Evaluations of UV curing with the fluorescence sensor

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1. Introduction

How do you evaluate if UV curing has been completed or not? In these years, UV cure resin is in widespread use because of its simple curing for the handling. Then it’s the causes of problems that products have been delivered in the market with short of curing and made hassles occasionally. Optical pick up that I know well is also using a lot of UV glue. And its 1st or 2nd causes of complaint in the market are “not good” at UV curing.

Not only with UV curing, but also for all of other gluing, it’s very difficult to check the gluing of products is OK or NG for all of them. It could be a check of hardness, or adhesive strength. In any way, it is destruction sampling inspection otherwise it could be a nondestructive inspection with weaker strength that cannot break the products. Who knows it is perfect? If you want to know clearly that the chemical reaction has been finished, you can take the way to use FTIR to see the composition of the chemical of glue. But it’s too complication for using on production as usual inspections. Mostly, they don’t like to set up the expensive equipments and employ an advanced engineer only to operate the equipments beside the factory.

Sentech Corporation has found out that UV cure glue changes to fluorescent material chemically after its curing and has developed the fluorescence sensor to evaluate how it is cured. The principle is highly chemical theory. It is not very easy to understand the details of the chemical reaction of the luminescence behaviors for a “not chemical” person. But to use the equipment is very simple and very useful compare to any method as known before.

I would like to make explanation about the evaluation of UV curing with the fluorescence sensor simply without technical words as possible.

You will find that I’m not a specialized person on this field because my explanation doesn’t give you satisfaction. But please guess what I want to say.

Yuki Nagaoka
2. What’s the fluorescence?

I would like to give explanations about the fluorescence itself and the principle of the fluorescence sensor before I go on the evaluation of UV curing with it. But I’m not a specialist of chemical fluorescence. If you know well about principle of fluorescence and the sensor, you can go to the chapter 5 directly without reading from chapter 2 to chapter 4.

“Fluorescence” is a general word you can see familiar around anywhere. You know fluorescence lightings and fluorescence agent in detergents. Or you should see fluorescent paint for night roads or for other goods. But from the point of the strictly physics, it needs to study quantum mechanics or quantum chemistry with the knowledge of molecular orbital energy to explain the phenomenon of fluorescence. So, I don’t mention about the complicate theory in this book. I’m talking only about the outline of the phenomenon.

“Fluorescence paint” gives you the impression that “Fluorescence” means the material emit luminescence when it is irradiated by other lights. Fluorescence is the phenomenon that the energy of lights from outside replaces to the energy of other lights from inside of the material. The material with this character is called fluorescent material and the light from outside to raise the energy for fluorescence is called excitation light. For instance, the fluorescent material is coated on inside of the fluorescent tube, and mercury atoms emit ultraviolet light and irradiates the material, the material emits fluorescence. Then you can see that the whole of the fluorescent tube is lighting. Fig2.1 from Mr. Nakamune of Sentech shows the structure of the phenomenon with some technical words.
When the material in the ground state is irradiated lights, the material absorbed the light and got higher energy (excitation state). Generally materials are stable when their energies are lowest. Then the high potential energy materials emit lights as energies and turn back to be in the ground state. This phenomenon is called as fluorescence. The time until the fluorescent material has been finished emitting since it was exposed in excitation lights is only $10^{-7} \sim 10^{-10}$ seconds. So, we can assume that the material emits lights only while exposed in excitation light as evaluation with the fluorescence sensor. I don’t mention about “phosphorescence” as the phenomenon with longer luminescence now.

The UV cure glue is exposed in UV (ultraviolet light) energy. After that, the energy will be spent for chemical reaction of curing and liberate thermal energy as extra. Then the other way for spending the extra energy for being in ground state is the “fluorescence”. Sentech has found the principle of the fluorescence from the extra energy. That is the clue of the development of the fluorescence sensor for evaluation UV curing”.

3. Relationship of UV curing and fluorescence

Now, I would like to explain the reason of why the fluorescence can be the tool for evaluation of UV curing. It related to chemical reactions of UV curing of course. The detail explanation of them needs higher chemical knowledge and need to use technical words like “monomer”, “polymer” or “oligomer” as not known for us very much. I’m not a specialist of that, then I pick up some summary and outline in a plain style. So, please understand this is not a thesis for specialists.

There are varied kinds of UV cure glue. I pick up radical reactivity as the most typical one. Radical reactivity is the only type for the evaluation with fluorescence sensor? It’s not true. Then all of radical reactivity glue can be evaluated with the fluorescence sensor? It’s not correct, neither. We can say that we have recognized most of radical reactivity materials are able to be evaluated with fluorescence sensor so far. Then I give explanation with only radical reaction as below.
Fig 3.1 shows the composition of UV cure glue material before chemical reacting. It contains chief material as monomer or oligomer which has small molecular weight as liquid. And photopolymerization initiator is contained.

The photopolymerization initiator absorbs light very well. When ultraviolet lights are irradiated on that, it will be change to radical state that is very reactive unstable condition.

The radical photopolymerization initiator catches monomer or oligomer near by soon and combines that. Next, the monomer or oligomer combined to radical initiator will change to radical.
Again, the radical monomer or oligomer pulls another monomer or oligomer and combine and let it be radical. Like these continuation behavior that pulls, combines and be radical, and one more pulls, combines and be radical, makes a small molecular weight monomer or oligomer to bigger molecular weight polymer as solid substance. That is the curing of UV cure glue and it is called as polymerization.

![Diagram of Polymerization](image)

The polymer that is already cured has “ex-photopolymerization initiator” absorbs light very well still in it. Meantime of polymerization progress, or the material is not stable yet, the given energy of lights was spend for several way as reaction in the material. But when the progress has done, the material is stable, the extra light energy irradiated cannot be used for anything of the curing reaction. For one way to spend the energy, the material emits luminescence as fluorescent light. That means the material has changed to fluorescent material.

![Diagram of Fluorescent Material](image)

That’s the reason of why we can evaluate how UV cured with fluorescence sensor by looking at the amount of fluorescent lights.
4. Principles and construction of the fluorescence sensor

Fig 4.1 shows the fluorescence sensor of Sentech Corp. As you can see, it is enough small to put on a desk in a general experimental laboratory room. It is composed of a sensor part and controller. The picture model is OL201 as a high sensitivity type in their lineup. There are variable resistances to control the sensitivity on both of the controller and the sensor part. They recommend this model for general-purpose properties. The exciting light wave length of OL201 is 365nm. And they have variety types as the wave length is 310nm and 280nm. It is better to choose the same wavelength as absorbed wavelength of the material for evaluation. At this moment, 365nm is the most standard one.

The lineup of fluorescence sensors of Sentech

<table>
<thead>
<tr>
<th>Model No.</th>
<th>Version (Wavelength)</th>
<th>Dimension (mm)</th>
<th>Spot size diameter (mm)</th>
<th>explanations</th>
<th>application</th>
</tr>
</thead>
<tbody>
<tr>
<td>OL301</td>
<td>Basic type (365nm)</td>
<td>W35xD50xH120</td>
<td>φ1</td>
<td>•Basic type</td>
<td>UV cure glue</td>
</tr>
<tr>
<td>OL201</td>
<td>High sensitivity (365nm)</td>
<td>W50xD75xH125</td>
<td>φ1</td>
<td>•Wider range for adjustment sensitivity •enable to adjust the light power of UV</td>
<td>UV cure glue</td>
</tr>
<tr>
<td>OL251</td>
<td>High sensitivity High output (365nm)</td>
<td>W50xD75xH125</td>
<td>φ2</td>
<td>•Higher light power than OL201 •UV cure glue •oil detection •trace chemical compound</td>
<td></td>
</tr>
<tr>
<td>OL202</td>
<td>High sensitivity Small spot size (365nm)</td>
<td>W50xD75xH125</td>
<td>φ0.5</td>
<td>•Smaller spot size •adhesion evaluation of small parts</td>
<td></td>
</tr>
<tr>
<td>OL221</td>
<td>High sensitivity (280nm)</td>
<td>W50xD75xH125</td>
<td>φ1</td>
<td>•With different wavelength for variety materials •280nm and 310nm prepared</td>
<td>UV cure glue</td>
</tr>
<tr>
<td>OL211</td>
<td>High sensitivity (310nm)</td>
<td>W50xD75xH125</td>
<td>φ1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4-1. Fluorescence sensors of Sentech Corp.
Fig 4.2 shows the contracture of the sensor part of the fluorescence sensor. There is an ultraviolet LED (UV LED) in the right side of the sensor part in the figure. And it irradiates exciting light. The light is folded at the mirror and exposures the test material. And the material emits the fluorescent light weepingly in all directions as the figure shows. The part of the fluorescent light arrives to the detector in the sensor and the detector shows the amount of the fluorescent lights.

The way of measuring is very simple. You can measure just when you put it on the table of the sensor and focus the exciting light on. The diameter of the spot is φ0.5~2mm (refer to table 4.1). The exciting light is invisible light, but it is easy to see the spot on a sheet of white paper or something as well. (Because white paper contains a lot of fluorescent material.) Please put protective glasses on.
The exciting light of this equipment is modulated light. It enables to measure under usual lighting as fluorescent lamp in an experimental laboratory room. It does not need specialized environment as a dark room. (But they recommend avoiding too closely lighting on a desk.) Even you can measure the process of the curing during adhering with UV-LED curing systems.

The fluorescence sensor in Fig4.3 is set on a table jig. It’s possible to be as stand-alone from the jig and put it on a part of factories where it is needed. And it’s also OK to put the sensor on an industrial robot to measure the data on variable places or angles.

As I have mentioned, the fluorescence sensor of Sentech have provided the method of analyzing the process of curing of UV cure glue through the fluorescent light come from the changing of interior structure of the materials. But it needs severely understandings for exercising this equipment. At the first, the fluorescence sensor measures the amount of fluorescent light, it never analyzes the changing of the material directly. Users had to research and recognize these behaviors of the materials which are analyzed as chemical reactions. (1) How the amount of the fluorescent light will be change? (2) How much the amount of the fluorescent light at the beginning? (3) How much the amount of it after curing? (4) What is the signal of finishing of the chemical reactions? After studying the detail, the measurer can judge it “OK” or “NG” seeing the figures of the equipment. When the construction of measuring and way to judge has been built, the equipment give marvelous convenience nobody had seen.

Fig4.4 is a graph that shows the process of curing glue with the fluorescence sensor. The trace of hardness of the glue is drawn regarding to the relationship of hardness and accumulated UV light power in a release book of the glue manufacture. And the trace of the fluorescent light power is added in the graph. Looking at this graph, some misunderstanding might be brought. Please mind that hardness of 50 of the maximum value on the left axis of the graph never indicate the absolutely the amount of fluorescent light of 40 on the right axis.
First of all, the figure of tracking of the graph as the process is just the remarkable notice for seeing the relationship of the fluorescent light and hardness (how cured). The adhering reaction is going on, how the amount of fluorescent light will be changing is the most important. Fig4.4 shows that Threebond 3056B has a property that the tracking curves of hardness and fluorescent light show very similar feature. When the each axis range is adjusted well, the curves are same on the graph as Fig4.4.

Many kinds of glue show this feature, but not all of glue has same property. For instance, Fig4.5 of Chemitech U-1582 and Fig4.6 of Chemitech U-406B show different characteristic curves.
Somebody thought that the fluorescence sensor is not useful for evaluating the UV curing when the character shows different curves of the hardness and amount of fluorescent light? I don’t think so. It is depend on what the measurers want to analyze. For instance, I agree with that fluorescent light cannot determine the moment of beginning of adhering of the glue of Chemitech U-1582. But if you want to know if it has been cured or not, who thought it is impossible? Both of Fig4.5 and Fig4.6 show the judgment of whether it has been done or not from the line of figure.

It has mentioned that the fluorescence sensor make the best use of its property when the relationship of what you want to see and how the trace of fluorescent light changes is clarified.

Notes:
1. The amount of fluorescent light doesn’t show the value of absolute.
2. First of all, it is necessary to see the tracking of amount of fluorescent light.

Temperature and quantity of the materials are also the condition to be considered.

Then I will mention the example of the applications in next chapter.
5. Evaluations of UV curing with the fluorescence sensor

5-1. UV glue to adhere components

The condition to curing should be classified into below four types.

(1) Voluntary cured when you pour it in air
(2) Mixing two kinds or more of glue material
(3) Thermal curing
(4) UV curing

Provided that you take (1) method, the curing will start as soon as you put the material in the case to keep abundant quantity for the work before you finish up it. If type (2), you need to be carefully about the ratio of the material mixed and stir up enough until there is no pure individual material in it. If you take (3), the components should be heatproof one than the curing temperature. And you need to take bigger process for the curing in the oven.

Compare to those method, type (4) UV curing start curing only when you give exposure UV light to the materials. You can determine the timing to cure when you want. You don’t need bigger process for curing glue.

Before these past years, UV curing was used to be only for optical components or something. But manufactures of glue in the world have paid much effort for developing excellent glue and achieved them. Now UV glue have diverse types and get enough reliability for using for everywhere in the market.

For instance, Optical pickup for DVD or BD (also CD), the component for reading or writing data on optical discs, uses many kinds of optical components. And almost all of the components are rigid by adhering with glue, not only for optical components but also for other mechanical components.

First of all, I’m going to mention about the glue at the objective lens. It’s the most important component of Optical pickup (OPU).
You need to be much attentive for the gluing the objective lens.

**Fig.5-2 Objective lens and the lens holder of Optical pickup**

Because Objective lens is very sensitive and much influenced by stress of adhering regarding the performance of OPU. The glue has cure shrinkage, of course, and also the changing of property of the glue for long term environment is much serious. Additionally, the strength of adhere should be enough for acceleration of shaking or drop impact. (I need to explain that the lens holder is sustained by four thin wires the diameter is around 100 micrometer.) It has never been acceptable to have tilt of lens or float of lens. Anyhow, you don’t have variety kind of glue for Objective lens. One of them, as known well in this industry, has very soft property its Shore hardness is A50. That is used as good glue for Objective lens widely.

One day, hypothetical accident, you get a complaint from the market and see the OPU gluing has removed and the Objective lens is dropped out from the lens holder.

How to assume the cause? You will watch the point of glued to see it is interfacial peeling or cohesion failure. You will pick the glue by a needle. And if you can, you will collect the piece of the glue on the lens holder and the Objective lens and will measure the weight of the glue. The weight should be only one or two milligrams. And you will search the data of the products in the past. And you will re-test of the drop and impact with normal products in your warehouse. Will you get reappearance or not? If not, you will never see what had been happened.

As you know, it’s difficult to measure the hardness property of one or two milligrams glue. What will you do? I suppose you will increase the frequency of the sampling test of the products. You will destroy the OPU samples day and day for the prevent reoccurrences and waste the products.

Even though, you know it’s very difficult to measure the accurate strength of gluing its Shore hardness is A50. It has resilience and extend before you feel it has been broken.
I suppose the fluorescence sensor is very useful for such a glue test. You can even 100% inspection with it.

The lens holder of OPU is assembled with four thin suspension wires and floating in the air. It should be very accurate. For instance, the tolerance of height should be below 0.1mm and the tolerance of tilt should be below 0.1deg. Then to achieve that, you may need to chuck the holder referring the hole for the Objective lens.

You see, you cannot glue the Objective lens when the lens holder is in stable position. It’s floating when you glue the Objective lens. You cannot measure the strength of gluing without damaging the product even if you push it by weak weight to test the adhesion.

As you know, if you take the sampling inspection, when you notice the problem of the gluing, the factory has made a lot of products already. It could be several thousands or several ten thousands. You have to throw away all of them. But, if you take the way of inspection with the fluorescence sensor, I expect you will get bigger benefit by it. You could inspect 100% or if it’s less than, you can inspect frequency as it meet the takt time as you want.

I suppose the volume of waste of products should be much less than the case of sampling inspection.

Of course, I know that the performance of adhesion doesn’t depend on only how curing it is. Also the condition of the face of components gives influence much. You need to inspect it on the other way.

But you should know the influence of not cured glue is too serious for the performance of the products. It damages other points of glue in OPU. OPU has other optical components else. It has same problem as well.
I would like to mention about the gluing of not optical components as the example of gluing of OPU. The developing of UV glue provide us the possibility to use UV cure for diverse components adhesion where the points they used springs, screws and heat thermal two-pack curing in the past. That brings benefits on reduction of process and makes the product line streamlined. The point indicated in Fig.5-4 should be most rigid for reliability. Required tolerance under determined environment is below 5~10 micrometer.

For your reference, the process of gluing the point of Fig. 5-4 takes biggest man-hour in the OPU production. They are eager to reduce the man-hour even one second or two seconds, if it is allowed for reliability. I suppose it’s also the suitable point to use the fluorescence sensor.

Especially, slim type Optical pickup used in lap-top PC or device in vehicle (refer to Fig.5-5) uses UV adhesion for fix the part of lens actuator and the sledge of OPU. (refer to Fig.5-6). It needs also strictly stability. The tolerance of the tilt of Objective lens regarded to the reference of OPU should be below 0.05deg under the determined environment conditions in determined term.
The amount of the glue for one point of these is around 5mg. It’s bigger compared to other gluing for optical components. And as it is different from Optical components, the components like metals or others cannot transmit lights (in this case UV light). So, sometimes it is a cause of un-cured because of short of exposure of UV light. It needs to be paid attention carefully.

Fig.5-7 indicates an automatic system of inspection for UV cure of Optical pickup. It can inspect point by point the UV cure automatically in the production. The sequence is programmed for each position of X, Y, Z and measure. One of OPU manufactures got a big benefit using this system.

I have a reason for spending long sentences for this explanation of the advantage of using the fluorescence sensor. The threshold of the judgment of that if it has cured or not cured is relied on the measurer or the developer of the system.

The developer of the evaluation system needs to understand how the material changes to a phosphorogen and study and see the relationship of the cure and the fluorescence. Then he or she can take the advantage of using the sensor.

You need to see that the value of fluorescence changes by the amount of the material, by the condition of incorporation and temperature. If there is other phosphorogen near the material, it also annoys you.

So, it’s depending on how you analyze that.
Those complicate conditions might bring confusion to you. If you want to inspect the glue like as viscous mud, it is complicate to see the judgment OK or NG because thickness of the material is not stable. But you will have the solution if you work desperately for it. And you are the only one who can achieve that as a developer of the products.

In the next chapter, I will mention about filmy UV curing that is easier to fix the judge of curing.
5-2. Filmy UV cure resin

The filmy UV cure resin in this chapter means the thickness of resin sheet is several ten micrometers ~ several hundred micrometers. It might be UV cure glue for laminated film with multiple films.

For instance, on Blu-ray disc as optical storage disc, there is a basis disc of 1.1mm thickness that has recording layer on it. The UV cure resin as a protector of 0.1mm thickness is applied with spin coat method or laminated as film of 0.1mm thickness. That needs very severe accurate mechanical dimensions.

Sentech made a measurement of Blu-ray disc of spin coat method with the fluorescence sensor. The sensor part of the equipment has been attached on the X-Y stage like as Fig5.8. And it shows the measurement data like as Fig5.9 as mapping data of fluorescent light.

I'm sorry that the Fig5.9 is the picture of white and black in this book. But actually it is very nice collared data easy to understand with eyes. The value of fluorescent light shows both of the thickness of the resin and how it has been cured. It is difficult to identify the thickness value and curing level from one measured value of data. But if the procedures for measurement and evaluation are optimized, it is good equipment for seeing both of the thickness and level of cured. Filmy types have advantage for judgment of “OK” or “NG” with suitable conditions because the distribution of thickness is smaller. Recently, UV cure resin is very popular for laminated products as film. Fig5.10 shows the example of the fluorescence sensor inspection of UV cure resin in a roll of laminated film in the factory.
And in another case of today, UV cure resin is used for electronic chip parts as an isolating material or packages. I heard one manufacture uses the fluorescence sensor for inspection of the level of curing whether “OK” or “NG” in their factory. Fig5.11 shows an example of the electric chip part using UV cure resin for isolating.

These examples show that the fluorescence sensor is very useful for inspection of how the resin is cured and how much the thickness of the filmy resin is. Especially in this case of films, measurers have to pay attention if other fluorescent materials are included in the laminate as base of the film or cover of the laminate or others. Polyethylene terephthalate (PET) is one of the examples and it used generally. Unfortunately, PET is a strong fluorescent material which of wavelength of exciting light is 365nm. It might be useful in some case, but it mostly disturbs the measurement when we like to see the other resin on the PET so far. But it’s not a problem if the engineer has enthusiasm. For instance, shifting the wavelength of exciting light of the UV cure resin by changing the reacting light wavelength of the material is one of the solutions.
While I have been researching the market of the fluorescence sensor, I was impressed with widespread UV ink. It is amazing that UV cure resin is in heavy usage at anywhere in the market. I have to be shamed that I have never known before. UV ink is used not only for housing of electronic hardware but also for package and printing of anything of products around. I know now that the UV ink also has some problem as peeling on appearance occasionally. The thickness of UV ink is below 10 μm that is thinner than filmy resin as mentioned in chapter 5-2. Sentech has verified that the fluorescence sensor can evaluate UV ink which of thickness is 6 μm had cured enough clearly.

Additionally, Litho Tech Japan Corp. as a specialist in the filed of lithography has announced in a specialty journal “Monthly The TRIBOLOGY 2010.2” that the fluorescence sensor is a useful equipment for evaluation of UV nano imprint.

We expect that the fluorescence sensor will have more opportunities for evaluation of UV ink from now.
6. for chemical researchers

I have mentioned in this book so far how UV cure glue and resin are used in widespread and how the fluorescence sensor is useful for the evaluation. This development of UV curing is based on achievements of many researchers and designers of resin itself. Especially Optical pick up mentioned in chapter 5 is one of the products that have received the biggest benefits on it. I have been feeling it in past. Working on the marketing of this equipment, I had opportunities to talk with developers of UV cure resin and I feel sure that the fluorescence sensor will exercise more in the stage of development and make many benefits soon. I feel it is very interesting.

7. Others

The principle of the fluorescence sensor is just an equipment to measure the amount of fluorescent light as irradiate exciting light on materials. I have mentioned only about UV cure resin in this book though, observation of fluorescent light is not limited on UV cure resin. There are many fluorescent materials around in the world. As mentioned in a technical release book of Sentech, the applications are not only for UV cure resin. For instance, to measure concentration of coumarin in water, to measure a thickness of oil film or to evaluate the effect of filter function as seeing fluorescent material in air are also the cases for the equipment. So, if it has never been known yet, someday some problems will be solved by studying fluorescent light behaviors of the material.

Recently, they found out that the fluorescent light observation is useful for evaluation of plasma treatment for surface modification that improves of wettability. It was not expected before. It was just like serendipity. Measuring the intensity of fluorescent light was not considered as accurate measurement so far, there are many possibilities with that idea from now.
Conclusion
I was impressed when I heard the fluorescence sensor for evaluation of UV cure glue first. I expected it would be change the ideas already known and spread widely soon. But it was not easy to send out equipment nobody knows in the world. The process of measurement is very simple. But it needs to know relationship of the property of material and fluorescent light at first.
It doesn't provide a result as soon as you turn on the equipment on the desk when you brought it from a shop. It needs something of aggressive. Finally, the fluorescence sensor is known in the world and they are trying to use it. I hope it will be widespread sooner.

I want to thank Mr. Hasebe and Mr. Nakamune as the president and the director of Sentech who have developed the fluorescence sensor, for patience to advices and explanations of detail, while I was working on this book.

I thank many people who have given cooperation in the market for my research for this book.

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[2] Documents from Mr. Nakamune of Sentech