secondary thiols shows high performance in UV curing system. We evaluated the addition effect of the multi-functional secondary thiol about UV curing in the system which used the acrylic monomer system below.

As evaluation of curing, the double bond conversion was measured about this composite which added the multi-functional secondary thiol shown in Figure.1 to bisphenol-A diacrylate (BPDA). Figure.2 shows the change of the double bond conversion by light exposure. Figure.2 shows that the reaction rate increases, in adding multi-functional secondary thiol “KarenzMT BD1”.

The result of having performed same measurement about other multi-functional secondary thiol is shown in Figure.3. It is showing that a double bond conversion improves with the increase in the amount of addition of each multi-functional secondary thiol. This knowledge shows that the number of residual double bond can be decreased, and the crosslinking density can be made to increase by adding the multi-functional secondary thiol to UV curing composite.

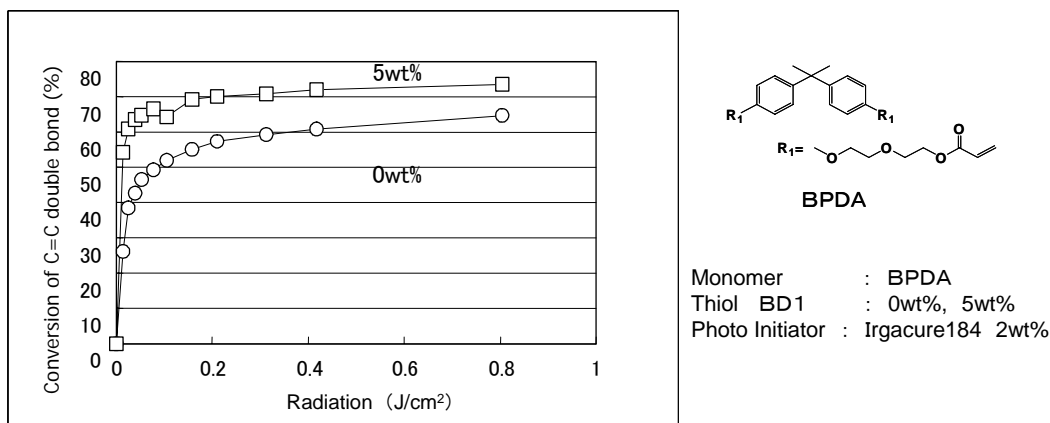


Figure.2 Conversion of C=C double bond vs. radiation

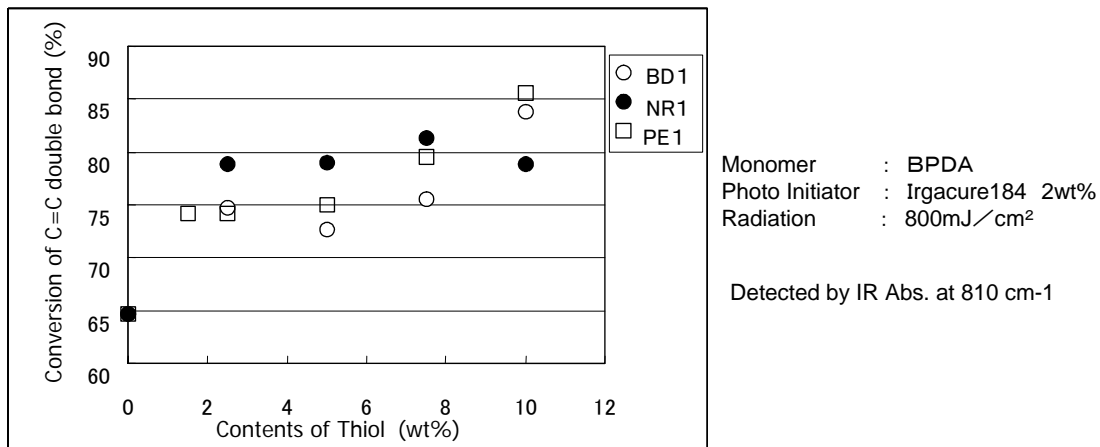


Figure.3 Conversion of C=C double bond vs. Contents of Thiol

4. Curing shrinkage

The curing shrinkage percentage at the time of adding multi-functional secondary thiol BD1 to BPDA is shown in Figure.4. As a result, although the double bond conversion increased by addition of BD1, it was shown that the curing shrinkage percentage decreased. This phenomenon is deeply connected with the flexibility.

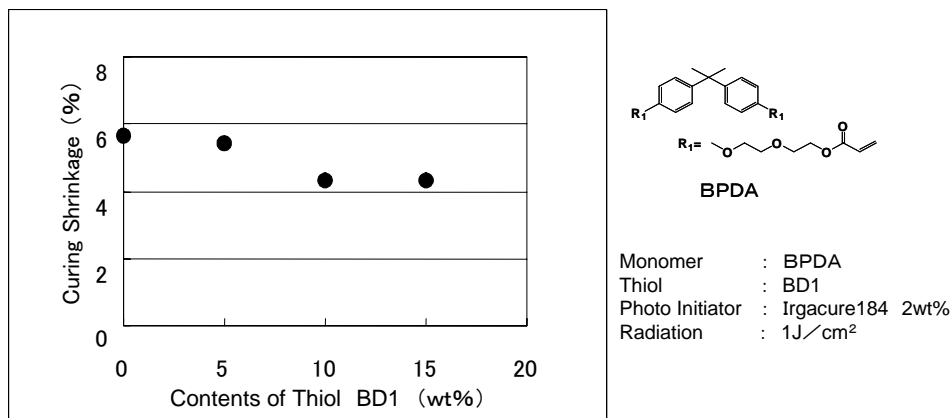


Figure.4 Curing Shrinkage vs. Contents of Thiol BD1

5. Adhesion with Substrate

The addition effect of multi-functional secondary thiol was evaluated for the acrylic monomer system about the adhesion characteristic of UV curing film. The composite which added multi-functional secondary thiol shown in Figure.1 to BPDA was applied to the glass substrate, and adhesion strength was measured after UV curing. Consequently, Figure.5 shows that adhesion strength increases depending on the amount of addition of the multi-functional secondary thiol. Since adhesion strength also increases according to the increase in a double bond conversion as this phenomenon is shown in Figure.6, the crosslinking density in an interface has influenced.

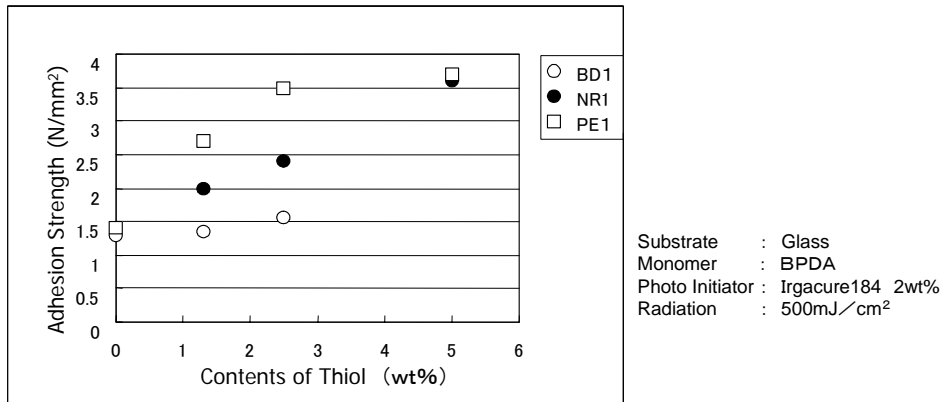


Figure.5 Adhesion Strength vs. Contents of Thiol

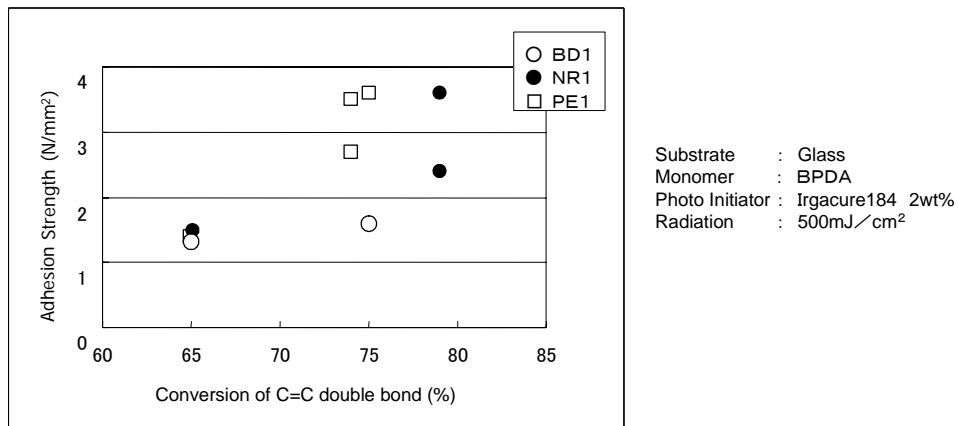


Figure.6 Adhesion Strength vs. Conversion of C=C double bond

6. Flexibility

Like measurement of adhesion strength, multi-functional secondary thiol BD1 was added to BPDA, UV curing film was prepared, and elongation percentage was measured by Tensilon testing. The result is shown in Figure.7, it was shown that elongation percentage is increased depending on the amount of BD1 addition. This phenomenon is considered with flexible structure that was introduced into UV curing film by adding BD1.

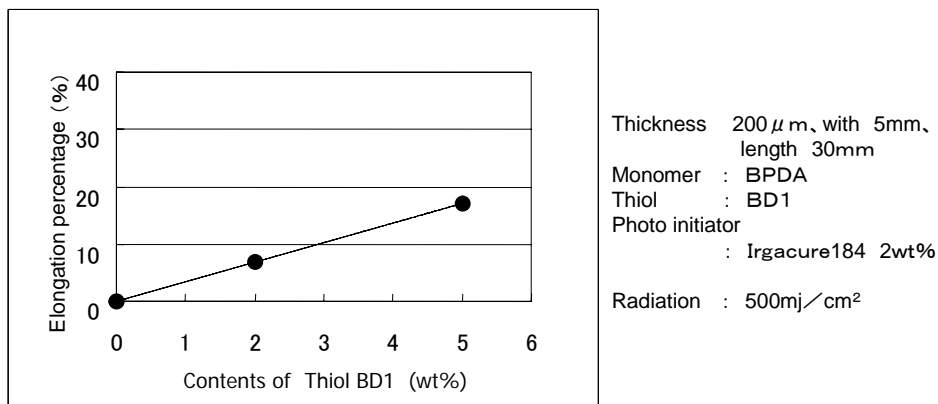


Figure.7 Elongation percentage vs. Contents of Thiol BD1

7. Transmission properties

At the optic material, in order to raise the optical characteristic, the materials design which made the sulfur atom often contain is carried out. Then, the transmission rate change at the time of adding the multi-functional secondary thiol was measured.

The transmission rate (T(%)) of visible light at the time of adding multi-functional secondary thiol BD1 to BPDA and long-chain alkyl diacrylate (HDA, Figure.8) was measured with the spectrophotometer. It was shown in Figure.8 that transmission rate increases depending on the amount of BD1 addition.

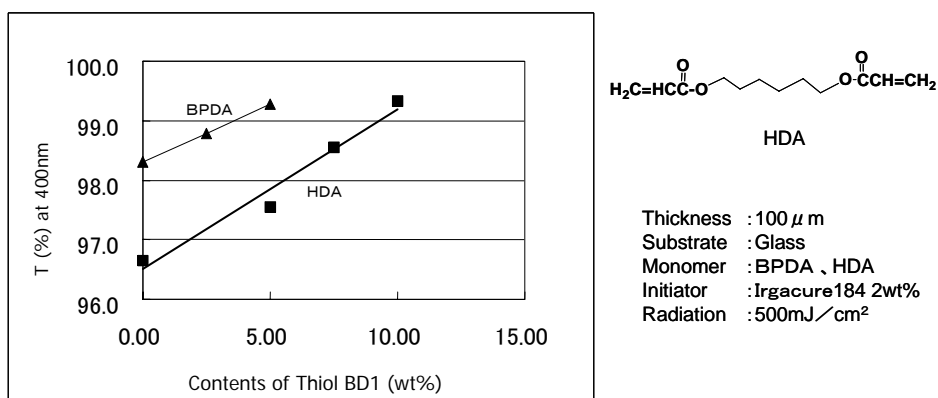


Figure.8 Transmission rate T(%) vs. Contents of Thiol BD1 at 400nm

8. Preservation stability

The viewpoint of the comparison of the primary and secondary of multi-functional thiol estimated the preservation stability of this composite. The composite which added the multi-functional secondary thiol of Figure.1 to the dipentaerythritol hexaacrylate (DPHA) was prepared, and viscosity change at 40 degrees C was measured with B type viscosity meter to it. Measurement of viscosity was performed at 23 degrees C.

A result is shown in Figure.9, the composite which added multi-functional primary thiol (PEMP) was gelled in tens of hours. However, the multi-functional secondary thiol addition systems carried out almost no viscosity change, and were stable. Since the large steric hindrance substituent inhibits an addition reaction to double bond, it is thought that high preservation stability is shown.

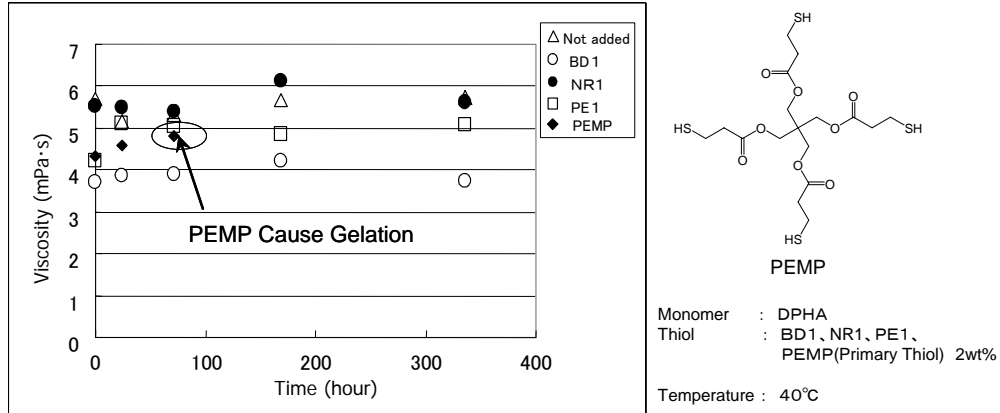


Figure.9 Studied by Analyzing Viscosity Change

9. Thermal addition reaction

A thiol compound causes the addition reaction (Michael addition reaction) to double bond with heat. The result of having measured addition temperature by DSC (temperature of peak top) to Figure.10 was shown. Whenever one methyl group increased, it was shown that addition reaction temperature increases from about 20degrees C to 30degrees C. This knowledge is suggesting also to the phenomenon of high potlife of the multi-functional secondary thiol.

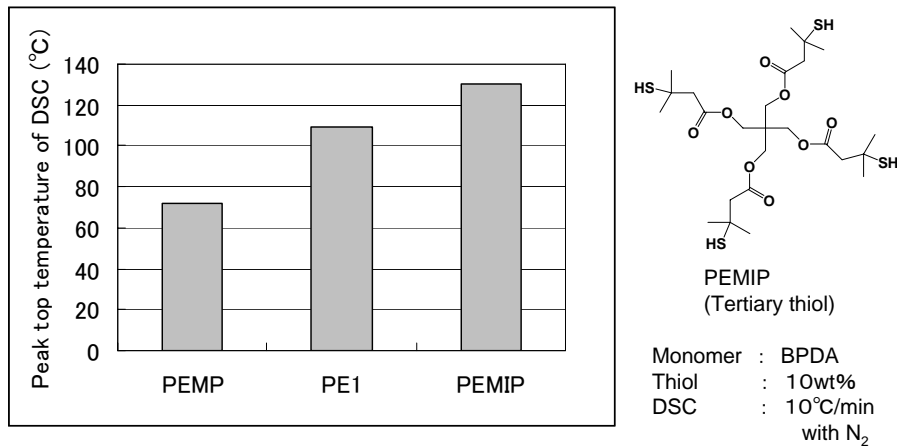


Figure.10 Temperature of addition reaction of the multi-functional thiol to BPDA

10. Addition reaction of epoxy monomer

Although there is an epoxy monomer that cured by the heat addition reaction, it is known that, as for thiol compound an epoxy monomer will react. Then, it measured about the curability and tensile strength at the time of adding the multi-functional secondary thiol to an epoxy monomer.

The result of having added the multi-functional secondary thiols to an epoxy monomer, and having measured viscosity change is shown in Figure.11. As a result, it was shown that the multi-functional secondary thiols has late addition time of onset as compared with the primary thiol.

Moreover, tensile strength of the curing film was measured by Tensilon testing (Figure.12). As a result, the secondary thiol shows high tensile strength. It is thought that this phenomenon is based on a large steric hindrance structure of the secondary thiol.

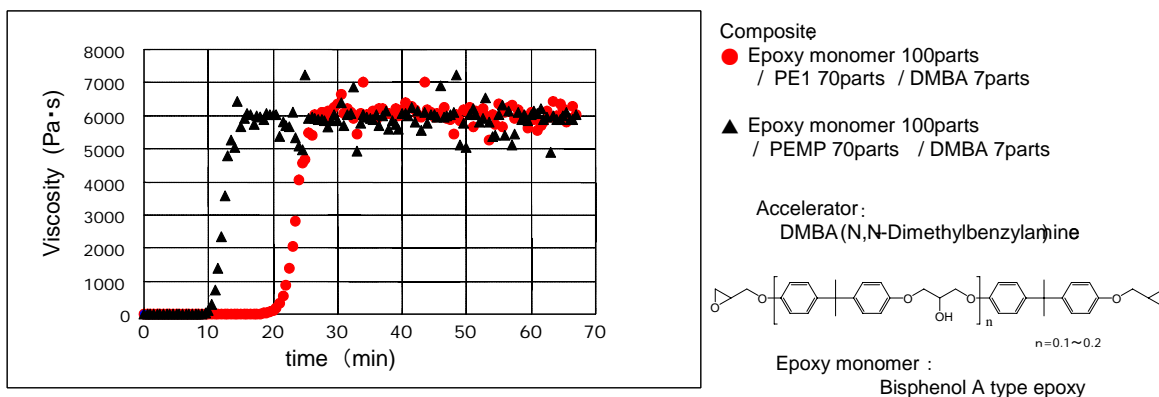


Figure.11 Viscosity change of epoxy monomer system

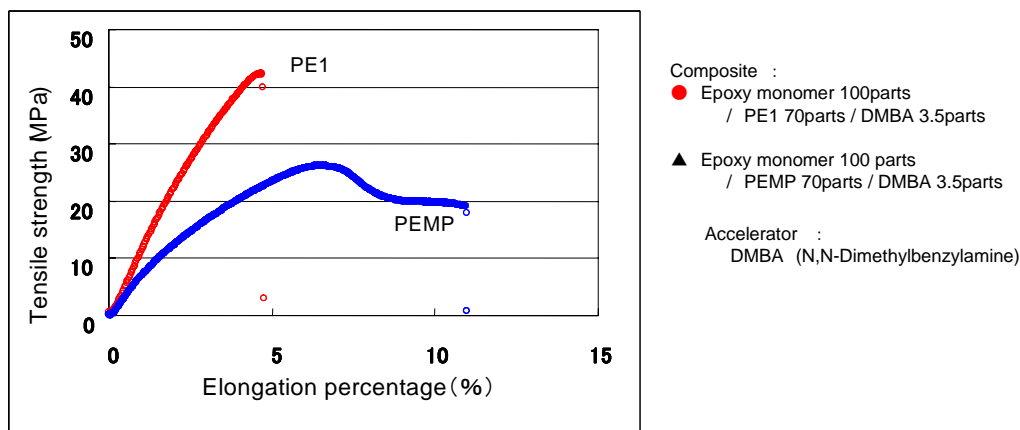


Figure.12 Tensile strength vs. Elongation percentage of epoxy-thiol system

11. Conclusion

By setting structure around of the thiol group to steric hindrance, the reactivity of the thiol group was controllable. Moreover, the feature was acquired by "curability", "curing shrinkage", "adhesion strength", "flexibility", etc. in UV curing reaction, maintaining potlife.

Moreover, the feature was acquired also the reaction with an epoxy group as a heat addition reaction.