Latest Progress and Prospects of UV/EB Curing Technology

By Koji Arimitsu

UV/EB-curing technology has been attracting a lot of attention as a clean form of energy-saving technology. It is used to manufacture ink, adhesives, electronic-related components and automotive components, making it an essential technology for many industries. This article describes the progress made in the key materials used in UV/EB-curing technology, and future noteworthy applications that will help expand its use.

Although some engineers may consider UV/EB curing to be a mature technology, new curing mechanisms can be used through the development of new photoinitiators, making it possible to develop new resins and expand the breadth of objects to be cured.

Photoinitiator Trends

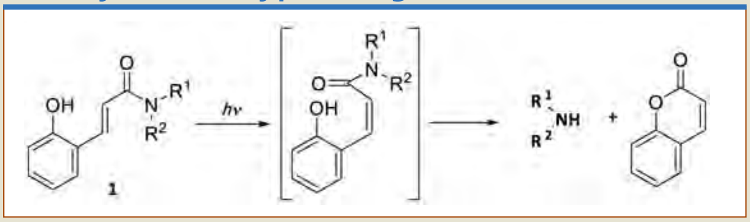
Some engineers who are working with UV/EB-curing technology have asked, "Why do we need to develop a photoinitiator?" After all, one could choose a required photoinitiator from a photoinitiator manufacturer's catalog. But new concepts require new photoinitiators. Although improvements have certainly been made to conventional products—such as better photoinitiator solubility and an expanded photosensitive wavelength band—it is also true that developing a photoinitiator based on a new concept is not easy. However, engineers should realize that sensitivity, curing behavior and the cured matter's physical properties are significantly influenced by photoinitiator performance, so they should recognize the importance of the photoinitiator. Currently, where UV/EB-curing technology has matured (i.e., assumed to have matured), we think it is necessary to develop photoinitiators based on new concepts and expand their application, as well as continue developing resins that are used in combination with newly developed photoinitiators.

Photobase Generator

Due to its mechanism, UV curing can be classified into radical UV curing, cationic UV curing and anionic UV curing. Radical UV curing is a leader in terms of UV curing materials currently put to practical use. However, it can cause problems such as oxygen inhibition, high volumetric shrinkage after curing and low adhesion. In cationic UV curing, these problems occur less frequently, but may contend with other issues such as metal board corrosion due to a superacid or any fluctuation in curing behavior due to moisture in the air. Anionic UV curing has the potential to improve almost all the weak points of radical and cationic UV curing. However, given its very low sensitivity, anionic UV curing has been considered difficult to put to practical use. Therefore, we have developed a new photobase

Figure 1

Photocyclization-type base generator



generator that generates various bases (between weak and strong bases) with high efficiency so as to improve the sensitivity of anionic UV curing.

Nonionic Photobase Generator

Almost all conventional photobase generators that generate aliphatic amine also generate carbon dioxide simultaneously when generating amine by UV-light irradiation. The generation of gas causes few, if any, problems when these photobase generators are used in non-enclosed thin film about 1-µm thick. However, the use of these photobase generators in thick film of a few µm in thickness or an enclosed film such as an adhesive does cause a problem. Therefore, we propose the use of photocyclization-type base generator 1 as a photobase generator that generates no carbon dioxide (Figure 1).[1] In practice, the resin could be cured without generating any bubbles when photobase generator 1 is added to the base-reactive liquid resin. There is one example where compound 1 was reported in the synthetic chemistry field.[2] However, we were the first to propose such application to photoreactive materials[1]—a proposal which was published in the 56th Symposium on Macromolecules in September 2007.

Ionic Photobase Generator

The desired base should ideally be freely and photochemically generated. As described earlier, however, only weak bases such as primary and secondary aliphatic amine were generated until now. To improve the sensitivity of anionic UV-curing materials, it is also important to generate strong bases photochemically and improve the efficiency of base catalytic reaction.

We first found out that carboxylate 2 and 3 generate free bases with high efficiency (quantum efficiency $\Phi = 0.6$ to 0.7) by light irradiation (Figure 2).[3] Weak bases such as aliphatic amine and strong bases such as amidine, guanidine and phosphazene base can be photochemically and freely generated by using these new photobase generators 2 and 3. The use of these photobase generators makes it possible to conduct anionic UV curing at room temperature which was previously difficult to do.[3c] (These photobase generators are partially sold by Wako Pure Chemical Industries, Ltd. and Tokyo Chemical Industry Co. Ltd.) Given this opportunity, the research and development of anionic UV curing will probably be accelerated from both the development of resins and the expansion of applications.

Photo-ring-opening Metathesis Polymerization Initiator

In conventional UV-curing materials, it was difficult to manufacture the cured film of aliphatic hydrocarbon. However, there have been recent reports about a ruthenium complex that produces ring-opening metathesis polymerization (ROMP) by UV light. The UV curing of cycloolefin monomer has made it possible to manufacture the cured film of hydrocarbon.

Currently, it is difficult to prescribe a photoinitiator that is high in heat stability with advanced dark reaction. However, it is an interesting photoinitiator. If the hydrocarbon-cured film manufactured by this photo-ROMP can be hydrogenated, we can expect the formulation of UV-cured film with excellent optical characteristics; that is, low in hygroscopic property, high in heat resistance, transparent and low in refractive index. The polymer synthesized by ROMP is generally low in solubility and difficult to handle; however, a monomer is easy to handle. Therefore, a cycloolefin polymer will be expanded in its application if the

Figure 2

Ionic photobase generator

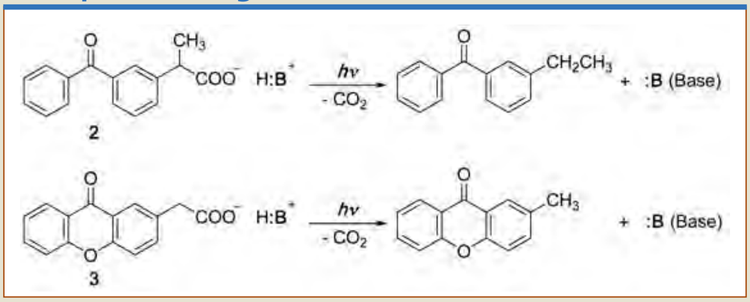
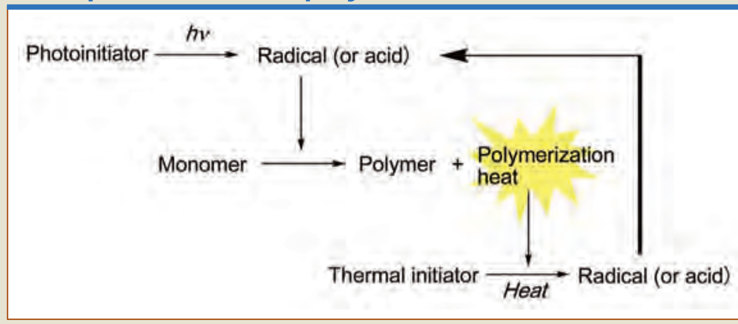


Figure 3

Example of a frontal polymerization



monomer can be polymerized by UV curing. Thus, a fourth UV-curing method following radical UV curing, cationic UV curing and anionic UV curing may become available.

Expectations for Anionic UV Curing

As previously described, UV curing can be classified into radical UV curing, cationic UV curing and anionic UV curing due to its mechanism. Radical UV curing accounts for about 90% of the UV-curing materials currently used in industry, while cationic UV curing accounts for about 10%.

In the present situation, there are only a few practical use examples of anionic UV curing. The main reason for this situation is that a photobase generator is low in base generation efficiency; the generated base is a weak base similar to aliphatic amine; and anionic UV curing is very low in sensitivity (as sensitive materials cannot be easily put to practical use). This proves that high-sensitivity anionic UV-curing materials can be constructed by using our high-efficiency photobase generator described earlier.

New anionic UV-curing materials can be constructed by simply combining our photobase generator with existing resins. For example, UV-curing materials in which metal board corrosion (i.e., a weak point of cationic UV curing) was improved can be constructed by simply combining the epoxy resin currently used for cationic UV curing with our photobase generator. Various organic chemical reactions are catalyzed using strong bases such as amidine, guanidine and phosphazene base.

There is also sufficient room for developing new resins suitable for anionic UV curing. In other words, anionic UV curing has yet to be sufficiently investigated in scientific and practical aspects. The real research and development of anionic UV curing are yet to come. The development of resins used for UV-curing technology has now matured, making it difficult to produce new resins. In almost all cases, resins were purchased from existing products according to the application. In the future, applications can be expanded in line with the development of resins suitable for anionic UV curing and the cured matter's physical properties. In UV-curing technology, more progress can be expected in terms of materials and the expansion of new applications.

UV Curing of Shadow Parts

UV curing for coating and ink applications has increased in importance as a processing technology in recent years, especially in the electronics industry for production of displays and other components for smart phones, tablets and similar devices. A limitation of photoreactive materials and UV-curing processing can be achieving full cure of the resins, particularly in thick coatings, inks or coatings which have high pigment and filler loadings, and also in shadow areas where the coating does not receive direct irradiation from the light source. In some cases, this limitation can be overcome by combining photopolymerization with thermally initiated polymerization to cure optically dense coatings or shadow areas. However, some parts and substrates are temperature-sensitive and cannot be heated sufficiently to complete the thermally initiated reaction, and some manufacturing processes do not allow sufficient time or space for ovens to heat the coated parts. In those situations, frontal polymerization can be considered an option to improve curing.

Many engineers are not familiar with the term "frontal polymerization," even though it has been studied since the 1970s. Figure 3 shows a representative example of frontal polymerization. The basic composition is a photoinitiator, monomer and thermal initiator.

UV-curing reaction is advanced when UV-light irradiation is applied to a coating film consisting of three components. At that time, a thermal initiator is resolved by polymerization heat to generate a new polymerization initiation species (radical or acid). The polymerization of a monomer advances in this case. Polymerization is advanced by the propagation of polymerization heat once polymerization is initiated with light serving as the trigger. Even for a coating film in which rays do not reach the depths of a film, curing reaction thus advances to the depths (i.e., the shadow part). It is desirable to advance frontal polymerization at the lowest possible temperature. Pot life is easy to sacrifice in this case. A UV-curing system that efficiently advances frontal polymerization is not necessarily constructed with ease, but we consider "UV curing of the shadow part" to be important keywords for the progress of UV-curing technology. Moreover, a variety of frontal polymerization systems should also be constructed.

Application to 3-D Printers

The 3-D printer has recently been adopted by each media and is attracting attention. In 2010, President Obama declared, "We will introduce 3-D printers into 1,000 high schools." In 2001, President Clinton worked out a nanotechnology strategy as a national policy. Given this opportunity, nanotechnology research and development accelerated globally at one stretch. Judging from this fact, significant advances in 3-D printer-related technology are also expected on a worldwide scale. The 3-D printer incorporates various systems and UV-curing technology is also used for 3-D printers. The 3-D printer is considered a new technology; however, the basic principle of this technology is the same as that of an older technology known as "laser lithography" (for which UV-cured resin was used).

In laser lithography technology, the three-dimensional model data prepared using CAD is converted into two-dimensional contour slice data on a computer. On the UV-cured resin surface of liquid, this slice cross section is cured and restored one layer at a time by using laser rays. Lastly, a three-dimensional image is prepared by accumulating this cross section. It takes a full day to make a molded object. Moreover, making a molded object is also low in productivity and entails higher costs. Therefore, this technology was used for special applications, such as medical care. It takes the same amount of time to make a three-dimensional image by laser lithography as that for a 3-D printer using UV-cured resin. The quantity productivity of a molded object by using laser lithography is very low. Moreover, it is difficult to make a device using a molded object as a component part because the molded object has low mechanical strength. In many cases, the molded object is currently used as a model.

The future goal for 3-D printers is to shorten the manufacturing time of a molded object (i.e., improvement of photosensitivity of UV-curable resin). As a matter of course, hardware performance must also be improved, such as printer operating speed and intensity of light. Moreover, it is also important to give mechanical strength to the cured object. Another important objective is to use UV to make a cured object with high mechanical strength.

Expanded Use in the Living Environment

Conventional UV/EB-curing technology has largely been used in electronic-related fields. To expand its use in other industries and outside the manufacturing realm, UV-curing must demonstrate higher functionality and higher added value. One of those new functionalities is the use of UV curing for coating furniture and floor materials. UV can also be used in the home repair field to fix peeling paint or cracks in a lavatory or prefabricated bath due to aged deterioration, making them look like new. By using UV-curing technology, homeowners can save both time and money on otherwise costly repairs or replacements.

UV is also garnering attention in the building industry, particularly in cured-in-place pipes. As worn-out sewage ducts begin to exceed the end of their designed lifetime (often defined as about 50 years), repairs and replacement can be costly and time-consuming. It can require large-scale construction that can cause traffic congestion and place a significant burden on drivers and neighborhood residents. For that reason, a seamless system method (photocuring method) has been attracting great interest.

In this method, a main liner (UV-cured resin) is drawn into an existing timeworn drainpipe for insertion, and then swelled by using compressed air. Then, the main liner is UV-cured as is. A special UV light source (called a light train) is inserted into the swelled liner, and the light train travels at a fixed speed to cure the liner while irradiating UV rays. Using this method eliminates the need to uncover timeworn sewage ducts, significantly shortens construction time and represents an epoch-making drainpipe regeneration method.

UV-cured resin plays an important part, even in this method. However, sensitivity and a cured matter's physical properties must also be further improved. The quantity of a UV-cured resin composition used in a seamless system method is very different from the number of electronic materials used. Consequently, we think that producing UV-cured resin that satisfies the performance required by the seamless system method will help to proliferate UV/EB-curing technology.

Conclusion

This paper describes future prospects for UV/EB-curing technology and notes progress made in key materials used in the technology and noteworthy future applications. Although some engineers may consider UV/EB curing to be a mature technology, we believe that new curing mechanisms can be used through the development of new photoinitiators, making it possible to develop new resins and expand the breadth of objects to be cured. Thus, there is still sufficient room for scientific and practical research and development.

UV/EB-curing technology is also expected to significantly contribute to the growth of using 3-D printers worldwide. Until now, UV/EB-curing technology was largely used in electronic-related fields, but research and development is now fueling growth in the home, such as the repair of a house or drainpipe. All of which will help to proliferate UV/EB-curing technology.

References

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