Smart UV/EB Curable Pressure Sensitive Adhesives

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Abstract

New materials that have the capacity to adapt to their environment and have a wide range of responses are continually emerging. Smart, Energy Curable Pressure Sensitive Adhesives (PSAs) are unique adhesives which allow for one set of properties, such as removable PSA, and then after a stimulus assume a second set of properties such as becoming a permanent adhesive or one which will debond on demand. Many stimuli can be used such as light or hydrolysable crosslinks but this study focuses on thermally responsive systems. Moreover, this study found that using thermally responsive oligomers can be used to target specific adhesive properties in order to tailor performance on demand.

Introduction

Photopolymerization is a method of obtaining polymeric materials via the use of actinic radiation, including UV/Visible light and electron beam sources. These photocurable resins are most commonly comprised of a photoinitiator, monomer, and oligomer. In a photocurable system light acts as the activating source and initiates the reaction by exciting a photoinitiator in order to generate radicals. The initiating radicals then react with vinyl groups, most commonly an acrylate or methacrylate moiety, present on the monomers and oligomers. Due to its fast initiation rates, photopolymerization is commonly used in coatings, printing inks, printing plates and adhesives.

In the field of UV curable adhesives, both monomer and oligomer choice are important. Monomers are frequently used to both lower the viscosity of oligomers while influencing secondary characteristics such as surface energy and glass transition which can further tune the ultimate performance of the adhesive. The choice of oligomer, meanwhile, governs the bulk properties of the photocured resin and acts to primarily dictate the adhesive properties of the material as measured by peel strength, tack, and shear resistance. In this study we examine a series of thermally responsive oligomers (TROs) which have the potential to exceed the properties of commonly available UV curable oligomers and while offering diverse properties which may be further altered based on choice of oligomer structure, monomer and other reactive diluent.

Experimental

Multivariable experiments were developed to study the effect of each component of a formulation and the parameters that apply. Different series of experiments were carried out to test variable monomers, oligomers, and secondary reactive moieties (SRM). The performance of the adhesive was evaluated based on its tack, peel, and shear.

Formulations were designed to examine unique, thermally responsive oligomers (TRO). These formulations included a high T_g monomer, a low T_g monomer, a photoinitiator, and a secondary reactive moiety (SRM) which allows for control of the final properties (e.g., stronger adhesion). A standard smart adhesive formulation is presented in Table 1.

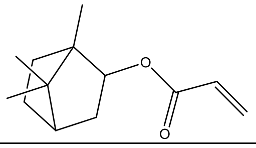
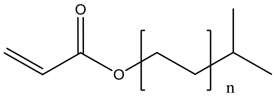
Component	**Smart Pressure Sensitive Adhesive**	**Role**
High T_g monomer	Monofunctional acrylate 	Modifies shear adhesion and helps prevent adhesive failure
Low T_g monomer	Monofunctional acrylate 	Modifies peel adhesion and helps prevent cohesive failure
Thermally Responsive Oligomer (TRO)	Proprietary	Governs the bulk rheology of the adhesive
Secondary Reactive Moiety (SRM)	Proprietary	Reacts with TRO after external stimulus is applied
Photoiniator	Irgacure 2022 (bis acyl phosphine/ α-hydroxyketone)	Initiates radical poplymerization after UV light exposure

Table 1. Base formulations for a smart adhesive

The adhesives were drawn down onto a facestock using a MFK-ASA II thick film coater as a 2.5mil film and then cured by using one pass under two 400 W power lamps of an Inpro medium pressure mercury arc lamp system with a speed of 50ft/min. In order to avoid oxygen inhibition, the adhesive film was cured with a release liner on top of it. All samples were annealed for 2 hours at 100 °C (212 °F).

The performance of each adhesive was evaluated through common adhesives testing such as tack, peel, and shear. Tack was tested using a probe tack PT-500 tester. Peel strength was measured at 180° angle using stainless steel substrates, a dwell time of 24 hours, and a 1 ft/min pull rate using an Instron tensometer. Shear resistance was done on stainless steel and was measured using a mass of 2kg and the tests were normally started after a 1 hour dwell time.

The solvent resistance of the PSAs was studied in acetone, isopropyl alcohol (IPA), and tetrahydrofuran (THF). Cured tapes were immersed in solvents and the time to delamination or dissolution was measured.

Results and Discussion

Photocured polymeric systems are well known for their rapid cure times making them attractive materials for high throughput processing. It has also been observed that by exposing a cured photopolymer system to temperatures above their T_g can cause the network to relax and additional cure to occur. The increase in cure is due to increased mobility of the polymer chains above the glass transition temperature. While not every industrially relevant process allows for this thermal processing, it is important to show the effects of a thermal annealing step on a standard UV PSA resin. In order to demonstrate these changes, a standard UV PSA using an acrylate oligomer was formulated and used as a reference for comparison with the PSAs utilizing the TRO chemistry. Fig. 1 shows the tack and peel strength of a standard UV PSA. Fig. 1A shows that there is a change of about 1 lbf (from 2 to 3lbf) for the standard UV PSA. This change is most likely due to an increase in low T_g monomer conversion. Fig. 1B meanwhile indicates that there is no significant change in peel strength performance of the UV PSA. The lack of change in peel strength is likely due to the bulk of the monomer system maintaining a similar rheology to before the annealing. Since the system has similar rheology it would make sense that the peel strength remains unchanged. Exposing the cured system to elevated temperatures doesn't alter how the network can wet out the stainless steel substrate and thus the values are relatively similar. Lastly, the UV PSA for both before and after annealing exhibited high shear resistance, greater than 3 days, and is not shown.

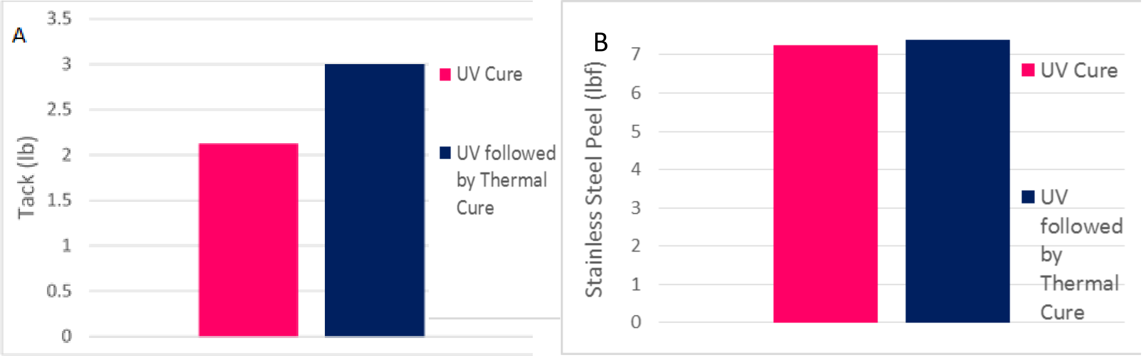


Figure 1. Tack (A) and Peel strength on Stainless Steel (B) for a standard UV PSA (no TSO oligomer) comparing only UV cure and UV followed by Thermal Cure.

Based on the observed differences in tack and the lack of change in peel strength and shear resistance, it was theorized that the introduction of TROs to traditional UV PSA formulations could make dynamic photocurable resins. These TROs would be able to produce either stronger or weaker adhesion depending on stimuli and formulation. To this end, as polyester-based backbones were identified as having better compatibility with the SRM, another series of TSOs were synthesized. The second series was made to target both high molecular weight >9000 Da, and low molecular weight, <2000 Da, blends. To characterize performance based on the oligomer used, either a 50:50 by weight ratio or a slight excess of low molecular weight oligomer, 40:60 by weight percent, were used. Fig. 2 shows the peel strength (3A), shear resistance (3B), and tack (3C) for the different molecular weight blends. Fig. 2A shows a dramatic increase in peel strength compared to the initial blends. Rather than showing almost no peel strength after UV curing, the peel is now approximately the same as that of a UV PSA for both the 50:50 and 40:60 blends. After annealing we see that the values increase to 9.5 lbf or greater. Fig. 2B also shows an increase in shear resistance performance from the gen 1 TRO blends. Rather than having shear times on the order of minutes, the gen 2 PSAs all hold for multiple days after photocuring. Reacting the SRMs further modifies the polymer networks and allows the TROs to have shear resistance values on the order of weeks. Lastly, as observed in Fig. 2C, the tack of the adhesive decreases after thermal treatment. These changes are due to the SRMs which allow for the adhesive polymers to increase the molecular weight between cross links within the polymer networks without compromising the low T_g required for wetting out the substrate which accounts for the increase in peel strength. The increase in molecular weight also accounts for the increase in shear resistance through molecular entanglements which prevents the adhesive from slipping. Lastly, the decrease in tack can be accounted for by the removal of the SRMs which act to promote tack prior to UV curing.

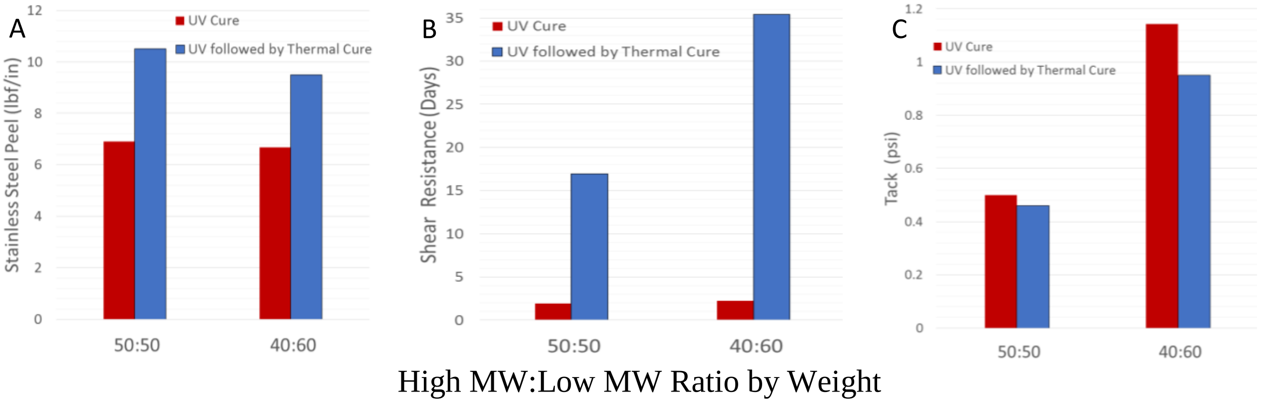


Figure 2. Performance of smart adhesives according to the ratio of High to Low molecular weight oligomers. Peel Strength on Stainless Steel (3A), Shear Resistance (3B), and Tack (3C) for ratios of a blend of TROs.

In addition to modulating the molecular weight of the TRO, it is possble to modify the SRM as well. A series of UV PSA formulations with higher reactivity SRMs were created and UV cured to determine how altering the functionality of the SRM would alter the adhesive properties of the resulting polymer networks. Moreover, using a blend of specific SRMs may produce an interpenetrating polymer network (IPN) after thermal cure step. Fig. 3A shows the effects of incorporating small amounts of a higher functionality SRM on peel strength. Here we can see that the initial UV step remains on par with a traditional UV PSA with small increases resulting from the thermal treatment. These small increases are likely due to some minor increases in the molecular weight between crosslinks and network relaxations to allow for greater substrate wetting after thermal treatment though due to the formation of a non-flowable network the peels are not as high as when using a less reactive SRM. Fig. 3B shows the shear resistance adhesion properties of the multi-SRM blends. Here the TRO has a much more pronounced effect, with 1 mol% of the higher functionality SRM extending the shear time with a 2kg mass to well over a month. Interestingly, the 0.5 mol% addition of higher functionality SRM actually decreases the shear resistance performance as compared to a less reactive SRM. It is believed that the decrease in performance is due to complex rheological differences and is an ongoing area of study. Tack, as observed in Fig. 3C, decreases to almost zero once the higher reactivity SRM is incorporated and the cured adhesive is allowed to thermally react with the SRM. The decrease in tack is also believed to be due to the formation of a secondary, non-flowing network which gives a fully cured, coating-like feel to the adhesive.

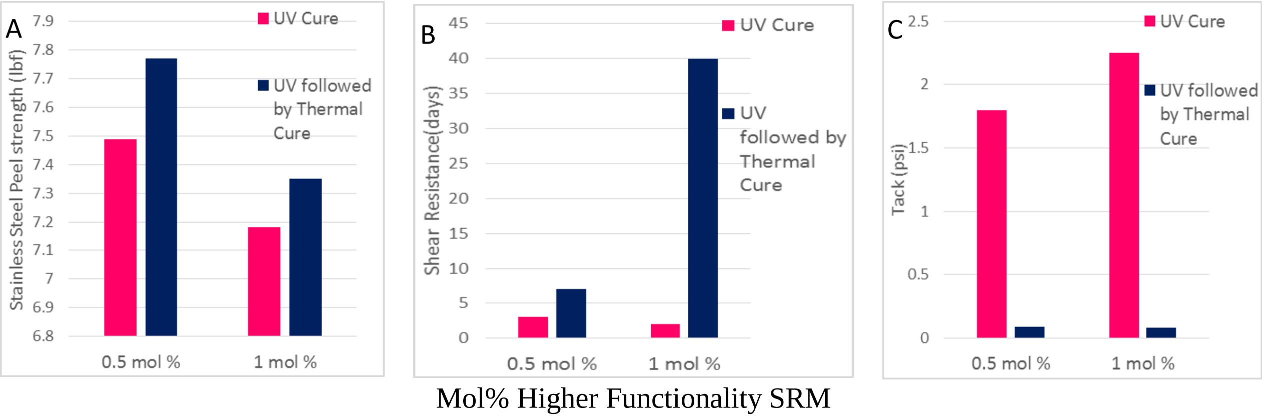


Figure 3. Peel Strength on Stainless Steel (A), Shear Resistance (B), and Tack (C) for two ratios of a blend of SRMs after UV curing and after UV and Thermal processing.

As the functions of the TRO and the SRMs are directly related, it is possible to alter the amount of SRM added to the formulation. By adding an off stoichiometric amount of SRM, it is possible to limit the extent of the thermally triggered reaction, and thus, further tune the adhesive properties. In order to explore the relationship between TRO and SRM, three formulations using 90%, 70% and 50% of the stoichiometric amount of SRM were made and cured. The stainless steel peel values are shown in Fig. 4A. The role of concentration of SRM appears to directly affect not only the UV cure but also how efficiently the thermal reactive step can take place. A decrease in as little as 10 mol% of the SRM produces a material with almost no peel strength observed after both processing steps. Decreasing the SRM concentration further shows that SRM still impacts the UV curing process while the peel increases after the thermal processing step, while peel increases once the SRM concentration is dropped to 50 mol%. The decrease in peel strength values until 50 mol% SRM is due to the complexity of the TRO formulations. Slight off-stoichiometric amounts appear to result in a nonflowable network, likely with some decrease in overall conversion of the acrylate groups. Fig. 4B shows the shear results of the same off-stoichiometric formulations. The close to stoichiometric SRM values show very low shear values, probably due to the resulting nonflowable networks. Once the SRM value is down to 50% it is possible that the thermal processing step creates something closer to the traditional UV PSA with a loosely crosslinked acrylic backbone governing most of the properties. The tack of the off-stoichiometric blends, as detailed in Fig. 4C, shows a complex behavior as the amount of SRM is decreased. After UV curing, the PSAs show increasing tack likely due to an increase in cure from the reactive monomer diluents as there is less competition from the SRM. After the annealing step a small increase is observed from 90% to

70%. It is believed that this result is due to the formation of a complex polymer network between the SRM, TRO, and monomer diluents. The tack meanwhile decreases to near zero once the SRM is decreased to 50%. The sharp departure from trend is attributed to the formation of something more akin to a crosslinked UV curable resin. Overall, the complexity of stoichiometric addition of SRM to TRO to monomer diluents is highlighted in this study, thus highlighting the complexity of formulations with TROs.

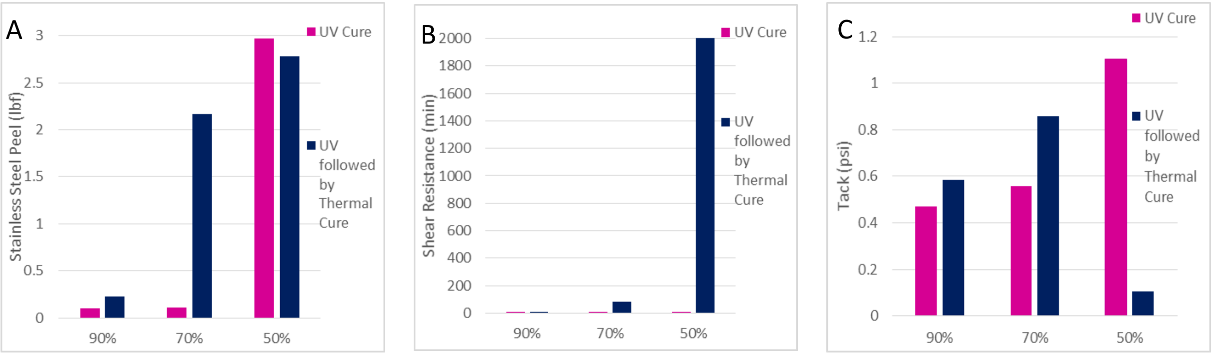


Figure 4. Peel Strength on Stainless Steel (A), Shear Resistance (B), and Tack (C) for three different amounts of SRMs while holding all other formulation concentrations constant.

As the functions and amount of SRM can imply significant modifications on the adhesive's performances, changing the nature of the SRM may change the properties of the formulation. Thus, using specific SRMs may produce an interpenetrating polymer network (IPN) after thermal cure step as it was showed previously using other SRMs may produce debondable adhesives. Indeed, for some applications, it is desirable to debond the adhesive and free the substrates. Using a different SRM we produced materials capable of debonding after thermal treatment as seen in Fig. 5.

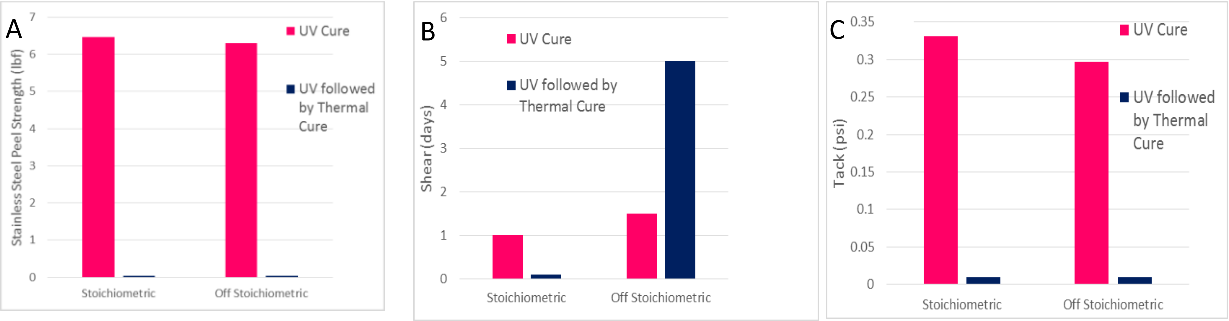


Figure 5. Peel Strength on Stainless Steel (A), Shear (B), and Tack (C) for two different formulation using the same SRM to generate debondable adhesives.

Figure 5 shows the peel (5A), shear (5B), and tack (5C) for two formulations similar to Fig. 2 but with a different SRM. The effect of SRM can immediately be observed as these samples have the opposite peel strength tendency than the previous ones. Indeed, the thermal cure step makes the stainless steel peel strength decrease to nearly zero as compared to a value of 6 lbf prior to thermal annealing. Interestingly, while the thermal annealing decreases the shear to zero for the stoichiometric blend as observed above, the thermal annealing actually increases in the off-stoichiometric blend highlighting the subtle interactions between SRM and TRO. Tack, as observed in Fig. 5C, also decreases to almost 0 for both blends indicating the capabilities of these materials to transition from adhesive properties to something more akin to a traditional UV curable coating.

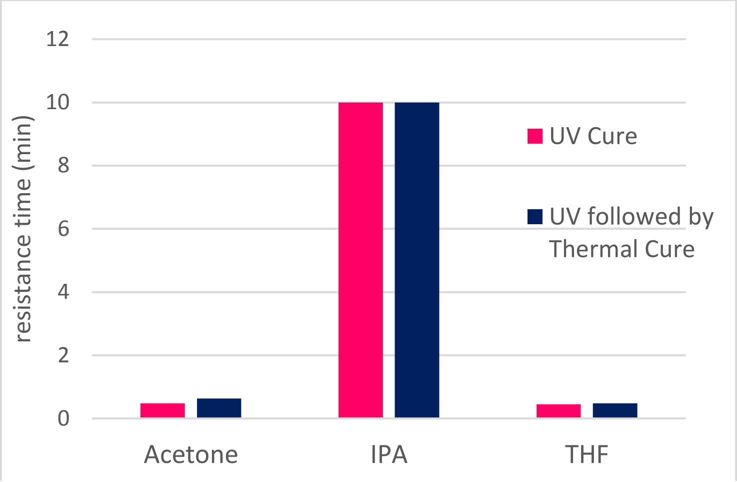


Figure 6. Solvent resistance of an adhesive without chain extender.

As TROs show significant changes based off of SRM and molecular weight, it was important to further characterized the network changes capable of TROs outside of adhesive properties. One method of probing these changes is to observe how soluble these materials are. Fig. 6 shows the time to delamination of a TRO blend after processing. It can be seen from the delamination time in Fig. 6, the SRO formulation that was tested showed high resistance to IPA, and much lower resistance to THF and acetone which would be expected for an aliphatic polymer system.

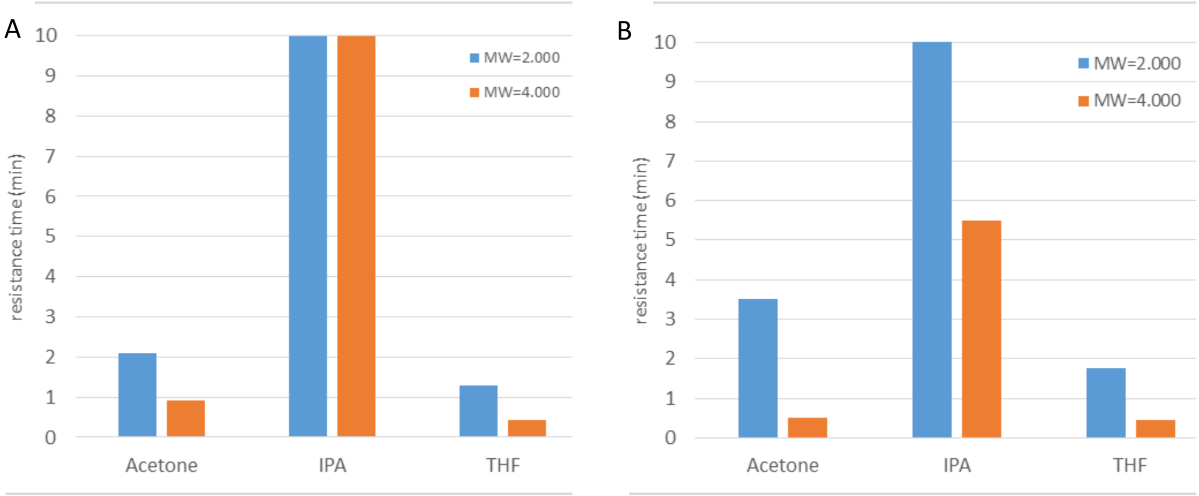


Figure 7. Solvent resistance of smart adhesives according to the SRM's molecular weight after UV curing (A) and after UV and Thermal Curing (B).

While it was observed that the TROs behaved like normal oligomers in the absence of a SRM, it was believed that tuning the size of SRM may further alter how the PSA may respond to solvents. Fig. 7A shows the solvent resistance after UV curing in the presence of a 2000 and 4000 MW SRM. Due to the aliphatic nature of the composition, resistance to IPA remains high. Interestingly, at lower molecular weight SRMs show longer times to delamination than the 4000 MW formulations. It is believed that the increased time to delamination is due to the SRMs potentially plasticizing the network prior to thermal curing with the higher MW SRM having a greater plasticizing effect. The difference in resistance times holds for acetone and for THF. THF is also a well-known solvent for polymers which alludes to the adhesives delaminating faster than in acetone. Fig. 7B on the other hand shows the solvent resistance for the TROs after the thermal processing step. After the thermal step, all formulations including the 2000 MW SRM show an increase in delamination time, with IPA still being the least effective solvent. Meanwhile, the 4000 MW SRM appears to decrease the time to delamination suggesting that the increase in SRM MW is likely decreasing the overall crosslink density of the network. By decreasing the crosslink density, the polymers can swell more easily leading to faster delamination from the substrate. The ability for solvent to better penetrate and swell the network is particularly reinforced when it is observed only after the TRO undergoes thermal treatment with a 4000 MW SRM does the adhesive delaminate in IPA.

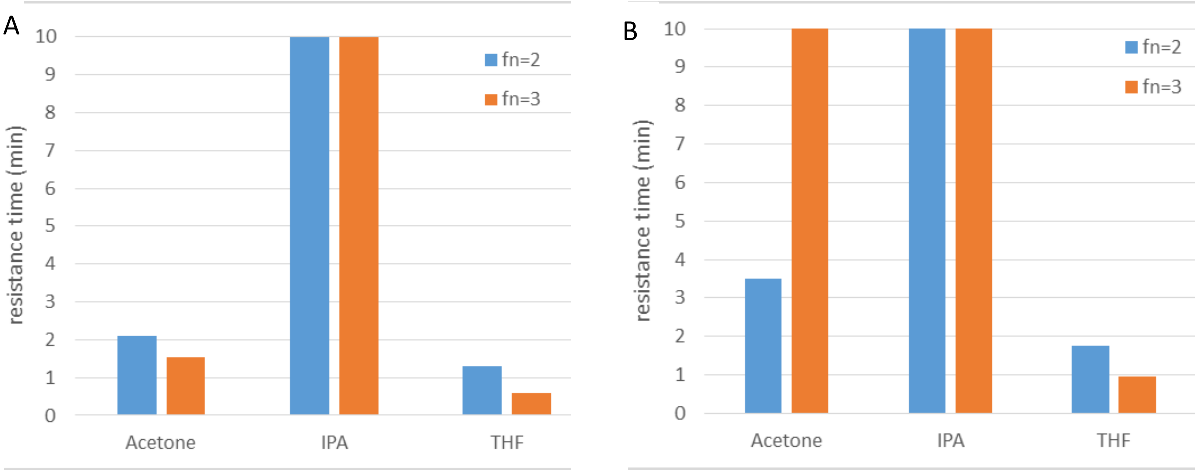


Figure 8. Solvent resistance of smart adhesives according to the SRM's functionality

In addition to controlling the nature of the TRO adhesive via the MW of SRM, it is possible to control the delamination time of materials by controlling the functionality of the SRM. Fig. 8A shows the solvent resistance of a TRO when UV cured in the presence of a 2 or 3 functional (fn) SRM. The aliphatic nature of the TRO continues to prevent lamination in IPA after UV curing. The presence of a trifunctional SRM appears to decrease the time to delamination, though, these changes are relatively small. Moreover, the differences in delamination time after UV curing are most likely attributable to the plasticization of the network by including a larger trifunctional SRM compared to the smaller difunctional SRM. The effects of SRM functionality are more significant after the thermal annealing step as seen in Fig. 8B. The effect on solvent resistance to acetone can be observed by the almost doubling when using a difunctional SRM and the adhesive reaching the maximum observed time of 10 minutes when using a trifunctional SRM. These changes in acetone solvency are likely due to changes taking place in the network which would prevent acetone from swelling and thus causing delamination. THF remains the best solvent for the TRO adhesive with small differences seen after the thermal annealing step, with a decrease in time to delamination observed for the trifuncitonal SRM.

Conclusion

We have successfully demonstrated the use of thermally responsive oligomers (TROs) in smart adhesive applications. We showed that first UV curing a PSA formulation can achieve one set of adhesive properties and with the use of an external stimulus (such as heat) change these properties. In one example, we were able to make a more permanent/stronger adhesive while in another example, the adhesive debonds or became easier to remove (in both cases after a thermal treatment). We can control the second set of adhesive properties through careful selection of several formulation features as discussed above. Future work will continue to explore the achievable property spaces of this technology as well as investigating other stimuli, such as light, mechanical, and chemical means. We also believe that TROs are a unique oligomer class that will pave the way for dynamic tunable properties, not only for adhesives but in other applications.

References

[1] Rudy J. Wojtecki, Michael A. Meador, Stuart5 J. Rowan, 2011, Using the dynamic bond to access macroscopically responsive structurally dynamic polymers

[2] Jean-Pierre Fouassier, Jacques Lalevee, 2011, Photoinitiators for Polymer Synthesis

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