# Highly efficient UVLED curing process with IR irradiation

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## Abstract

Novel UV curing process by LED irradiation has been developed to enhance capability of UV curable materials. The process is featured by IR irradiation prior UV irradiation. UV curable materials are activated by IR irradiation just before UV irradiation (hereafter, pre-IR irradiation) and higher double bond conversions are observed for cured materials, compared to those obtained by merely UVLED irradiation. In this paper, two initiation systems were examined; one is Tri-phenyl phosphineoxide (TPO) initiation system and the other is hydroxyl cyclohexyl phenyl ketone (HCPK) initiation system sensitized by an anthracene derivative. Pre-IR irradiation provides much faster curing speed for both initiation systems.

## Introduction

It is well-known that diphenylphosphonoyl radical generated by photo-cleavage reaction from TPO is more sensitive to oxygen inhibition and sometimes it is difficult to obtain tack free surface after UV irradiation by LED, due to lack of shorter wavelength emission from LED. A lot of marvelous research works have been reported to overcome oxygen inhibition[1-3]. The chemical approaches proposed are to utilize an oxygen scavenger like triphenyl phosphine[4] or chain transfer compounds like thiol[5, 6] derivatives in formulations. It is clearly demonstrated that those chemical approaches are successfully and efficiently used in TPO initiated formulations to overcome oxygen inhibition.

However, those additives cannot be always used in formulations, because they may cause unknown effects to the final performance of cured materials for some applications. UV irradiation process by using LED is examined from process technology point of view, in order to obtain tack free surface without using additives. Photo-initiated polymerization behavior observed in TPO initiation system is demonstrated with the data obtained by several analytical approaches.

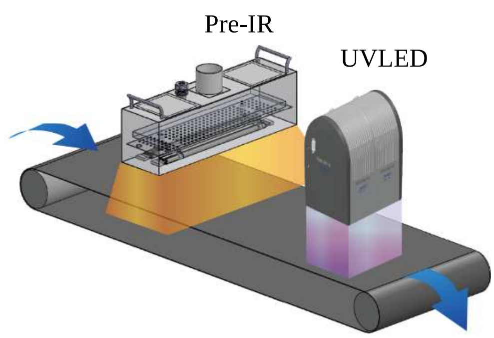


Fig.1 The schematic lamp layout for Pre-IR plus UVLED used for experiment.

In this paper, intermittent and/or continuous UV irradiation processes by LED with and without IR irradiation were examined by using the irradiation system designed as shown in Fig. 1, that is, pre-IR irradiation was carried out just before UV irradiation by LED.

Furthermore, the effect of new irradiation process was also examined for the sensitized initiation system. Generally phenyl ketone type photo-initiators do not show good absorption spectrum matching against UVLED emission and it is difficult to use them in formulations targeted to the monochromatic emission from UVLED. 9,10-Dioctanoyloxyanthracene is used as a sensitizer for phenyl ketone type photo-initiators and the effect of pre-IR irradiation was examined for curing speed.

## Experimental

### *Material*

Polyester acrylate oligomer, Aronix M-8100 was obtained from Toagosei and methoxy polyoxyethlene acrylate (NK Ester AM-90G) were obtained from Shin-nakamura Chemical. Irgacure TPO and 184 (HCPK) were obtained from BASF. 9,10-Dioctanoyloxyanthracene (Anthracure UVS-581) used as a sensitizer was obtained from Kawasaki Kasei Chemical.

### *Sample preparation*

10μm thickness films were prepared to measure tack free point. AM-90G containing 4% TPO and containing 8% HCPK with 1% UVS-581 were prepared to measure rheology change by LED irradiation.

### *Equipment*

A Semray 4003 395nm (Power output: 14W/cm2) from Heraeus was used as a light source to measure absorption spectra changes of TPO. An Altair75 395nm (Power output: 3.7W/cm2) from Heraeus was used as a light source to measure rheology change by irradiation. 4 rows of carbon emitters, CRS1000/300G (Power output: 3.2kW), from Heraeus were used for pre-IR irradiation. A Hitachi U-3010 was used to measure absorption spectra change. A HAAKE MARS III with a Nicolet iS10 was used to measure rheology change and double bond conversion change at the same time by LED irradiation. An EIT Power PuckII with UVA2 range was used to measure irradiation UV energy.

## Results and Discussion

### Curing process in TPO initiation system

#### *Curing behavior observation*

As reported previously[7)], diphenylphosphonoyl radical generated by photo-cleavage reaction from TPO is highly reactive and presumably terminates polymer propagation radical easily, via radical recombination. In order to prevent the termination reaction of propagation radicals by highly reactive radicals, it was shown that the intermittent LED irradiation was efficient to restrain radical recombination, because propagation radicals can be survived for longer time during dark time, and because the diffusion rate of highly reactive radicals for termination was reduced, due to increase of micro-viscosity in reaction media by step-wise polymerization.

Figure 2a and 2b show curing test results with continuous and intermittent irradiations in the M-8100/AM90G/TPO (60/40/6: high viscosity) and (20/80/6: low viscosity) systems. As can be seen in these figures, continuous irradiation requires more energy to obtain cured material, compared to intermittent irradiation. It is found from Fig.2 that this phenomenon is amplified in low viscosity system and that the intermittent irradiation process with shorter emission time is more efficient to get cured material.

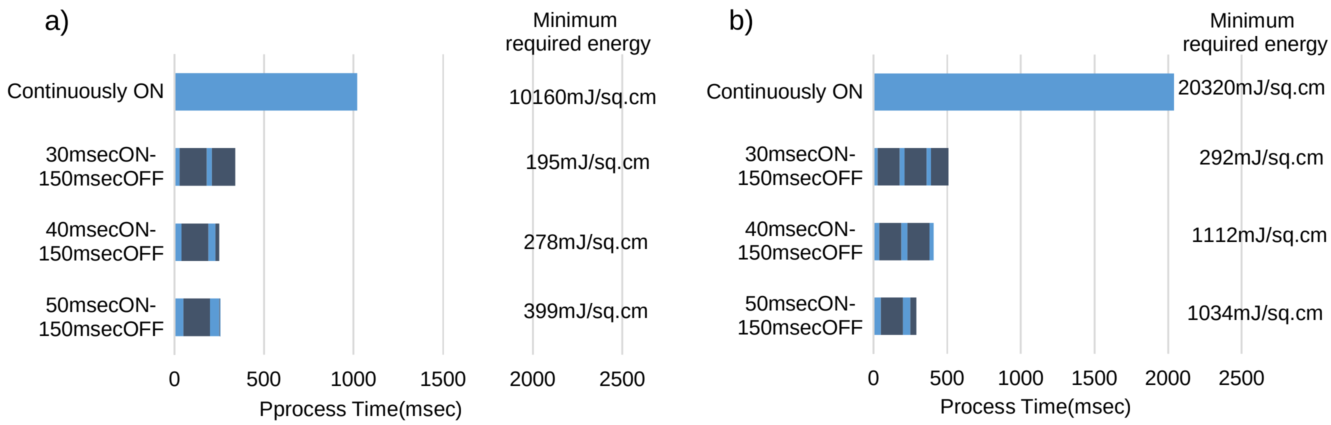


Fig. 2 The curing test results for continuous and intermittent irradiations. a) M-8100/AM90G/TPO =60/40/6: high viscosity system, b) M-8100/AM90G/TPO =20/80/6: low viscosity system, ■ Irradiation period, ■ Dark period

***Polymer analysis***

Simplified photo-initiated polymerization was conducted to clarify the phenomenon observed in intermittent irradiation process. AM-90G, mono-functional monomer, containing 6% TPO was used to obtain a linear polymer. AM-90G was irradiated under continuous and intermittent irradiations (20msec irradiation and 150msec dark time interval) and the obtained polymers were analyzed by GPC. The analytical results for the obtained polymers were summarized in Fig. 3a and 3b. The polymer conversion is essentially same against irradiation energy as shown in Fig 3a, however, the number average molecular weight for the obtained polymers showed very different behavior between two irradiation systems. That is, the number average molecular weight for the polymers obtained by continuous irradiation system shows almost constant against irradiation energy. On the other hand, those for the polymers obtained by intermittent irradiation are increased with increasing total irradiation. These results support the advantage of intermittent irradiation process for curing in TPO initiation system. More propagation reaction can be proceeded during dark time in intermittent irradiation process.

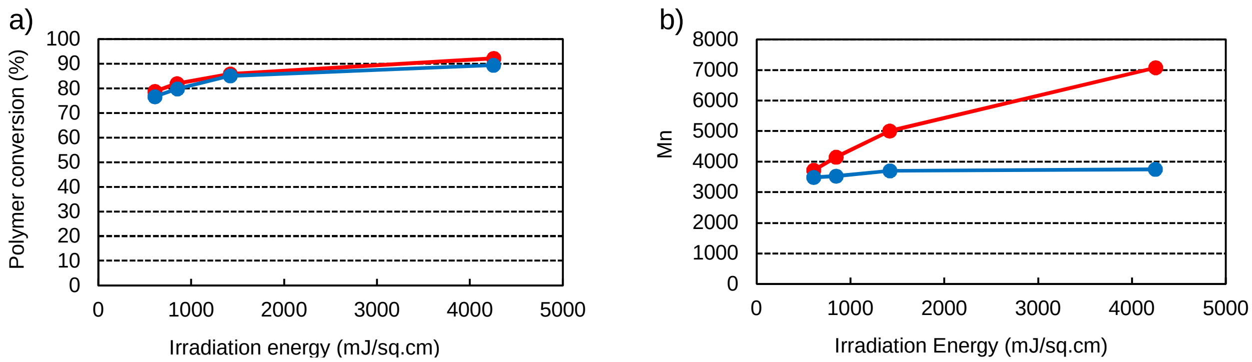


Fig.3Analytical results for the obtained polymers. a)Polymer conversion against irradiation energy. Polymer conversion is almost same in both irradiation processes, b) Number average molecular weight for the polymers obtained by Intermittent irradiation (20msecON-150msecOFF) and by Continuous irradiation.

***Rheology analysis***

In order to clarify curing behavior precisely, rheology measurement was conducted in continuous and intermittent irradiation processes by using the equipment shown in Fig.4. The rheometer is connected to LED lamp and rheology change can be measured by irradiation. At the same time, double bond conversion of acrylic group can be also measured by RTFTIR. Rheology change was measured for AM-90G with 4% TPO system. The obtained results were shown in Fig.5. As can be seen in Fig.5a, it is observed that the double bond conversion is increased with increasing irradiation energy by intermittent irradiation and that the storage modulus is also increased with increasing double bond conversion at the same time. On the other hand, much higher double bond conversion is observed in continuous irradiation, compared to intermittent irradiation, whereas storage modulus is not increased even in high conversion area and does not overcome loss modulus. This is one of the direct observations for contribution of intermittent LED irradiation in TPO initiation system.

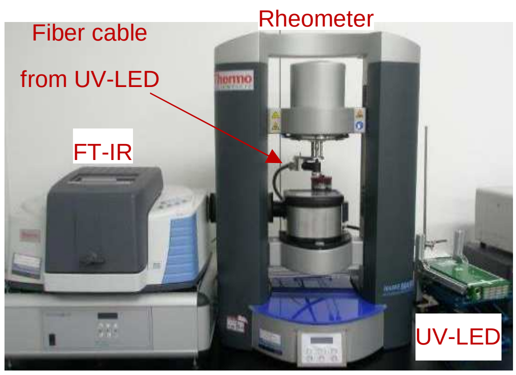


Fig4. The equipment for rheology and conversion measurements. The rheometer is connected to UVLED lamp. RTFTIR is connected to rheometer. Rheology change and conversion change can be measured at the same time.

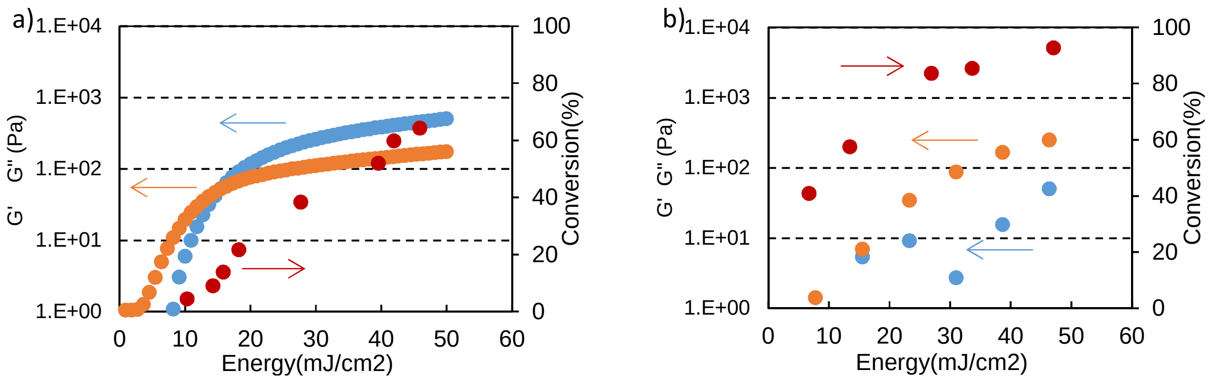


Fig.5 Double bond conversion and rheology changes. a) Intermittent irradiation (20msecON-150msecOFF), b) Continuous irradiation, ● G', ● G'', ● Conversion

***Pre-IR plus LED irradiation process in TPO initiation system***

It was demonstrated in the previous sessions that intermittent LED irradiation is efficient process to get cured materials in TPO initiation system. New irradiation process was examined to accelerate curing speed by using carbon IR emission with UV irradiation. Figure 6 shows emission spectrum of carbon IR emitter used and all organic compound can absorb IR energy directly before UV irradiation. Molecular motion, especially photo-initiators, is activated by IR irradiation and UV absorption efficiency would be increased, due to increase of transition moment. The curing behavior of M-8100/AM-90G with 6% TPO system was summarized in Fig.7. It is obviously shown that pre-IR irradiation can accelerate curing rate for all conditions. Especially, the curing speed was remarkably increased by pre-IR irradiation in continuous LED irradiation process. Total required energy for cuing is also reduced in all intermittent irradiation process.

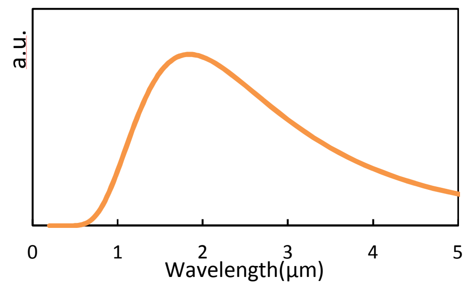


Fig.6 Emission spectrum of carbon IR emitter

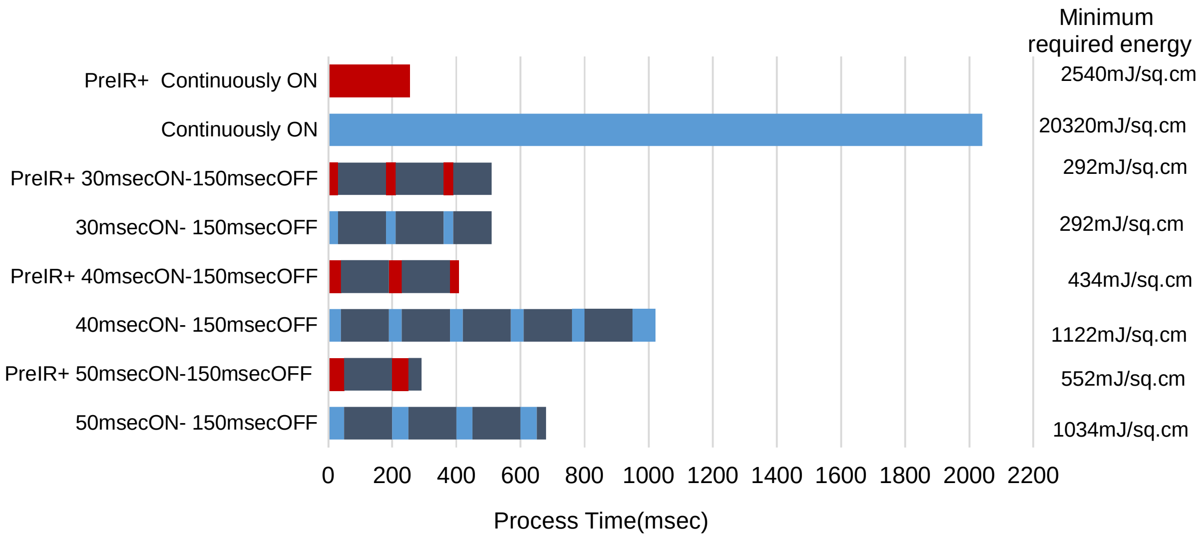


Fig.7 The curing behavior of TPO initiation system with Pre-IR irradiation. Pre-IR irradiation can accelerate curing speed, UVLED Irradiation period, Dark period, Pre-IR + UVLED Irradiation period

***Double bond conversion under continuous irradiation in TPO initiation system***

Double bond conversion was measured in M-8100 with 6% TPO system under the continuous LED irradiation with and without pre-IR irradiation. The obtained results were shown in Fig.8. As can be seen in Fig.8, higher double bond conversion is always provided by pre-IR irradiation under the continuous irradiation process.

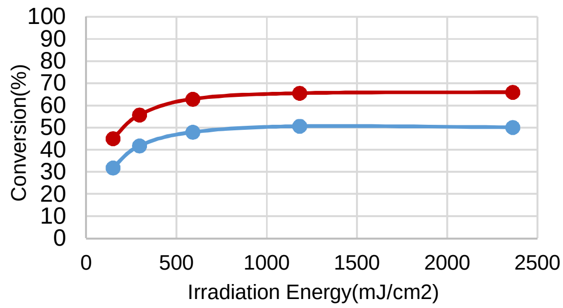


Fig.8 Double bond conversion against continuous LED irradiation energy.

PreIR+UVLED, UVLED

## Curing process in sensitized system

***Curing behavior observation***

Sensitized curing behavior containing 8% HCPK with 1% UVS-581 was examined in M-8100/AM-90G system, in the same as TPO initiation system. The obtained results were summarized in Fig.9. As indicated in these figures, the curing behavior of the sensitized system is quite different from that observed in TPO initiation system. The total amount of required energy for curing can be reduced by intermittent irradiation, however, more LED irradiation process time is required, compared to continuous irradiation process. No process advantage can be found in intermittent irradiation process for the sensitized system. The differences of curing behavior was presumably caused by the difference of radical generation mechanism between two initiation processes.

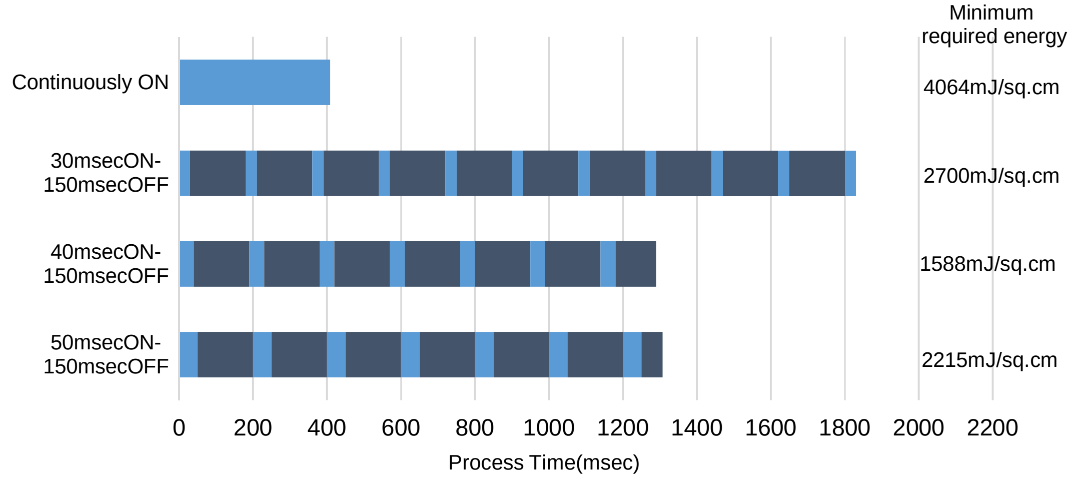


Fig.9. Curing behavior of sensitized system. No advantage for process time was observed with intermittent irradiation in the sensitized system. ■ UVLED Irradiation period, ■ Dark period

### *Rheology analysis*

Rheology change was also measured for the sensitized system in continuous and intermittent irradiation systems, although no significant advantage was observed for process speed point of view. The measured rheology behavior obtained by two irradiation processes was summarized Fig.10a and b. It is found in Fig.10a that faster storage modulus is observed by intermittent irradiation, compared to continuous irradiation, although process speed of intermittent irradiation is much slower than that of continuous irradiation.

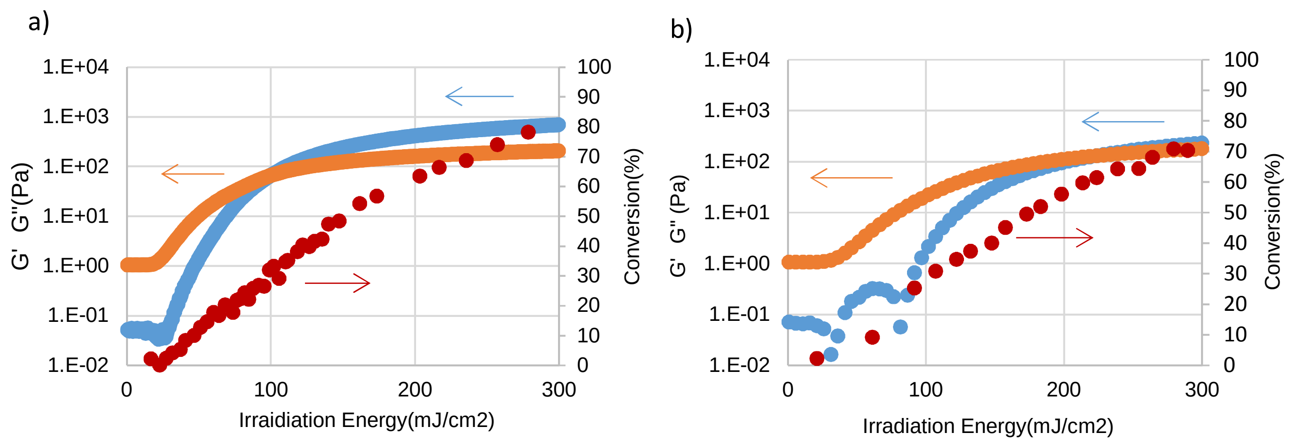


Fig.10 Rheology and conversion changes. a) Intermittent irradiation, b) Continuous irradiation, ● G', ● G'', ● Conversion

### *Pre-IR plus LED irradiation process in TPO initiation system*

As described previously, no process advantage was observed in intermittent irradiation process in the sensitized system, that is, the continuous irradiation process showed the fastest total irradiation time. Pre-IR plus LED irradiation was conducted, in order to accelerate irradiation process rate. The result was shown in Fig.11. As can be seen in Fig.11, total irradiation process time was remarkably shortened and the minimum required energy to get cured material was also reduced by pre-IR irradiation in the sensitized system.

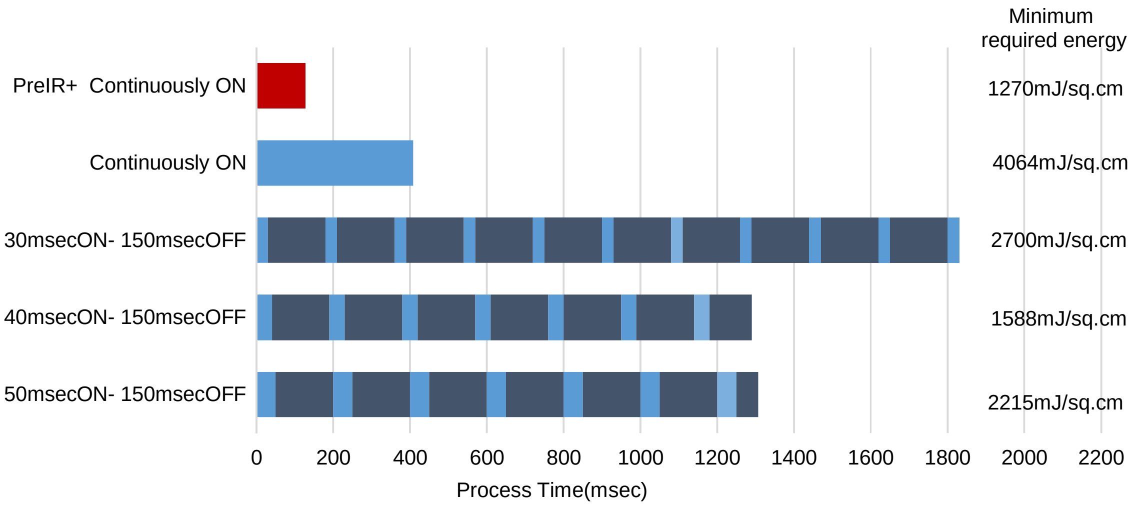


Fig.11 Curing process time for the sensitized system. Pre-IR irradiation accelerates remarkably irradiation initiation process time. UVLED Irradiation period, Dark period, Pre-IR + UVLED Irradiation period

### *Double bond conversion under continuous irradiation in sensitized system*

Double bond conversion was measured in M-8100 with 8% HCPK/1% UVS-581 system under the continuous LED irradiation with and without pre-IR irradiation, in the same way as TPO system. The obtained results were shown in Fig.12. As can be seen in Fig.12, higher double bond conversion is always provided by pre-IR irradiation under the continuous irradiation process, which is the same effect as observed in TPO initiation system.

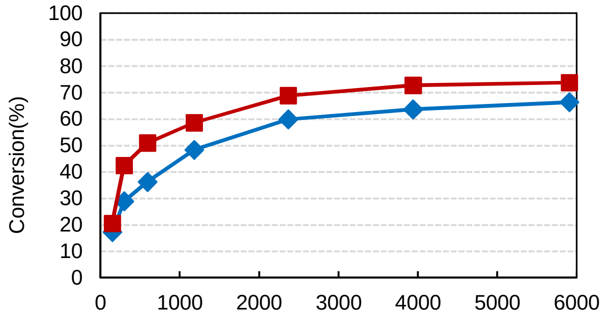


Fig.12. Pre-IR irradiation provides higher double bond conversion. UVLED irradiation, Pre-IR+UVLED irradiation

## Conclusion

It is indicated in this paper that the intermitted irradiation is very efficient to get cured material in case initiation radical is highly reactive like diphenylphosphonoyl radical generated by TPO. Termination reaction of propagation radicals by radical coupling can be reduced by intermittent irradiation, compared to continuous irradiation process. Furthermore, much faster and efficient curing reaction can be provided by pre-IR plus LED irradiation, since initiators are activated by pre-IR irradiation and since more radicals are efficiently generated by LED irradiation. These process technologies can contribute to developing new UV curing world provided by UVLED.

References

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