

UV Cationic Acrylic PSAs

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Introduction

Solvent based acrylic PSA are well known as the premium system in the market place due to their durability and high performance either as one or two pack formulations. Acrylic polymers also offer great synthetic versatility in that a wide range of monomers are commercially available and the polymer formulator can readily control the resulting polymer architecture during polymerisation. This briefly explains the unique position the solvent borne PSA have in the market place. However, this technology has major limitations of processing thick coatings (100+gsm) at high coating speeds. Existing UV acrylic hotmelts overcome the processing problem but introduce a depth of cure issue with coatings at 80+ gsm. This paper will provide details of our approach to designing a UV cationic acrylic hot melt curing adhesive that aims to overcome both the thick film and depth of cure challenges with existing acrylic technologies.

1 Background

With increasing pressures on reducing environmental emissions from factories and energy costs the industry is seeking alternative approaches to solvent based adhesives. Hotmelts are an obvious choice, but in order to apply such adhesives a number of compromises must be made with molecular weight for application and with the use of different crosslinking chemistries which are stable at elevated temperatures. The use of UV radiation is believed to be a viable solution to this technical challenge.

Over the past several years the UV PSA hotmelt development for the merchant markets has consisted of the following reported approaches.

- * Acrylic polymers with bound PI ¹
- * Acrylic Hybrid polymers containing (meth)acrylate groups ²
- * Styrenic block copolymers with either bound or added PI ³
- * Epoxidise isoprene with added PI ⁴

Each of these systems has a different set of application and adhesive properties, but the most successful to date has been the acrylic polymer with bound photoinitiator (PI) as it affords the adhesive and durability properties more closely related to solventborne acrylic adhesives.

Table 1
Properties of different UV hot melts

Property/system	Acrylic	Hybrid	Styrene Block	Isoprene
Crosslinking	Graft	Radical	Graft	Cationic
Base polymer	Acrylic	Polyurethane	Styrene/Butadiene	Isoprene
Max coat Wt	@ 80 gsm	@ 100 gsm	@ 80gsm	@ 100 gsm
Application temperature	130C	90C	180C	90C
Durability	Good	Moderate	Poor	Poor

2 Discussion

The utilisation of UV curing technology for the PSA Tapes and labels business sector appears to be the future technology platform. The key challenge is in identifying the optimum technology; as customers have an extensive range of demands, some of which are mutually exclusive. However it is apparent that different technologies offer different opportunities to our customers. One key weakness of existing offerings is that of obtaining high coat weights of >100 gsm with acceptable coating speed, quality and depth of cure. Secondly, with the higher costs for energy any new system should have an enhanced UV curing efficiency. This paper will report on the latest developments on Cationic cured acrylic polymers to meet these needs.

One key advantage of Cationic cure is that it offers the opportunity to make thick coatings. This is achieved because of the curing mechanism. With free radical chemistry the photoinitiator must receive a photon of UV energy to form an active species. This then initiates cross linking, but the lifetime is very short and the reaction is completed in under a second. So if the film is thick the UV photons may not penetrate deep enough in sufficient amounts to achieve full cure. The Beer Lambert law allows for a detailed description of the relationship between absorption and intensity of the radiation at different levels. The equation for absorption is given as

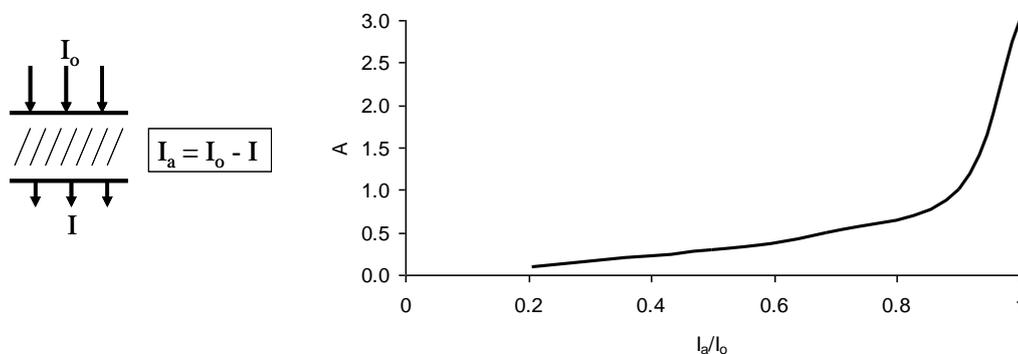
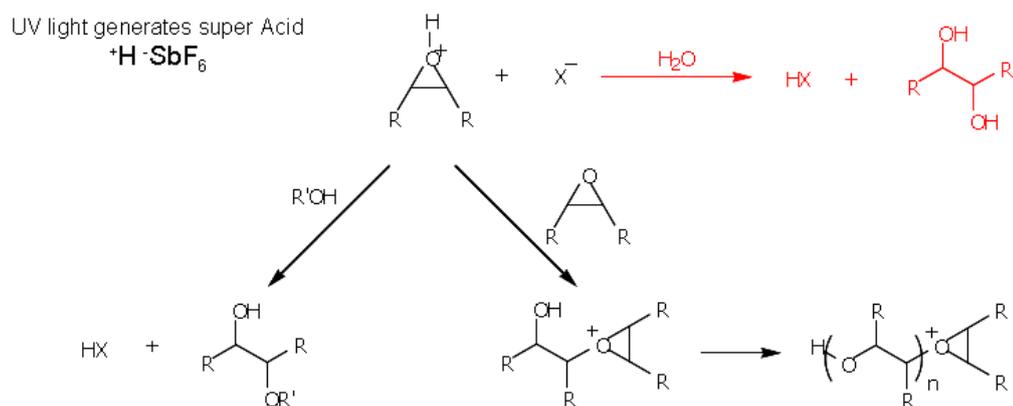


Figure 1

$A = \epsilon c l$, in which ϵ is the extinction coefficient, c is the PI concentration and l is the thickness of the film. The overall absorbance of the film, A , will govern the rate at

which the incident light is absorbed. As can be seen in Figure 1, this is an exponential relationship. The effect that the absorbance, A , has on the amount of light that is absorbed can be calculated⁵. Essentially, at a fixed UV dose, the underside of a thicker film will not get exposed to sufficient UV dose due to the absorbance of the photo initiator, and under cure will occur.

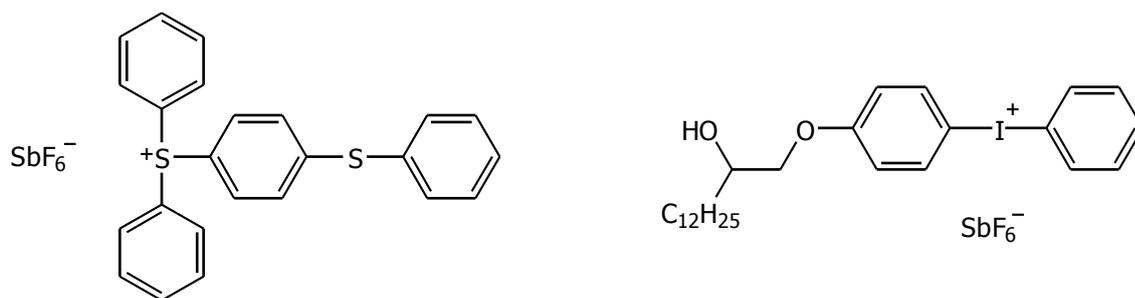
In a cationic system the crosslinking chemistry is via the ring opening of epoxy functional groups using an acid catalyst. On exposure to UV radiation the cationic photoinitiator undergoes photolysis resulting in a Bronsted acid. This then forms an oxonium ion with epoxy functionality, initiating a “living polymerisation” with other epoxy groups until they are all consumed. This acid remains in the film and will migrate throughout the whole film ensuring complete cure. This process is often referred to as “Dark Cure” in cationic systems and is generally complete within 1 to 24 hours. This migration has the benefit of giving good though cure in the system. It also allows for lower radiation doses to be used as the photoinitiator is being used as a catalyst in the curing system.



Overall mechanism for cationic cure
Figure 2

2.1 Photoinitiators

Fortunately, in the wider field of UV curing chemistry cationic cure is well established, and a number of commercial photoinitiators are available, which are used in the inks and electronic industries⁶. Many suppliers are in the process of developing new catalysts. When these PI's are exposed to UV light @ 350 nm, they decompose to form a strong acid. The cationic curing mechanism requires this acid to initiate ring opening polymerisations as shown in Figure 2 above. As only catalytic levels are required UV absorbance is not a major issue as it is with free radical curing systems.



Typical Cationic Initiators

Figure 3

2.2 Epoxy Functionality

Typically, cationic formulations are blends of epoxy, vinyl ether, and oxetane monomers to give a low viscosity fluid at room temperature. On curing, these syrups give highly crosslinked polymer networks. For a PSA tape the crosslink density must be controlled so that only a low crosslinked network is formed. The choice of epoxy functionality was proven to be extremely important. Our approach was to have the reactive functional groups polymerised into the acrylic polymer to control the cured network density. The most common epoxy monomer is glycidyl methacrylate. Prototypes using this monomer gave encouraging adhesive results, but the thermal stability at 130°C was extremely poor with gellation occurring rapidly within an hour or so Figure 4. Alternatively, epoxy/functional monomers were sought, shown in Figure 5. It was discovered that other cycloaliphatic or aliphatic epoxy monomers gave better thermal stability at elevated temperatures depending upon their structure. In addition to epoxy functionality, vinyl ether groups are also useful in this curing technology.

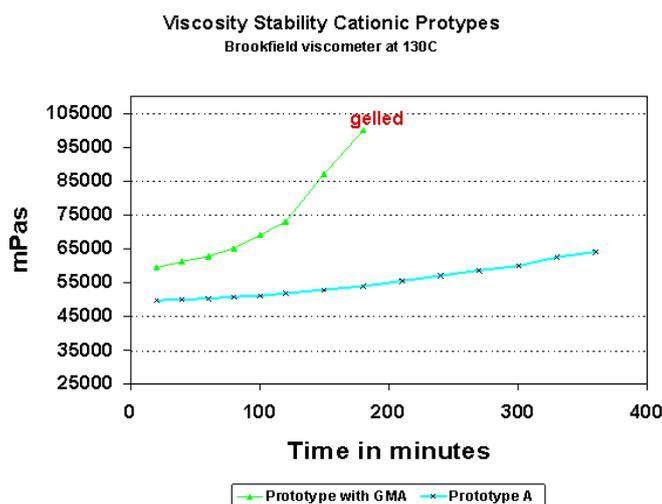
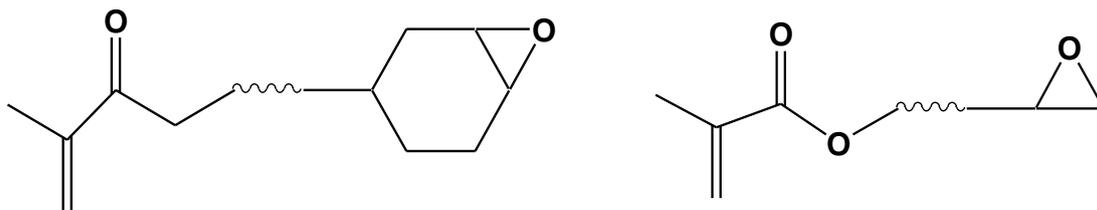


Figure 4

Using the appropriate epoxy functional monomer a prototype has been synthesized to give a hot melt polymer. The viscosity stability was measured to ensure the epoxy functional resin gave stability at the highest end of application temperature at 130°C.

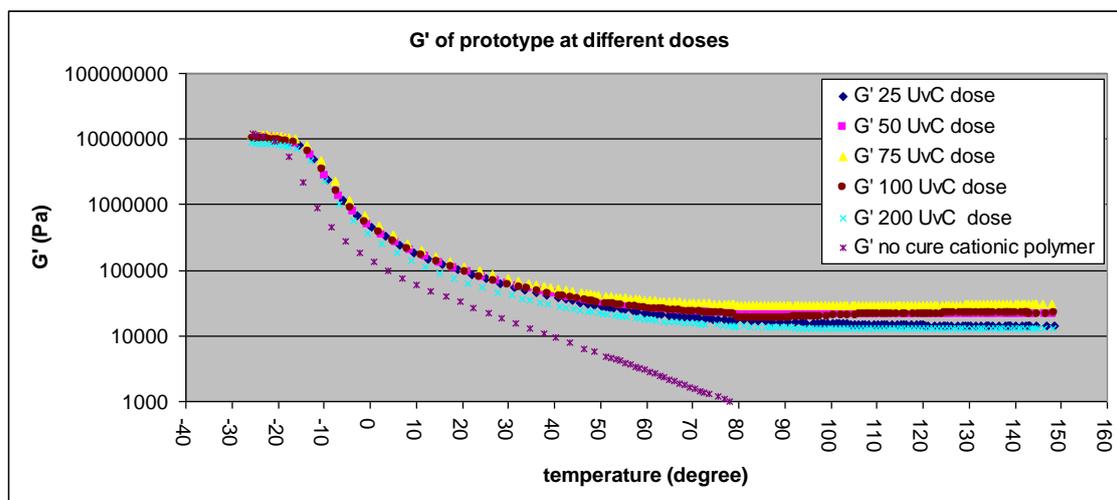


Examples of different epoxy functional monomers

Figure 5

2.3 Adhesive Performance

The above approach has led to the design of several prototype cationic curing polymer systems. These have been evaluated for their physical and adhesive properties. Thermal analysis was undertaken to study the level of cure using rheological methods. For these experiments a cured coating was layered so that approximately 2 mm thickness was obtained and then analysed for G' , G'' and Tan delta. Figure 6 is a plot of the G' vs. UVC dose applied to a 100 gsm coating. It can be seen clearly that a low dose gives a G' plateau at the same level as the coating with a high dose.



G' measurement made within 24 hours of curing 100 gsm coating

Figure 6

The rheology data showed that good cure was achieved even at low dose levels. This indicates that the prototype can be cured with a greater efficiency of UV radiation compared to UV acrylic systems using the grafting crosslinking mechanism. Figure 7 makes a comparison for peel adhesion between the cationic prototype A, a free radical UV acrylic and a solvent based acrylic (SBA). Data is shown for each with the prototype having a dose of 10 mJcm^2 UVC dose while the free radical UV curing acrylic hotmelt required 140 mJcm^2 UVC.

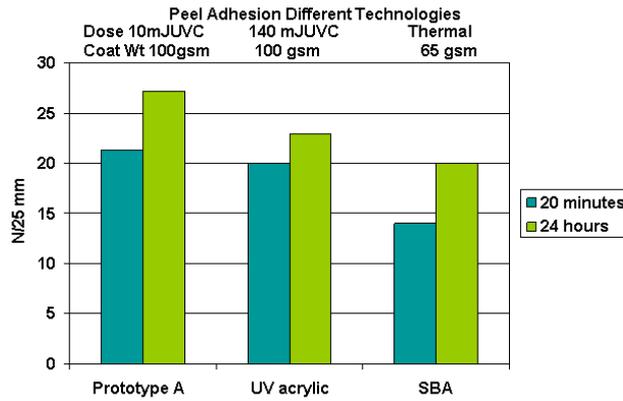


Figure 7

Figure 8 shows the data for the same technologies SAFT performance. What was very surprising was that the thermal cohesion was also excellent at the low UV dose levels for the cationic system.

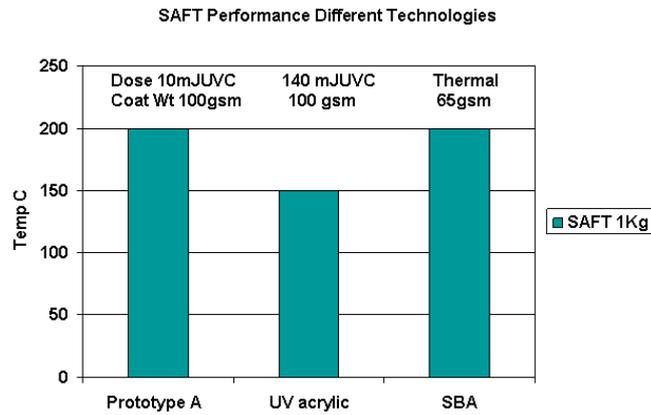


Figure 8

The main advantage of cationic systems is that thicker coat weights can be cured especially compared to free radical curing. Figure 9 shows some data to illustrate this feature. Coatings were made at 100, 150, and 200gsm and cured for both cationic and free radical system. The free radical system will not cure at these higher coat weights, but the cationic prototype will give a 1Kg SAFT failure to 200°C.

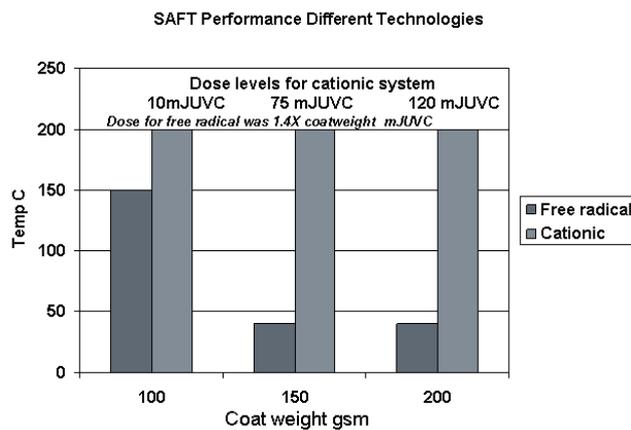
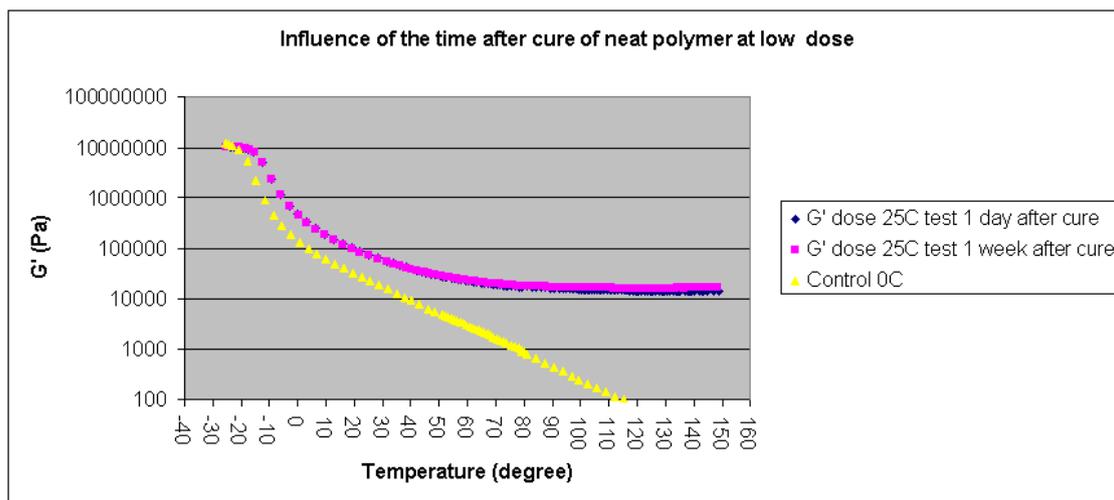


Figure 9

With cationic curing technologies “Dark Cure” is always an issue to be understood. This is due to the fact that the curing chemistry continues after the initial UV dose until all the reactive species have been consumed. In order to investigate any “Dark Cure” in our prototype A, rheology tests were performed on a 24 hour sample and a sample aged for a week that had been cured with 10 mJcm² UVC. The plot in Figure 9 shows that prototype A has reached its final cure crosslinking after 24 hours and no significant change occurs in the next week. This indicates that “Dark Cure” has completed within 24 hours and no change to the rheology/adhesive properties occurs after this point in time.



G' data for 100gsm coating after one day and one week

Figure 9

Conclusions

The paper has shown some very encouraging results for a prototype UV cationic cured acrylic polymer system. The polymer contained bound UV reactive groups that could be cured at significantly lower doses than existing UV acrylic systems. Thick coating weights greater than 100 gsm can be cured. This acrylic prototype has similar application properties to that of state of the art acrylic technology and comparable peel adhesion and cohesion values. The “Dark Curing” of these coatings appears to be fully completed within 24 hours.

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