

CATIONIC CURE UV ACRYLIC HMPSA

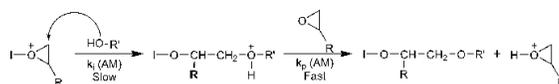
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Introduction

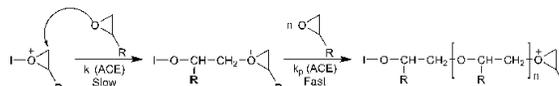
Traditionally, UV cured pressure sensitive adhesives are strongly dependent on intense UV emission in the UV-C range. However, some cationic photoinitiators show potentially useful absorptions well up into the UV-A range. With recent developments in LED technology, UV LED has become more powerful and more economic every year. Purely from a chemistry and formulation design point of view, the major difference of mercury vs LED is that mercury is broad spectrum light with UVA, B, C coverage, while UV LED has a narrow spectrum but with much higher peak intensity. Therefore, the match of the photoinitiator UV absorption with the lamp emission is very important for UV LED cure. Currently, high intensity UV LED Lamps only cover UVA region, namely $> 365\text{nm}$.

Usually, cationic cure UV acrylic HMPSA (hotmelt pressure sensitive adhesive) contains pendant oxirane, oxetane, oxazoline and/or vinyl ether functional groups in an acrylic polymer. In the presence of a cationic photoinitiator, it undergoes crosslinking by UV light. The cationic curing mechanism is generally believed to be as follows:

Activated monomer mechanism (AM)



Activated chain end mechanism (ACE)



In this paper we report the study of cationic cure UV acrylic HMPSA with UV LED. With 365nm UV LED lamp, a similar curing level can be achieved by using 365nm LED lamp as with using a mercury H bulb.

Experimental

Henkel UV Adh A is a cationic cure UV acrylic HMPSA, containing pendant cycloaliphatic epoxy groups and a commercial sulfonium salt photoinitiator. The product can be effectively cured by mercury H bulb. The cure efficiency and properties have not been previously studied by using UV LED lamp.

The photo-rheometer used in this study has a quartz window bottom plate, through which a UV light source can be introduced to initiate UV cure reaction while the rheometer monitors the physical changes of the curing material. The UV light sources include a medium pressure mercury arc light source, and UV LED lamps with 365nm, 375nm and 405nm independently. Each LED lamp has a power of $2\text{W}/\text{cm}^2$ at its specific wavelength.

Rheology samples of UV Adh A were made by dissolving the hotmelt material in ethyl acetate solution. The solutions were cast into film and were fully dried. A dried and bubble-free film was placed on the rheometer and then heated to 80°C to mimic a curing temperature of typical hotmelt coating process. After a few minutes equilibrium at 80°C , UV light from either mercury UV light or a UV LED light was turned on for a specific time, while the modulus change was monitored throughout the experiment.

Results and Discussions

As shown in the Figure 1 below, the modulus of UV Adh A increased significantly at the time when the mercury UV light was on, and continued to increase up to $\sim 10,000$ Pa, indicating an effective and complete UV cure reaction. Under 365nm LED light, the modulus increased similarly but not as fast as in the case of mercury light, suggesting slower curing reaction at $200\text{mW}/\text{cm}^2$ power. LED light with 375nm, however, triggered almost no cure reaction at the first 5min, and the modulus only slightly increased over 20 min of continuous exposure to the light. Apparently, UV Adh A is not reactive under 375nm light. As the UV spectrum shows (Figure 2), UV Adh A appears to be most reactive in UVC and UVB, with its absorbance tail extending into UVA range, and thus can still be cured by 365nm LED light, given its high irradiance and dosage.

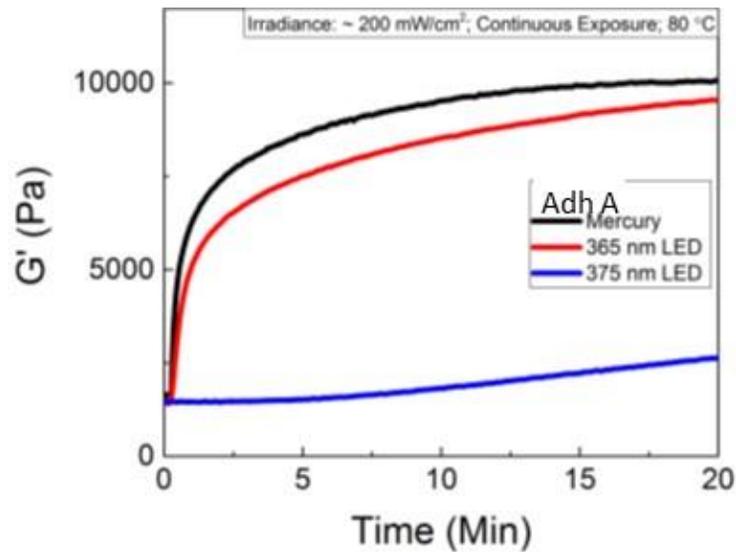


Figure 1. Modulus versus time

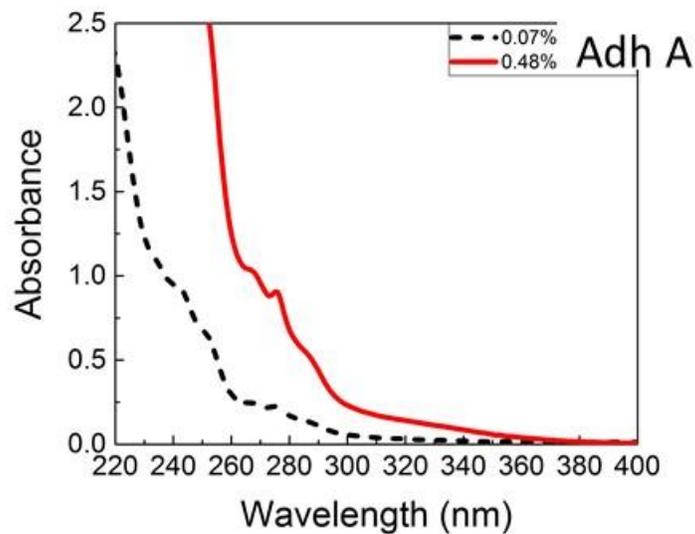


Figure 2. UV spectrum of Adhesive A

UV Adhesive A exhibited similar and significant dark curing behavior under both mercury and 365nm light sources, as shown in Figures 3 and 4. It took more than 20sec to reach full modulus after lights were turned off. For LED light, it can be translated to about 4000mJ energy for curing of 200 μ m thick film. For a typical 50 μ m film the dosage will be about 1000mJ/cm².

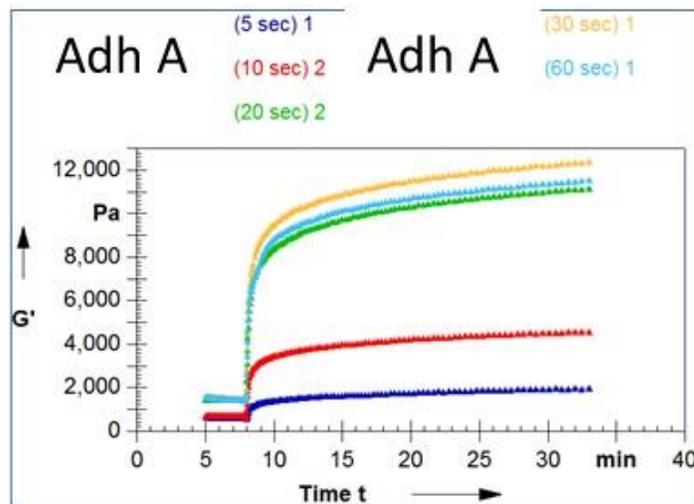


Figure 3. Modulus versus time (Hg bulb)

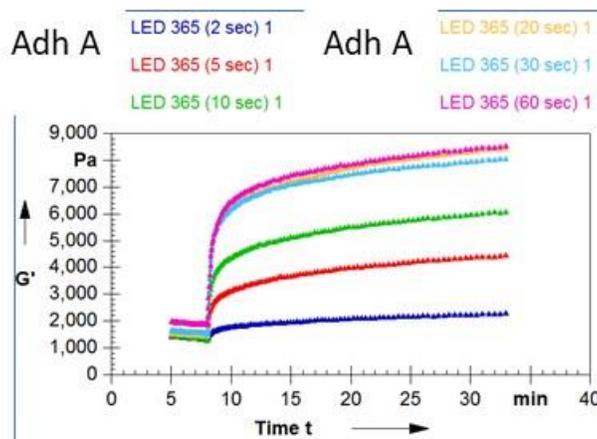


Figure 4. Modulus versus time (LED 365nm)

Photosensitization was investigated to improve UV Adh A cure efficiency under 365nm LED. Figure 5 below shows the results of different combination of photoinitiators and photosensitizers. The photoinitiator was used at 0.2% and photosensitizer at 0.1% in UV Adh A. The 365 nm LED light with 150 mW/cm² was turned on after 3 min equilibrium at 80°C and stayed on throughout the experimental runs.

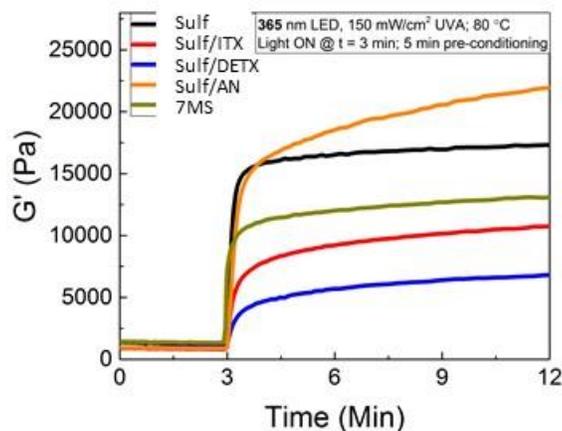


Figure 5. Modulus versus time (photosensitizers)

The black curve labeled sulf (sulfonium) was a control sample. Replacing sulf with a redshifted iodonium photoinitiator Sylanto* 7MS, with UV absorption peak at ~350nm, provided little improvement. The resulting modulus was lower than the control sample. Addition of thioxanthone sensitizers ITX or DETX caused reduction in modulus. The extent of modulus reduction was smaller for ITX than DETX. In contrast, the addition of anthracene sensitizer (AN) increased the final modulus significantly, by almost 30%.

An Iodonium salt Oppi demonstrated very high reactivity under 365nm, both with or without ITX as a photosensitizer, as shown below (Figure 6). The 365 nm LED light with an irradiance of 300 mW/cm² was turned on for 5 sec after 3 min equilibrium at 80°C. The experiment was conducted at 0.1% strain, 200-um gap, 10 rad/s. In addition to trimming sample edges at the elevated temperature, the same set of 8-mm stainless steel upper plate and quartz bottom plate were used to minimize data scatter.

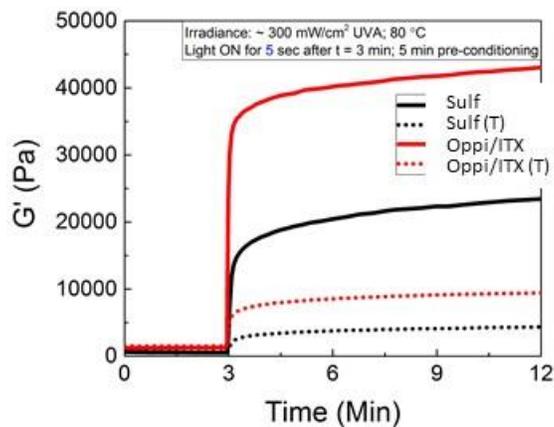


Figure 6. Modulus versus time (sulfonium vs iodonium salt)

The black solid curve labeled sulf is again the control sample. When the iodonium salt Oppi and ITX were used together, the resulting sample (red solid curve) shows a modulus nearly double that of sulfonium control. The cure kinetics was also faster, as suggested by the steep upturn in modulus upon UV LED exposure. However, if a tackifier was added to the control, a diminished cure speed and significant reduction in modulus of about 80% were observed, as shown by the black dotted curve sulf

(T). Oppi/ITX (T) (red dotted curve) still maintains faster cure and is higher modulus than sulf (T). Dark cure was seen in all these cases. Once initiated, the cure continued for the rest of the test runs. This is due to living nature of the UV cationic polymerization process. This feature is beneficial for achieving large cure depth, thick coatings, and shadow cure.

The concentration and ratio of the photoinitiator and photosensitizer exhibited significant impact on the cure profile of UV Adh A. The numbers in the legend indicate the relative weight percent of Oppi (p-octyloxyphenyliodonium hexafluoroantimonate) and ITX, where 10 and 5 represent 0.2 and 0.1 phr, respectively. A 365 nm LED light with an irradiance of 300 mW/cm² was turned on for 5 sec. The experiment was conducted at 0.1% strain, 200-um gap, 10 rad/s, and 80°C. As seen in Figure 7 below, the dark blue curve labeled 5-2* was a sample with equivalent moles of Oppi and ITX.

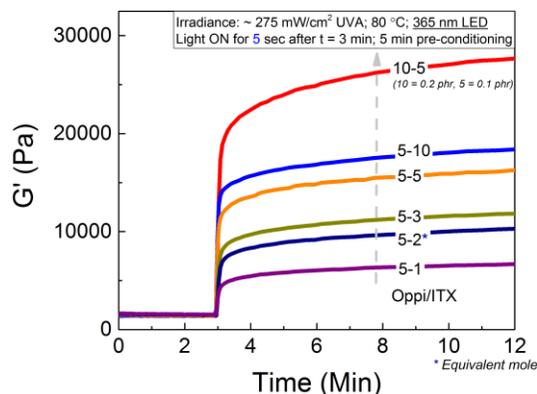


Figure 7. Modulus versus time ()

Interestingly, the final modulus continued to increase with increasing ITX amount (vertical arrow added for aiding visual comparison). However, when comparing Oppi/ITX 10-5, 5-5, and 5-10, increasing the photoinitiator amount was shown to be much more effective in enhancing the cure or final modulus. Finally, the addition of UVA radical photoinitiator to UV Adh A proved detrimental to the cationic cure process (figure 8 below)

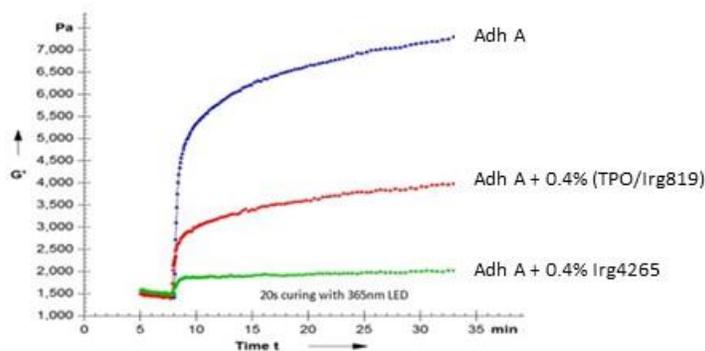


Figure 8. Modulus versus time (combination with UVA photoinitiator)

Multifunctional epoxy monomers and oligomers can affect the cure profile and final modulus, as one would expect (Figures 9 and 10). Addition of small amounts of an epoxy monomer like Syna*

Epoxy 28 in UV Adh A increased dramatically the final modulus but exhibited a long and slow dark cure process. The curing reaction might well not have been completed over 35min of the experimental duration. Addition of aliphatic epoxy monomer like Vikoflex* in UV Adh A showed similar effects on modulus and dark cure.

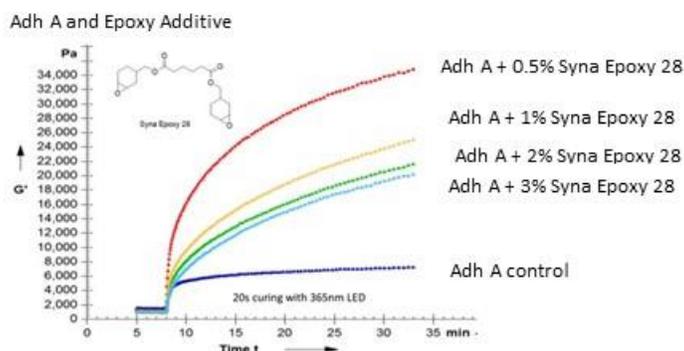


Figure 9. Modulus versus time (multifunctional epoxy)

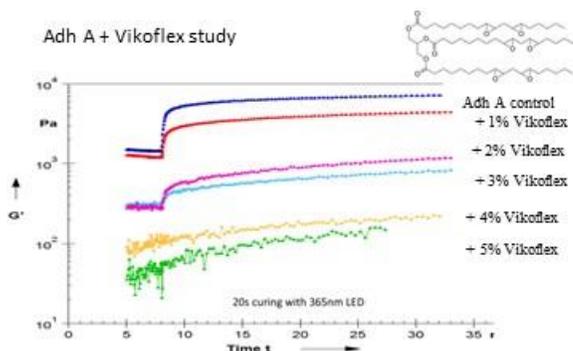


Figure 10. Modulus versus time (multifunctional epoxy#2)

Conclusions

UV LED 365nm light was proved to deliver similar cure effectiveness as mercury UV light for Henkel UV Adh A acrylic HMPA, with high irradiance and dosage, or in a slower line speed. UV LED cure efficiency was further improved by using more reactive iodonium salts and ITX as a photosensitizer.

Acknowledgements

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