DEVELOPING NOVEL PSAs USING A HIGH THROUGHPUT WORKFLOW

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Abstract
Developing next generation PSA products has been traditionally a time and people intensive process. The wide parameter space due to a myriad of synthesis and processing variables has always made it challenging to traverse the space in order to detect optimum performance characteristics. We describe a High-Throughput workflow for discovering new aqueous and solvent based PSA products and also for improving existing products. The approach combines use of automated equipment in conjunction with sound experimental design principles, statistical modeling and rapid data visualization tools. The utility of the High Throughput process in identifying and modeling synergistic effects of additives in blends of existing acrylate and polyurethane adhesive products will be used to exemplify the advantages and limitations of this approach.

Introduction
Offering innovative products and differentiated solutions to customers is imperative for sustainable growth for any corporation. Accelerating the process of innovation, while maintaining the pace for new product development is a challenge for most R&D organizations. The pharmaceutical industry, one of the early adopters of High Throughput techniques successfully applied the tools to fast-track drug discovery. This was quickly followed by chemical companies for catalyst discovery[1]. More recently, specialty chemical companies have embraced these tools for developing coatings formulations[1,2,3]. DOW has been one of the leading companies in the chemical industry that have strategically invested in High Throughput research (HTR) and successfully applied it for catalyst discovery, and developing coatings, personal care formulations etc. However, high throughput tools have had limited success in PSA research for many reasons.

First and foremost is the complexity of automating various application tests that comprises a portion of PSA workflow. Due to the 'soft' nature of the polymers that deliver PSA properties, PSA testing is extremely sensitive to test conditions and sample handling. The skill sets required for developing robotics to accomplish such tasks with precision and robustness are often not readily available and require in-house capability building. A PSA workflow (see Figure 1) in the context of HTR refers to an integrated set of robotic instruments that can be used to formulate PSA compositions, prepare samples on a variety of substrates, and analyze both formulations and PSA samples for key properties. The workflow is completed with statistical modeling and data analysis feedback to discover and develop unique products and solutions. Another critical step in a workflow is developing models for structure-property relationships. A key requirement

for developing robust predictable models is availability of good quality data, and HTR is ideally suited for that purpose.

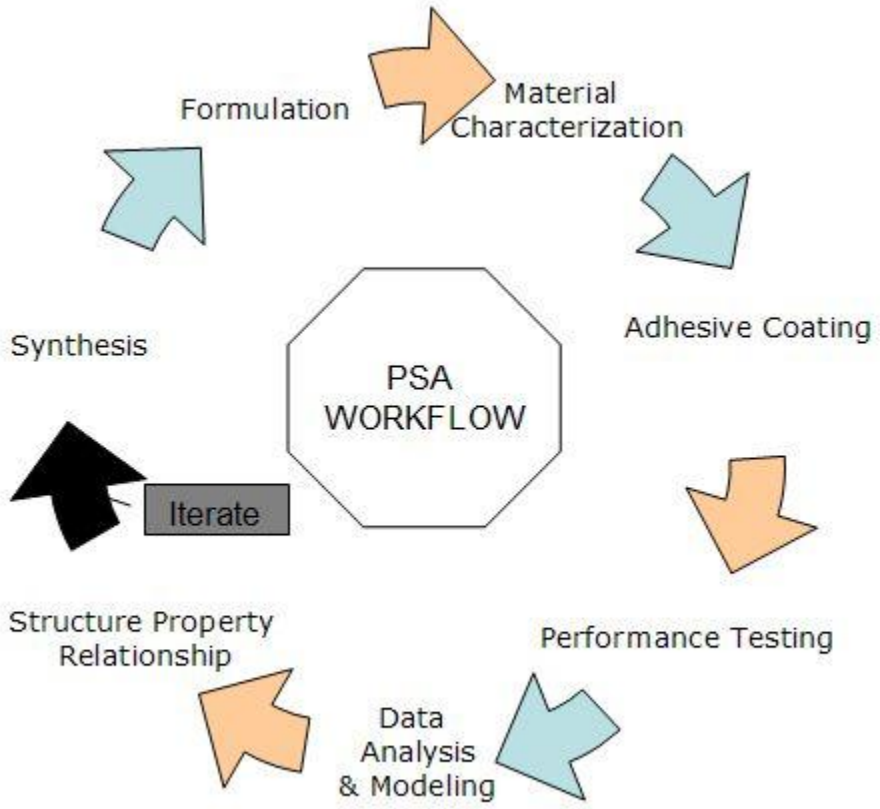

Figure1: Schematic of a Pressure Sensitive Adhesive Workflow

Secondly, the investment required to achieve a complete workflow is significant. The Dow Chemical Company has made a strategic investment towards High Throughput Research (HTR) and fully embraced it in its R&D culture.

In this work we demonstrate the successful development of a PSA workflow with two specific examples. The integrated approach of HTR is leveraged to develop high performance waterborne acrylic PSAs with unique balance of adhesion and cohesion. Ability to formulate multiple additives is demonstrated along with a design of experiments strategy that uncovers unique formulations. The objective of this study is to understand the complex interactions between multiple formulation variables and uncover synergistic interactions to develop high performance PSAs. It is practically impossible to execute a complete mixture-design study without high-throughput tools.

The second example demonstrates the versatility of the PSA workflow developed where polyurethane dispersions (PUDs) are synthesized from a variety of isocyanate terminated

prepolymers using aromatic and aliphatic isocyanates in combination with dimethylolpropionic acid (DMPA) and aliphatic polyether and polyester polyols of varying molecular weights and functionalities, followed by neutralization with triethylamine and chain extension with aqueous aliphatic diamines to the desired % solids content. The performance properties of these PUDs were then evaluated using the PSA workflow. The variables that can be studied for PUD systems is immensely large, and HTR is ideal for such research projects.

High Throughput Principles and Methodology

A high throughput workflow is a process combining elements of parallelization, serial automation, miniaturization, experimental design, primary and secondary screening methodologies and, last but perhaps the most vital link, software integration. Information resources such as database sample tracking, data mining and data analysis are critical as it allows conversion of a conventional materials research process into a seamless high throughput experimentation workflow. Further, the workflow is also typically an iterative process so that the insight into structure-property relationships of materials gained by executing the process is utilized to improve the experimental designs in the subsequent rounds. Over time, a library of solutions is available and predictive models are generated that allow continuous improvement in the product performance.

However, high throughput experimentation is not to be confused as a process to replace a scientific research methodology with brute force searching.[4] Despite an increased throughput, typically 10-100 times the throughput obtained using a conventional discovery process, scientific knowledge and experience is critical for generating a sound experimental design, data analysis and developing structure-property relationships. Experimental design forms an integral part of any high throughput workflow and is imperative for it to be cost and time efficient in finding an optimum solution or discovering the next generation product. Until now, discovery of next generation of products that will satisfy the customer requirements has been largely a one variable at a time experimentation process or an informed search utilizing the knowledge base of the researchers. Such a strategy is woefully inadequate for a large parameter space with multiple variables and the solution is likely to be not an optimum solution. Another pitfall of this strategy is the confounding that occurs due to the interaction of multiple variables. As an example, a lower peel performance of a pressure sensitive adhesive could be due to a number of synthesis variables such as the molecular weight of the polymer or the formulation additives such as surfactants used in the product or the coating quality and thickness. Further, there are interactions between these variables that are difficult to quantify and scientifically model using one variable at a time experiments. Experimental design using a factorial or screening approach can thus not only allow rapid discovery of optimum solutions and next generation products but also make it very efficient by providing a scientific basis to solving problems that are presented to the community in the future. Typically software programs such as JMP are used for this purpose as it allows the researcher to generate designs that are tailored to the problem including fractional factorial, screening or custom designs.[4]

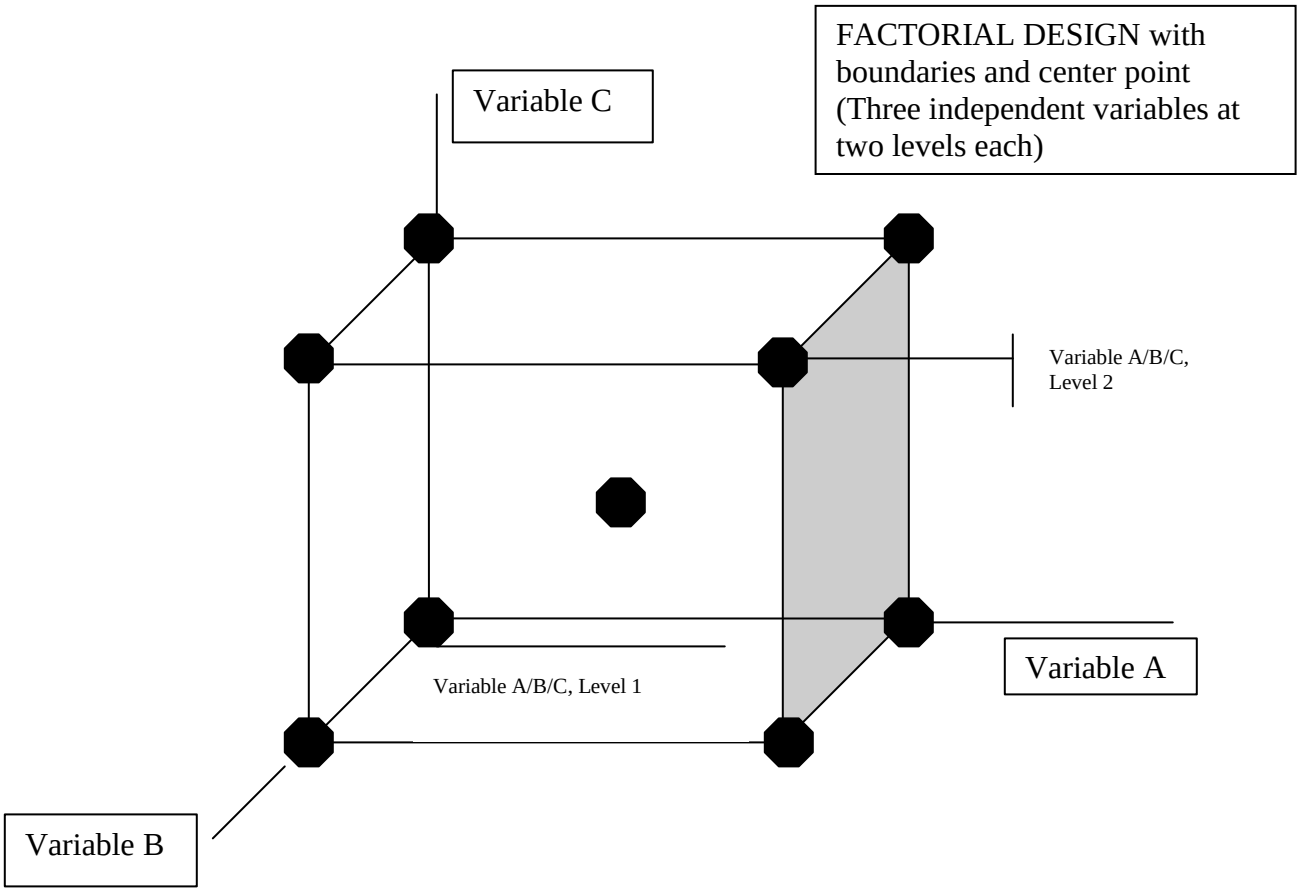

Figure 2: Factorial design depicting data points at the boundaries and center point for three independent variables. The two levels form the boundaries of the experimental space.

The increased throughput is typically a strong function of the parallelization achieved in the standard workflow. Typically, conventional techniques are replaced with equivalent methods that correlate well with the standard synthesis, formulation or characterization methods.

High throughput pressure sensitive adhesive characterization presents a number of challenges to parallelization of the workflow due to the absence of fundamental measures of performance and the critical dependence on practical but inherently error-prone testing such as peel, tack and shear property testing. However, synthesis and formulation techniques, which are typically the predominant bottlenecks in a standard adhesive discovery process, can be executed in a parallel fashion by leveraging other material science research high throughput workflows such as those used for coatings research[4,6]. Parallel formulators, widely used until now for drug discovery, but increasingly becoming popular for materials research such as Hamilton, Tecan etc. allow formulation of 4-96 samples at a time as shown in the figure below. The adhesive performance testing part of the workflow is difficult to execute in a parallel fashion but lends itself very well

to serial automation which, although not as fast still allows fairly rapid (10x) experimentation. Furthermore, it eliminates operator-to-operator variability in sample preparation, conditioning, loading and testing because of the repeatability of robotic systems.

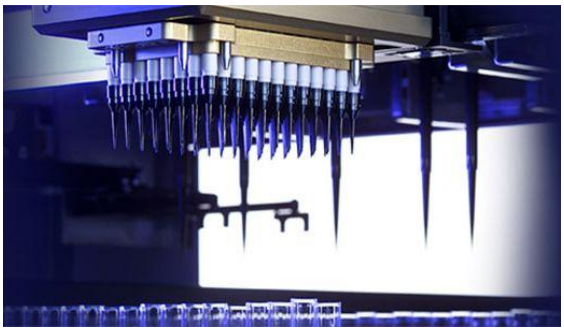

Figure 3: (a) Hamilton Liquid handling robot with 96 channels (www.hamiltonrobotics.com)
(b) Standard micro titer plate with 96 (1ml) vials.

Due to an increased parallelization and rapid characterization, there is a continuous push towards using smaller samples, and miniaturization is another principle that is widely employed in high throughput experimentation. This approach has been widely adopted in the academic community where microfluidics and lab-on-a-chip have generated a lot of interest in the last decade.[5] Microfluidic devices are being developed for performing parallel reactions and material characterization, especially in the drug discovery field, such as biochemical assays and pathogen detection. For adhesive and coatings area research, a sample size of the order of ~5-10 ml is used as the number of screens and replicates for each screen are large. Typically, standard titer plate formats are used so that sample tracking in databases is automated and one example of standard titer plate with 96 samples in shown in the figure above.

On the flip side, high throughput experimentation requires a strategic focus, significant capital investment and people commitment. It is possible to automate a single piece of a standard workflow to de-bottleneck a conventional discovery or optimization workflow but to realize its full potential in terms of acceleration of new product discovery and development, it is essential to integrate all the blocks to seamlessly track samples, analyze high sample density data and use iterative designs to find solutions.

High Throughput Pressure Sensitive Adhesive Workflow

Pressure sensitive adhesive workflow presents a number of challenges to a fully automated parallel workflow, as was alluded to in the earlier section, and has been described in considerable detail by Crosby[6] (2003). This is primarily due to the absence of fundamental properties that correlate well with pressure sensitive adhesive performance in applications. Hence, primary screening of the product performance typically relies on the measurement of peel, tack and shear properties in order to evaluate them for a host of applications. A host of other properties such as water whitening resistance, chemical resistance, dry flow etc. are also measured depending on the particular application area.

Fortunately, most of these primary screens are neither tedious nor time consuming as compared to some of the other building blocks in the workflow such as formulation using different additives and synthesis of base polymers. This feature makes them ideal candidates for serial automation and even without parallel measurement techniques it is possible to have sufficient throughput in these devices (of the order of 100 measurements in a day). Rapid parallel adhesive screening is however possible for certain combinations of variables such as for application testing that requires screening of adhesive properties as a function of temperature. Researchers at NIST and their collaborators have built some novel devices that can perform rapidly peel and tack tests at multiple temperatures using a temperature gradient on a single sample.[7,8] Probe tack test, in particular, has been the focus of a number of high throughput research efforts since the spherical probe tack test can be used to understand fundamental adhesive failure using the work of adhesion as an evaluation criterion[9,10]. A number of designs have been already described in literature for performing probe tack in a serial or parallel manner[11,12].

Synthesis of base polymers and polymer characterization is a time consuming step and typically the bottleneck in a conventional pressure sensitive adhesive workflow. There are commercial reactors available for polymerization and homogenous or heterogeneous catalytic reactions from a number of companies including Symyx Technologies and Chemspeed Technologies. They typically have 4-24 parallel reactor arrays with multiple inlet lines, mixing, weighing and heating capabilities. Peil and others (2004)[1] at Dow have also previously published the use of high throughput technology in optimizing catalytic reactions. Typically, liquid handlers such as the Hamilton or Tecan liquid handling robots are then used for formulating the adhesive dispersions using a number of additives such as tackifiers, wax, rheology modifiers, neutralizers, surfactants etc. Heating, mixing capabilities are quite universal among these robots but they typically differ in their dispensing methodologies, either gravimetric or volume dispensing, and their viscosity handling capabilities, as shown in the figure below. Many of the liquid handling robots have 4-96 channels which enable us to formulate multiple dispersions in parallel thus significantly increasing the throughput as compared to a conventional PSA workflow.

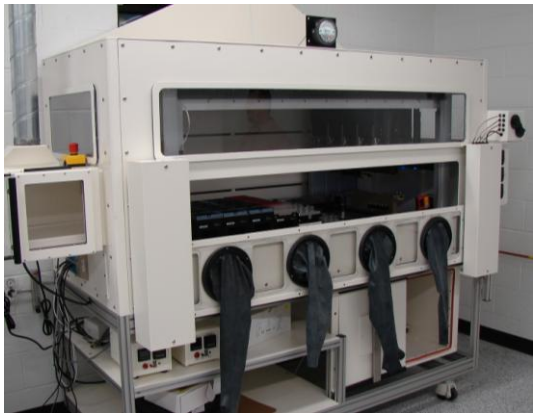

Figure 4: (a) Hamilton liquid handling robot with custom enclosure for waterborne and solventborne adhesive handling **(b)** High Viscosity Formulator for gravimetric dosing and mixing of high viscosity materials.

Formulated adhesives are characterized for a number of properties, chief among them being particle size, pH and rheology. In case of polyurethane systems, spectroscopy and titration are also used for material characterization. A host of automated tools, some of them commercial, while others custom-built, are used for performing these characterizations. An example of a tool that was custom-built as a collaborative effort between Dow and Anton-Paar and which is now commercially available is an automated cone-plate rheometer from Anton-Paar (HTR 301) shown in the figure below. The instrument which will be described in further detail in a separate article provides detailed rheological characterization and has automated sample loading and cleaning for unattended operation. The ability to walk away from instruments is critical in increasing throughput as the researcher is able to operate multiple characterization tools in parallel despite each individual tool operating in a serial fashion.

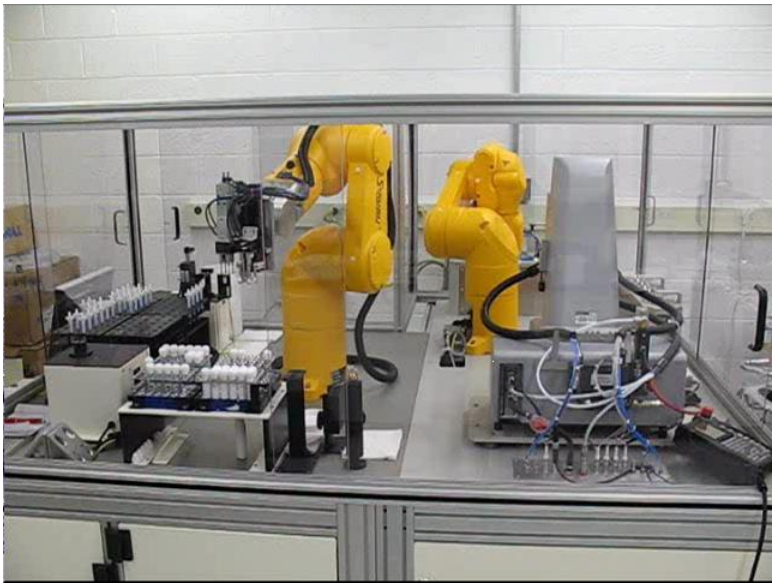

Figure 5: High Throughput rheometer with automated sample handling, loading and measurement.

A reproducible and defect-free coating with controlled thickness is a pre-requisite for understanding adhesive performance and an automated system helps in eliminating the operator to operator variation. Coating stations are also becoming more common in the industry due to their use in high throughput coatings workflow[13] and are now available from Symyx Technologies and hte AG among others.

Figure 6: Symyx Coating Station with ability to coat 1-8 coatings on a single test panel. Coatings can be made at different thicknesses and on different test panel materials.

Primary screening of pressure sensitive adhesives typically consists of understanding peel, tack and shear behavior[14]. These correspond directly to desirable properties in a PSA such as the ability to stick upon simple contact, to be peeled without leaving residue and minimizing creep over time.

A number of designs for executing the probe tack test have been published in literature and have also been described earlier in this section. A tack tester from Symyx Technologies that can perform an automated probe tack test on a number of substrates at different temperatures and using probes of different materials is shown in the figure below. This allows the user to test the tackiness of the adhesive on various facestocks while applying different compressive loads.

A particularly daunting test that is a part of the PSA high throughput screening workflow is the holding power test which is an inherently long test, as the observation entails recording failure over time. Acceleration of this test would significantly improve the throughput but in the absence of such an accelerated shear test, it is possible to overcome the throughput issue by having a large number of sample stations available where the failure mode is being observed and recorded in parallel so that it does not present a bottleneck to the complete workflow.

Peel test measurement strongly depends on a number of factors such as the backing, construction of tape, peel angle and test speed besides the pressure sensitive adhesive behavior. It is also a critical test in quantifying the performance of the adhesive product in an actual application. The complexities of performing the test in a controlled manner and the absence of fundamental properties that correlate with all of the above extraneous factors that strongly affect the peel measurements implies this test is best suited for serial automation. A custom-built automated peel tester, shown in the figure below, uses a six-axis robot to execute the complex tasks an operator performs during sample preparation and can take samples directly from the coating station. Sample loading, peel measurements and cohesive adhesive failure analysis are all done automatically and can be tracked in the database allowing the researcher to find the best solutions.

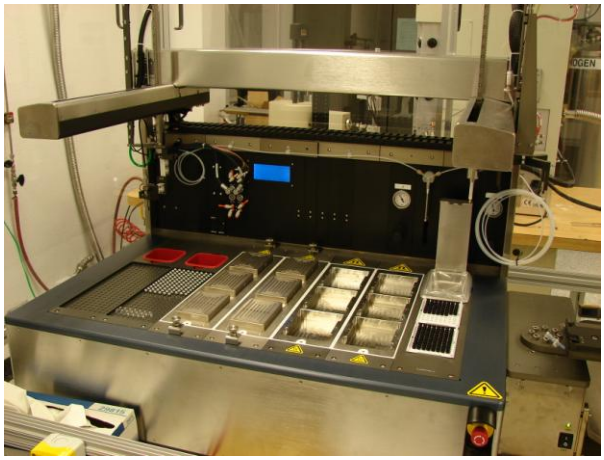

Figure 7: (a) Symyx Tack Station with automated probe tack test. Probe tack is performed using ¾" diameter spherical probes which can be different materials such as steel, glass etc. **(b)** Automated Peel tester with ability to perform 180 degree and 90 degree peel test on different types of test panels (HDPE, Glass, Stainless Steel etc.)

Top candidates that pass the primary high throughput screens are often subjected to additional secondary screening tests to better understand its performance relative to customer requirements. Secondary screening is typically done manually using the standard test protocol. It is also quite common to utilize the automated instruments to perform secondary screens if minor tweaks can adapt the instrument to the test method. An example is to test water resistance it is fairly straightforward to condition the sample in water for a 24 hour period before performing the peel test.

High density data analysis is performed using statistical analysis softwares such as JMP and other imaging and modeling tools such as Miner3D and Matlab are also frequently used. Sample and measurement tracking in the database during the entire workflow allows quick data import into these softwares for predictive model development. These

models typically correlate with existing fundamental structure-property relationships or help develop new fundamental models by estimating important interactions among variables.

The high throughput workflow is typically iterated to generate a library of solutions and the findings from each iteration help guide the latter experimental designs in search for global maxima and minima and products with optimum adhesive properties.

Experimental Methods

Materials

Waterborne Acrylic Formulation Development

The objective of this study is to utilize HTR to identify high performance PSA formulations. Waterbased acrylic PSAs were used as the base emulsion. The formulation latitude was tested by including various additives such as tackifiers and other performance additives. The table below summarizes various materials used for the study. A range of PSAs were selected with varying balance of adhesion and cohesion strength. PSA 1 has the highest shear and lowest adhesion, and PSA 5 is just the opposite. To test the ability of the formulating tools to make multiple formulations, five different additives were chosen for the study. All the additives were in a dispersion form.

PSAs used for the study	PSA 1 (high shear, low peel)	PSA 2	PSA 3 (med shear, med peel)	PSA 4	PSA 5 (Low shear, high peel)
Additives used for the study	Tackifiers	PA 1	PA 2	PA 3	PA 4

Polyurethane Dispersion based Adhesive Development

There are a number of drivers for use of water based polyurethane dispersions as adhesives, chief among them are environmental constraints such as reduction of VOCs and their ability to provide adhesion to a wide variety of surfaces.

The PUD synthesis process involves a number of synthesis variables including type and molecular weight of polyol or mixture of polyols used, type of isocyanate and isocyanate functionality etc. There are a number of polyols used commonly for synthesis of PUDs including polyether polyols such as polypropylene glycol (PPG) , polytetramethylene glycol (PTMG) etc. and polyester polyols such as polycaprolactone and adipate glycol based diols etc[15,16]. The functionality of the polyols can also vary and typically diols and triols are used by themselves or as mixtures with monols or short-chain diols. The mixture ratio and the functionality determines the degree of crosslinking in the system

and as such is fairly important in determining the PSA performance. The MW of polyols can also be varied and a number of pressure sensitive adhesive systems[17,18] use mixtures of high and low molecular weight polyols to give a rich library of adhesive properties. The polyether polyol used for this project is a 2000 molecular weight polyol with a functionality of 2 based on propylene oxide with ethylene oxide capping. The ethylene oxide capping provides a hydrophilic nature to the particles and helps in the dispersion process. The second polyol used is a polyester polyol which also has a functionality of 2 and similar ethylene oxide capping but has a higher molecular weight of 3000 and a much higher monol content.

A number of different isocyanates are used to produce the urethane linkages and can be either aromatic or aliphatic in nature leading to differing adhesive properties. Some of the commonly used ones include IPDI, ADI, TDI, H12MDI and MDI and their usage has been reported for a number of PUD systems for coating and adhesive applications.[15,16] These isocyanates have been used to produce the urethane linkages in the current project. Also, the PUD synthesis process provides the chemist a rich toolbox in terms of chain extenders and emulsifying agents to obtain a good dispersion. Some of the chain extenders used in the current study include water, ethylene diamine and 1,2-propanediamine. Emulsifying agents include 2,2-dimethylolpropionic acid (DMPA) and surfactants used include sodium lauryl sulfate (SLS) and sodium dodecanesulfonate (LDS).

Experimental Techniques

A host of instruments, both automated and manual have been used for the projects described in this article. Many of these instruments form part of the high throughput pressure sensitive adhesive workflow and have been described in the earlier section.

The rheological and thermal properties of the samples were measured using a Rheometrics ARES melt rheometer and a TA Instruments Q2000 respectively. The rheology experiments were carried out on a 8mm disc samples using a frequency of 1 Hz. The temperature range used for each sample was -70 ^{o}C to 180 ^{o}C and experiments were performed in both temperature directions.

Coated adhesive samples were prepared on 2mil thick mylar films and the dried sample had a coat weight of around 18 g/m^2. All tests were performed in controlled environment of 50% relative humidity and temperature of 21 ^{o}C and the average result from three or more replicates was recorded.

RESULTS AND DISCUSSION

Example Project I – Development of high performance PSA formulation

Getting optimum adhesion - cohesion balance with waterbased acrylic PSAs to match the solvent-based performance is a holy grail. Additives are often used to modify the

adhesion and cohesion behavior. Objective of this study is to improve adhesion to HDPE surface with the use of additives while maintaining the cohesion.

Experimental Design

Typically, one variable at a time experimentation is carried out to improve the cohesion-adhesion balance for waterborne systems but there are a large number of formulation, synthesis and experimental variables that are important and need to be considered in experimental designs. The goal of this project was to utilize existing monomer streams and optimize the adhesion to HDPE substrates by focusing on the formulation variables. For an initial screening design, five formulation variables were evaluated including the latex and a performance additive type, additive amount, wax and tackifier amount. The focus of this screening was to select the monomer stream with the highest potential and to understand the critical interactions among formulation additives that determine the adhesive performance. Five monomer streams were selected and acrylate systems that are known to span the broad range of peel, tack and shear properties were chosen as described in the experimental materials section. Ranges for the amounts of the formulation additives were chosen based on formulations used for a broad range of applications as shown in the table below. The experiments were designed in such a manner such that the performance additive could be chosen from a broad range of additives such as oils, surfactants, other polymers based on polyurethane or acrylate chemistry etc. Keeping the goal of project to improve adhesion to HDPE substrates in mind, three waterborne additives from the large library of chemicals available at Dow were chosen.

Sample Cell	*Latex type*	*Additive type*	*Additive amount*	*Tackifier amount*	*PA1 amount*
A1	PSA4	PA4	30	3	3
B1	PSA5	PA3	5	3	3
C1	PSA2	PA3	30	0.5	3
D1	PSA1	PA4	5	0.5	0.5
E1	PSA3	PA3	17.5	1.75	1.75
F1	PSA4	PA3	5	0.5	0.5
G1	PSA3	PA3	30	3	0.5
A2	PSA3	PA2	17.5	1.75	1.75
B2	PSA3	PA2	5	0.5	3
C2	PSA5	PA2	30	0.5	0.5
D2	PSA1	PA2	30	3	3
E2	PSA2	PA2	5	3	0.5

Table 1: Screening experimental design for a 5 variable parameter space. Mixture of performance additives used with additive 1 common for all formulations. 5 existing base polymers used for improving adhesion to low energy substrates

Formulation

Since an existing library of five polymers was chosen, the synthesis step in the high throughput workflow was skipped and the Hamilton liquid handling robot as described in the experimental method section above was used to make the formulations. Library Studio software was used to program the recipes obtained from the experimental design so that the robot can dose different cells with the set amounts of additives. The robot has 8 channels which allowed us to formulate 8 samples at a time and a library of 12 samples was rapidly generated. The Hamilton robot uses a volume based dosing approach and is faster than some of the other liquid handlers using gravimetric dosing. In order to confirm that the set amount of additives were added, we confirmed the weight using a custom-built automated weighing station and the desired versus actual weight comparison for one of the components with replicates is shown in the figure below. Each formulation has its own unique descriptor which is a combination of the cell name and barcode for tracking results for each sample.

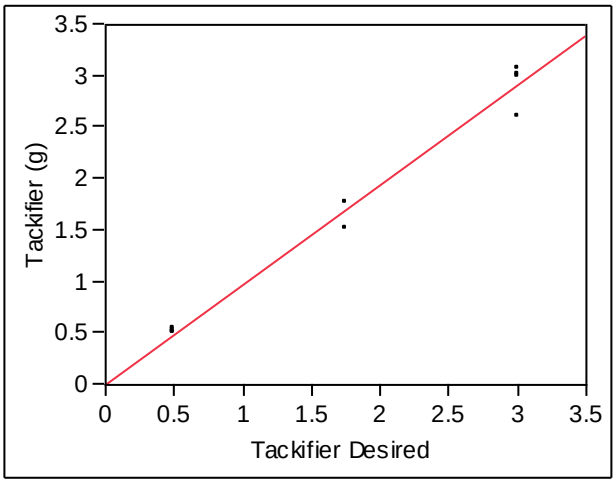

Figure 8: Validation of the Hamilton liquid handling capabilities. Tackifier amount actually dispensed into the formulations as compared to the desired amount as per the experimental design.

Material Characterization and Coating

The viscosity, pH and particle size of the formulations were determined using a combination of automated and manual tools as described in the experimental techniques section. Coated samples were then prepared by direct coating the formulated adhesive onto mylar films (2 mil thickness) using the Symyx Coating Station and also using traditional manual drawdown techniques. The coated samples were then post-cured in an oven at 83 degree Celsius for ten minutes and coat weight was confirmed to be 18 g/m^2.

Adhesive Performance Testing and Data Analysis

The adhesive performance was characterized using tack, peel and shear behavior as primary screens. Peel test was performed using the automated peel tester on both stainless steel and HDPE test panels with a 30 min (initial) and 24 hour dwell time respectively. The peel test was performed in accordance with PSTC-101 Test Method A and the average measurement from three replicate measurements was used for evaluating systems.

This screening design was also used to validate the high throughput workflow by executing the design using a standard manual PSA protocol including formulation using overhead mixers and coating by hand. The average peel results for both steel and HDPE test panels are compared in the figure below for adhesives formulated using the high throughput workflow with those formulated using the standard manual protocol.

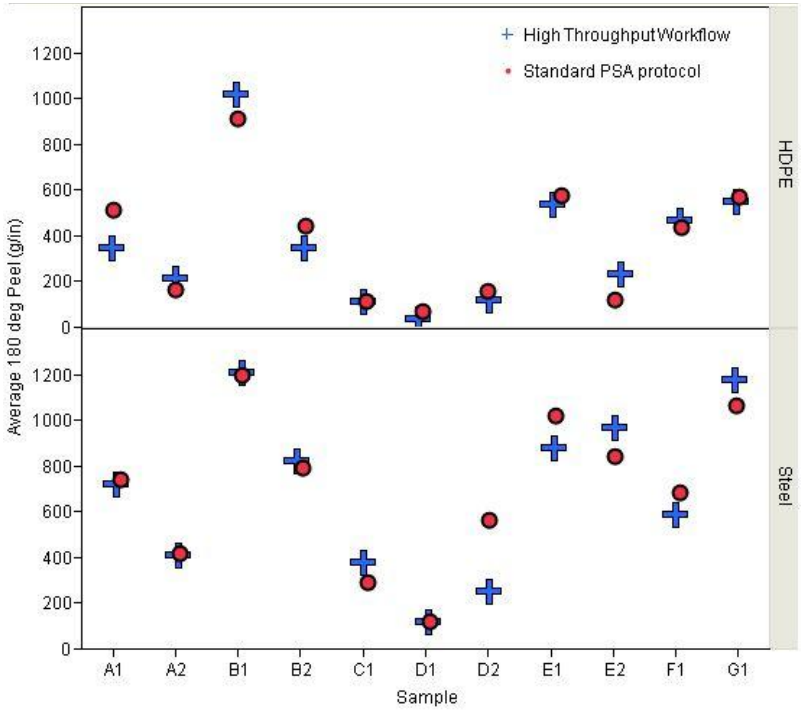

Figure 9: Average 180 degree peel results for the formulations on stainless steel and HDPE substrates. The peel results obtained using the high throughput workflow (plus markers) are also compared to results obtained using a standard (manual) PSA workflow showing excellent correlation.

The cohesion adhesion balance of properties was used for evaluating the different formulations and as expected due to the choice of the base polymers, systems spanning the whole range of peel and shear behavior were obtained. However, results not intuitive to those familiar with the art of formulating PSAs were also observed and synergistic combinations of certain base polymers and performance additives (B1, E1, G1) led to surprisingly good adhesion to low energy substrates while maintaining the high creep

resistance. The results are shown below where the three axes correspond to the 180 degree peel measurement on stainless steel, HDPE and the holding power test.

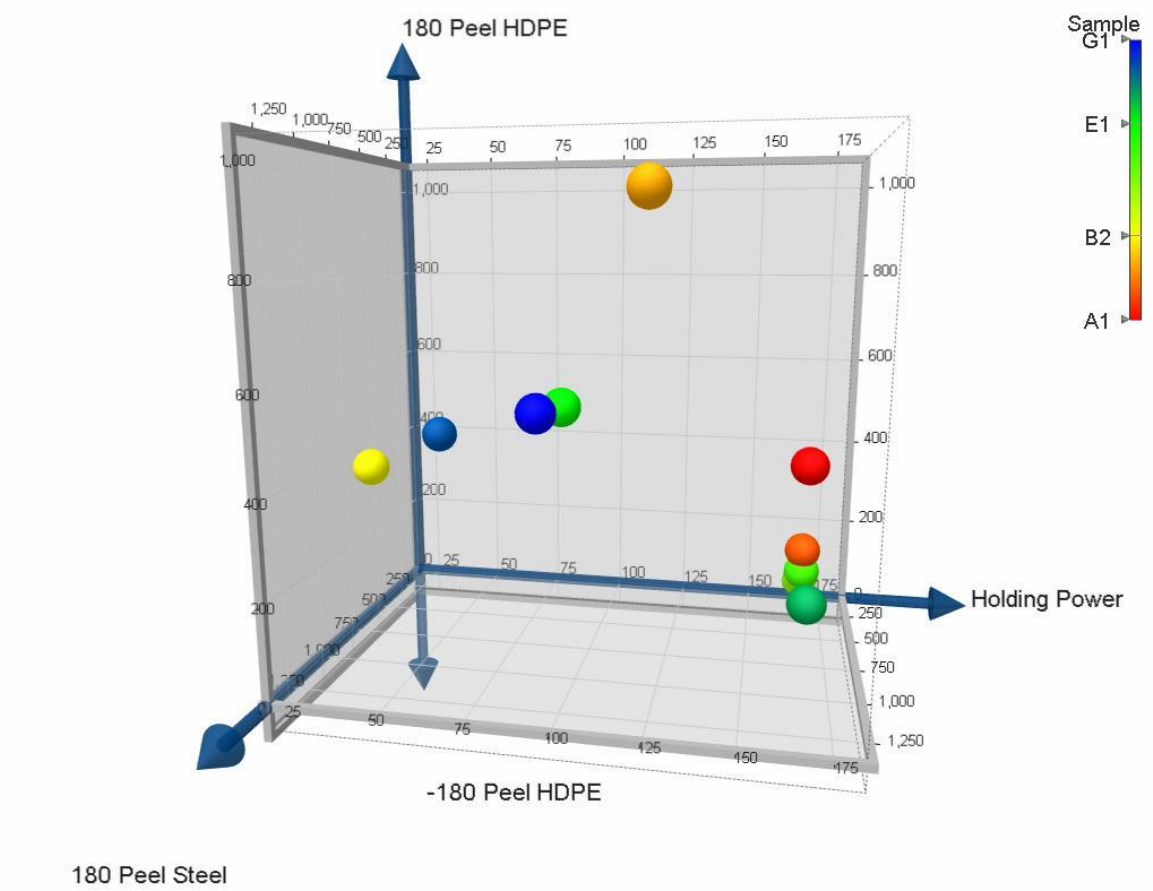

Figure 10: Primary Screening results in a 3 dimensional plot with the shear test results on the x-axis, 180 degree steel results on the y-axis and 180 degree HDPE results on the z-axis. Samples B1 (light orange marker), E1 (green marker) and G1 (blue marker) were hits and satisfied the customer requirements

Statistical software such as JMP was then used to model the variables and interactions important in controlling the adhesive performance. Based on the results from this screening design, the high throughput process was iterated to elucidate the structure property relationships leading to these unexpected but exciting results. Further, multiple experimental designs were also launched to develop predictive models in order to understand the synergistic interactions of certain combinations of performance additives with base polymers.The results from the experimental designs that were subsequently carried out to map out the experimental space around the three successful recipes (B1, E1, G1) are shown in the figure below. The plot below shows the testing results for 36 formulations (12 formulations around the parameter space for each of the hits) with additional information such as the performance additive amount (size of marker) and tackifier amount (color of sample) also depicted using a 3d visualization tool. As can be

seen from the results below, a library of solutions that satisfied the project goals was generated using multiple combinations of performance additives with existing polymers.

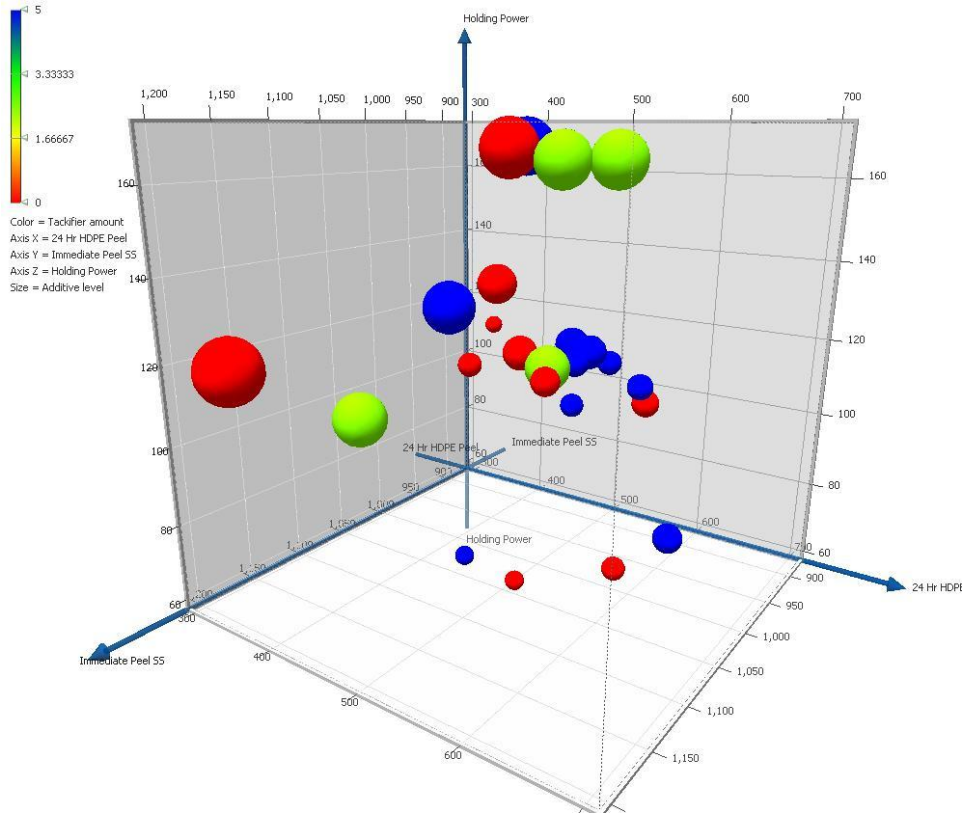

Figure 11: Results from subsequent experimental designs executed in order to map out the experimental space. The 3 dimensional plot shows HDPE peel (x-axis), SS peel (y-axis), shear results (z-axis), tackifier amount (color) and performance additive amount (size). Library of solutions that satisfy the project requirements was thus generated.

This experimental design based high throughput approach was thus highly successful in not only generating a library of solutions from a toolbox consisting of existing polymers and additives but also in generating models that can be applied to solve future customer problems.

Example Project II – Polyurethane Dispersion based Adhesives

Background

In spite of significant efforts during the last several years to design and develop PSAs based on aqueous acrylic emulsions with similar performance parameters as solvent based acrylic PSAs, several gaps exist. A few of the critical unmet needs are:

- Clarity of adhesive in clear label, unaffected by environmental conditions (temperature, moisture)
- Resistance to moisture
- Resistance to chemicals (gasoline, vinyl plasticizer, etc.)
- Resistance to temperature changes (adequate adhesive properties at cold and hot temperatures)
- Higher shear without loss in tack
- Consistent tack and peel strength over time
- Adhesion to low energy substrate materials

It has been hypothesized that aqueous polyurethane dispersions and polyurethane/acrylic hybrids, especially with high solids, could be designed in a cost competitive way to bridge the gap between waterborne acrylics and solventborne acrylics. The progress in this direction is illustrated by several patents and publications, where inherently tacky PUD polymers were developed without the addition of plasticizers or tackifiers, and a balance of permanent tack and cohesive strength was achieved by controlling the polymer design parameters[17,18]. PUDs that can be tailored to have a wide range of peel adhesion and shear strength properties have also been described in the literature[17]. Our goal is to expediently develop a library of PUD systems with a range of viscoelastic properties and unique balance of tack, peel and shear strengths using the high throughput workflow.

Experimental Design

The large number of synthesis, formulation and processing variables important in determining the behavior of PUD system performance provide a significant challenge to the researcher in finding an optimum solution that satisfies all of the customer requirements. Hence, we have used an experimental design generated by using a six-sigma approach to study effect of multiple parameters and their interactions in determining the performance properties of the dispersion.

In this article, we will describe one of the experimental designs that was undertaken to compare two aliphatic diols - a polyether and a polyester polyol in combination with two isocyanates – isophorone diisocyanate (IPDI) and Dow's proprietary aliphatic diisocyanate (ADI). The other experimental variables that are also considered in this screening design are the % hard segment which quantifies the ratio of the hard to soft segments in the polymer and also the type and amount of the surfactant used for the dispersion process. The reaction was catalyzed using dibutylin dilaurate and the chain extender used for this design is 1,2-propane diamine. No emulsifying agent such as DMPA was used during the dispersion process.

An experimental design with 22 dispersions was chosen to map out the parameter space and the design is shown schematically below. Replicates were done at the center points to quantify the variation in the system properties. Also, two combinations of surfactant and isocyanate type were utilized at each boundary and center point as depicted in the design below by different shape and color of the markers respectively. This fractional factorial

design was specifically chosen such that it can be used to statistically model the parameter space including pairwise interactions between different variables.

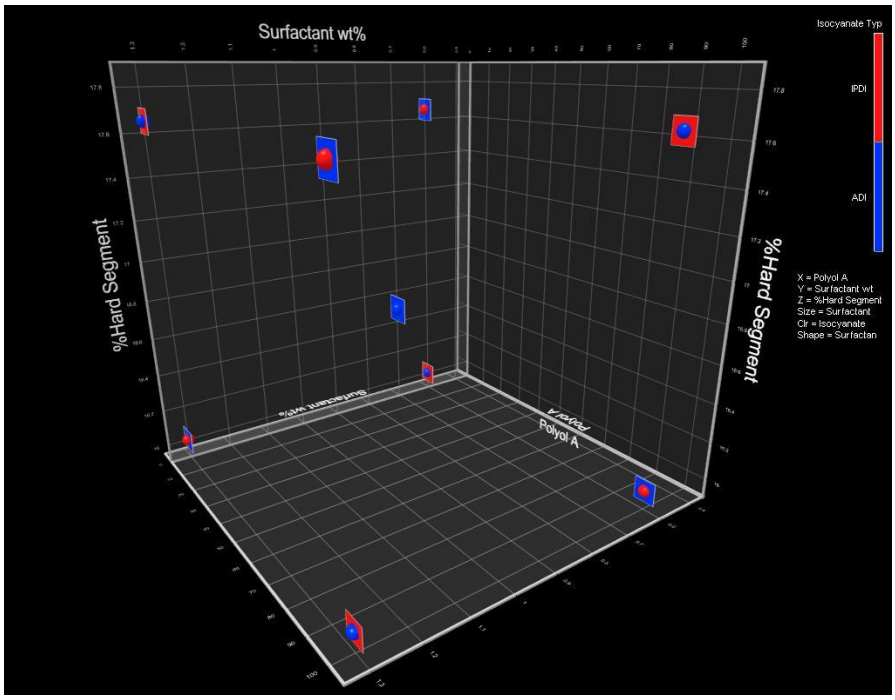

Figure 12: A 5 variable fractional experimental design for PUD systems based on a mixture of polyols (x-axis), two aliphatic isocyanates (color) and three different surfactants (y-axis). Also, %hard segment (z-axis) and the amount of surfactant (size) is varied in the design.

Synthesis and Formulation

The prepolymer synthesis was carried out in a high throughput manner and titration of the prepolymers synthesized indicated that the resulting prepolymers had % NCO levels very close to the design levels and were within acceptable limits of variation (standard deviation ~ 0.1%).

The dispersion process was carried out in the absence of any solvent such as acetone or NMP and vigorous mixing was used to aid the chain extension step. 19 systems out of the 22 system design formed good dispersions without evidence of any agglomeration of particles or change in particle size over a week. The particle size for the different systems varied between 100 nm to 1 microns and the median particle size was around 400 nm.

Material Characterization

The adhesive materials were also characterized using standard thermal and rheological techniques as described in the experimental section above. It was found that the glass transition temperature of the systems was strongly dependent on the

type and mixture of polyols used. Also, the plateau modulus (G') at room temperature was consistent with the Dahlquist criterion for pressure sensitive adhesives (G' (RT) ~ 0.1 MPa). Also, if all other experimental variables were held constant, it was found that plateau modulus could simply be modulated by changing the % hard segment in the recipe as shown in the figure below. This observation is not surprising since % hard segment determines the ratio of hard to soft segments and determines the microphase separation in the system similar to adhesives that are based on block copolymers.

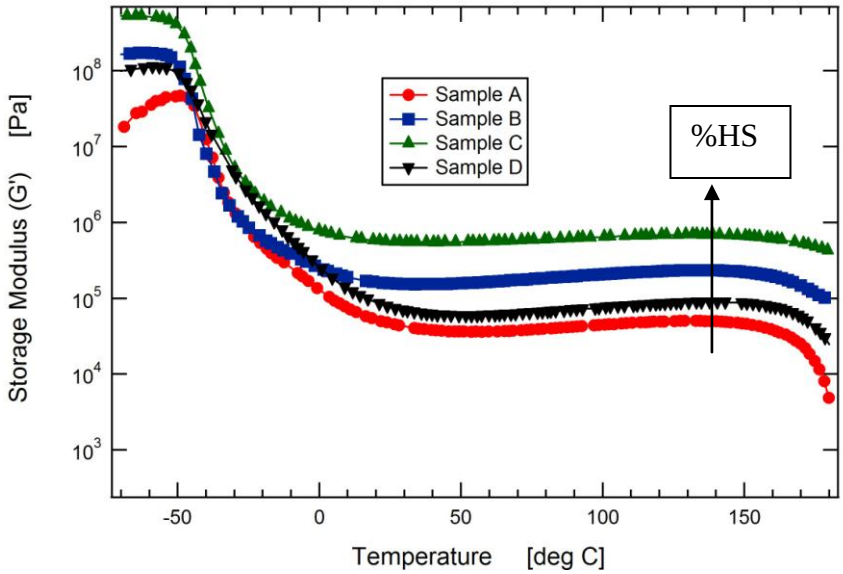

Figure 13: Representative storage modulus results depicting a G'@RT directly dependent on the % hard segment. Curves green to red represent a decreasing % Hard segment. Dahlquist criterion suggests a room temperature storage modulus ~ 0.1 MPa

Adhesive Performance

Primary screening is critical for increasing the throughput in the discovery of a new material as described in the earlier sections. This helps to weed out the majority of the samples that do not show promising behavior. Many project and customer specific screens are then performed only on the promising samples thus reducing the experimentation time and effort involved.

For the purpose of this project, it was deemed important to have a cohesion-adhesion balance and hence, 180 deg peel test on stainless steel substrates and shear test were chosen as the primary screens for this project. Tack of pressure sensitive adhesives was also considered as a primary screen as it is a fundamental property of pressure sensitive adhesives to stick on application of light pressure. Polyurethane dispersions are known to have a number of desirable properties such as good water resistance and

chemical resistance[15,16] and these along with others such as adhesion to low energy substrates formed the secondary set of screens for this study.

The 180 degree peel test and the shear test were performed using the automated mechanical test Frame and shear test rig with samples and data being recorded in the database using barcode information. The results from this preliminary experimental design are shown in the figure below. All systems were found to have extremely good shear properties while the peel performance was found to vary across the board and needed improvement.

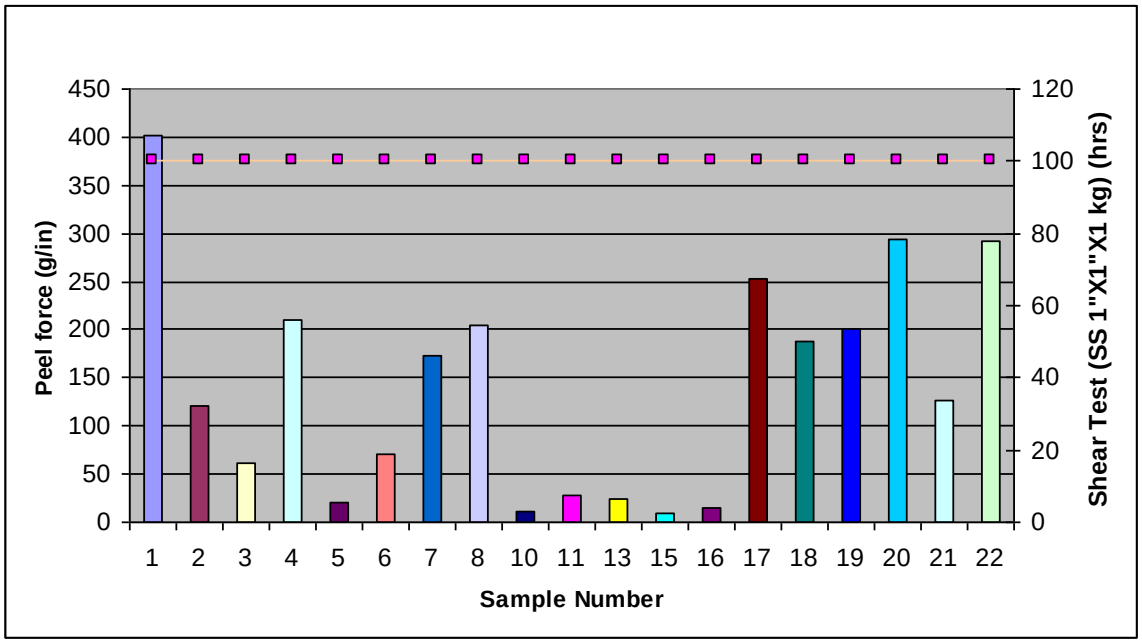

Figure 14: Screening results for the preliminary experimental design showing excellent shear properties but peel properties on stainless steel varying from low to medium.

Statistical modeling of this screening experimental design, which is described in greater detail in the next section, allowed us to find regions in the parameter space that had the potential to give improved adhesive performance. Subsequently, a larger full factorial design was undertaken to explore these regions with high potential and a subset of the results is shown in the figure below. Many of these systems showed the classical cohesion adhesion trade-off wherein increase in the peel performance was attained by sacrificing the high shear performance but at the same time, a few solutions that had the optimum peel performance while maintaining the excellent shear behavior were also discovered.

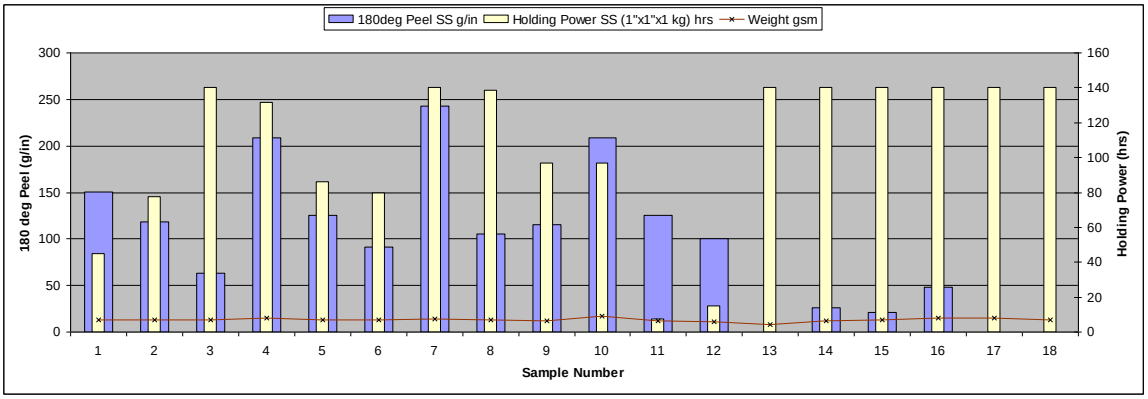

Figure 15: Sample results from a subsequent experimental design showing a wide range of cohesive-adhesive properties. Successive experimental designs were guided by the predictive model results and structure property relationships developed by earlier designs.

Data Analysis and Visualization

Data generated in the experimental designs shown earlier was fed into multiple plotting and modeling softwares such as JMP, MATLAB etc. The model generated not only allowed us to understand the effect of a number of important variables such as polyol type, isocyanate type, % hard segment and the role of formulation additives such as surfactants in determining the adhesive performance, but also allowed us to predict regions in the parameter space with potential for improved performance. These predictive models were then used for guiding the subsequent experimental designs and with each successive design the solution library grows and results that were unexpected in manual experimentation based on informed searches are found.

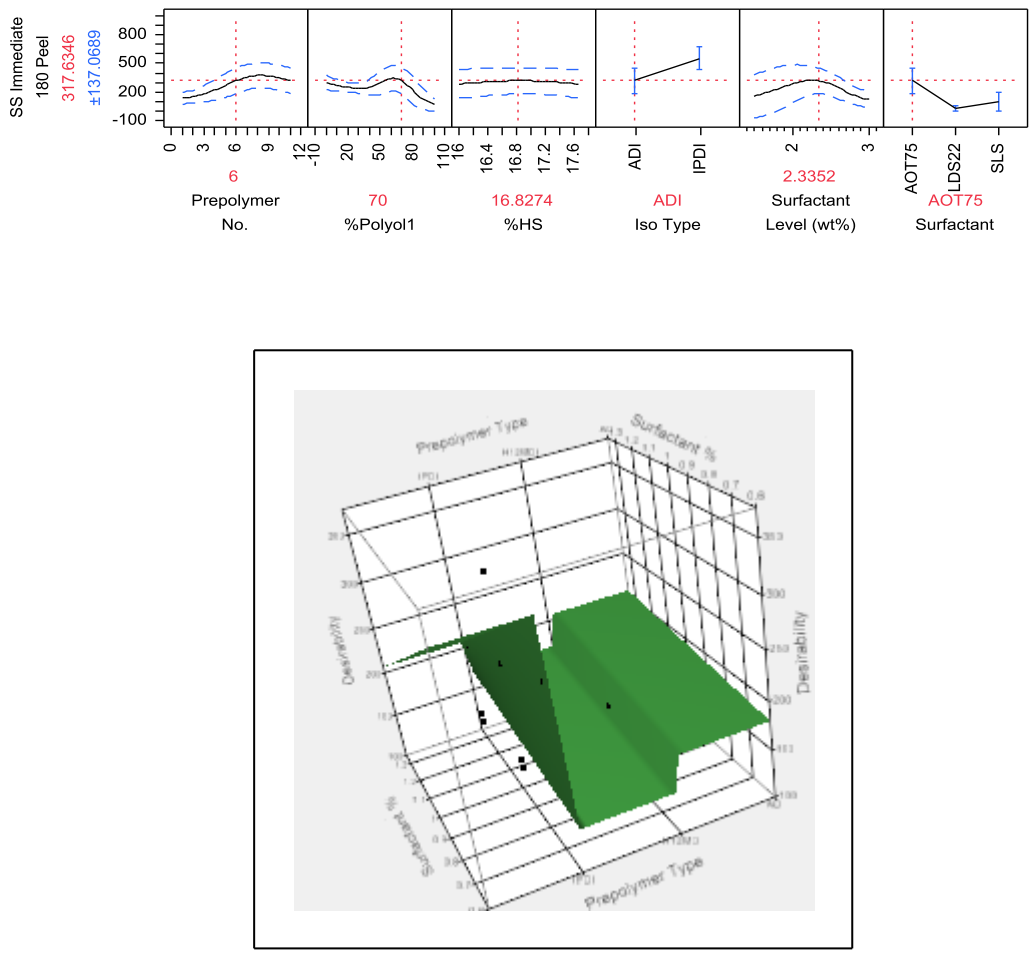

Figure16 : Predictive model developed using the screening results. Also shown is a surface profiler for quick visualization of trends.

The high throughput approach for this project thus helped us map out large parts of the PUD parameter space, elucidate the dependence of adhesive properties on many different synthesis, formulation and processing variables and helped us design polyurethane dispersion systems with optimum adhesive properties for a number of applications.

CONCLUSIONS

The high throughput workflow based on sound experimental design and a seamless, iterative process can hence be successfully applied to both product optimization and new product discovery type of projects. The two examples helped highlight the flexibility of the high throughput PSA workflow developed in tackling challenges and scope that is unique to these efforts. In the first case study we tested the ability of the PSA workflow to formulate with multiple additives viz. tackifiers and other performance additives. Interestingly, we were able to identify formulations using existing base products that had a unique balance of adhesion and cohesion. This exemplifies the capabilities of High throughput research as an enabler for complex multiple variable designs. Similarly for the

PUD system discovery project, the high throughput workflow helped rapidly map out a large experimental space while developing a library of solutions for a host of applications.

In conclusion, we have successfully developed a high throughput workflow that complements standard testing by allowing faster approach to a solution space and eliminating unnecessary experimentation. The high throughput approach in conjunction with the standard PSA protocol can thus be used to expedite solution delivery to a multitude of current and future customer problems.

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