The identification and screening of lower toxicity solvents for contact adhesives

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ABSTRACT

Contact adhesives, which bond to themselves upon contact, frequently contain hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) that detrimentally impact human health and the environment. Commercial formulations containing polychloroprene, SIS, and other rubbers and resins impose demanding requirements that balance solubility, viscosity, evaporation, color, odor, and cost. In this paper, solvent compositions that contain safer solvent alternatives to the hazardous air pollutants, toluene and hexane, and which retain the solubility of contact adhesive polymers and resin in contact adhesives, are predicted with Hansen Solubility Parameters (HSP). A database of solvents selected based on health and environmental data from those available in the *Hansen Solubility Parameters in Practice* (HSPiP) software was used to identify binary and ternary solvent blends based on solubility, evaporation rate, and density. Promising new solvent blend candidates are experimentally tested for solubility, evaporation rate, adhesive application and edge bond strength and their performance compared to commercial formulations.

1. Introduction

Contact adhesives are adhesives that are tacky but non-bonding when contacting other surfaces, but aggressively bond to themselves upon self-contact. This class of adhesive is typically used to bond items with large surface areas; common examples are plastic laminate countertops in kitchens and bathrooms, or any laminate that is bonded to wood or particle board [1,2]. Contact adhesives are rapidly and easily applied to these surfaces by brush or spray equipment; after the evaporation of a solvent component, the surfaces coated with the tacky adhesive are brought into contact under pressure to be bonded [3]. There is a time window during which the bonding can occur, which is known as the open time; the open time is typically between 5 and 60 min after spraying. Some advantages of contact adhesives are that they bond rapidly, possess high shear strength, and are durable [3].

Solvent-based contact adhesive formulations typically consist of a solvent or solvent blend, in which rubber, resin, and additives such as fillers, antioxidants, and curatives are dissolved. The rubber component of the formulation is typically natural, butyl, nitrile, styrene-butadiene rubber (SBR), or polychloroprene rubber [3]. The strength of the adhesive is dictated predominantly by the rubber component [4]. The resin component is added to improve tack, while antioxidants are added to prevent oxidative degradation [3].

Solvents that are used in these adhesives are often primarily selected for technical function and cost, with physical and human health hazards as secondary concerns. Toluene, hexane, methyl ethyl ketone, xylene and methylene chloride are chemicals in commercially available contact adhesives. These solvents, with the exception of methyl ethyl ketone, are classified as hazardous air pollutants (HAPs) by the U.S. Environmental Protection Agency (methyl ethyl ketone was removed from the HAPs list in 2005). Exposure to these chemicals can cause polyneuropathy, pulmonary edema (i.e., fluid in the lungs) and can harm the reproductive system causing birth defects [5]. Beyond human health effects, contact adhesives with flash points below room temperature have the potential for dangerous physical behavior. Their flashpoints, the lowest temperature at which the chemical vapors will ignite, range from − 26 to 6 °C [6]. In the late 1970s, approximately 130 burn injuries and 15 deaths were attributed to fires and explosions caused by the vapors from contact adhesives within a 7 year reporting period [7]. These documented hazards resulted in a ban of containers larger than one-half pint (0.24 L) for extremely flammable contact adhesives that have a flash point at or below 20 °C [7]. The focus of this paper will be on the replacement of the hazardous air pollutants toluene and hexane. Toluene is also a volatile organic compound (VOC),

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meaning that its vapors participate in photochemical reactions with the sun to produce smog [8]. Long-term inhalation exposure to toluene may permanently damage the brain and cause loss of speech, hearing, muscle control, and memory [8,9]. Toluene inhalation can also cause central nervous system (CNS) depression, which decrease a person's breathing and heart rate resulting in a coma [8]. Hexane is a VOC and is highly flammable [10]. Long-term inhalation exposure to hexane may lead to numbness in the hands and feet, which can result in peripheral neuropathy, i.e., paralysis of the arms and legs [10,11].

The primary function of the solvent blend is to dissolve the solid rubber and resin components, a function that must be met for any suitable replacement solvent composition. The solubility of polymers within solvents can be predicted by the use of Hansen Solubility Parameters (HSP). HSP consists of three intermolecular bonding forces (i.e., parameters) to characterize the interaction of a chemical with other components. These parameters are the dispersion parameter (∂D), the polarity parameter (∂P), and the hydrogen bonding parameter (∂H) [12]. The HSP values of a solvent blend is calculated based on the sum of individual solvent component HSP values multiplied by their respective volume fractions as seen in Eqs. (1)–(3) [13]:

$$\partial D_{blend} = \sum_{i=1}^{n} \partial D_n \varnothing_n \tag{1}$$

$$\partial P_{blend} = \sum_{i=1}^{n} \partial P_n \varnothing_n \tag{2}$$

$$\partial H_{blend} = \sum_{i=1}^{n} \partial P_n \varnothing_n \tag{3}$$

Polymer solubility within a solvent is predicted by similarity of their respective HSP values [14]. Every polymer has a solubility sphere defined by a center and a radius located in the ∂D, ∂P, ∂H parameter space [13]. Solvents that reside within the volume of the polymer (solute) solubility sphere, are predicted as likely to dissolve the polymer. The closer a solvent is located to the center of a polymer solubility sphere, the more likely it is to dissolve that polymer.

HSP values can also indicate similar solubility properties of solvents based on the location of each solvent; the nearer that solvents are positioned to each other in HSP space, the more alike they are in terms of solutes that they can dissolve [13]. The distance between HSP points in solubility space, δ, is calculated by Eq. (4):

$$\delta^2 = 4(\partial D_1 - \partial D_2)^2 + (\partial P_1 - \partial P_2)^2 + (\partial H_1 - \partial H_2)^2 \tag{4}$$

The coefficient of four associated with the ∂D parameter is an empirical coefficient that adjusts the ellipsoid into a sphere [13]. The relative energy difference (RED) provides a metric for relative solubility and is calculated by Eq. (5):

$$RED = \delta/r \tag{5}$$

where r is the radius of the sphere [13]. A perfect match of the solvent and solute corresponds to a RED value of 0. A solvent positioned on the surface of the solute sphere has a RED equal to 1. If the RED > 1, then the solute/solvent mixture is considered incompatible, while if the RED < 1 the solute/solvent mixture is considered compatible. The lower the RED value, the more soluble the solute will be in the solvent blend [13]. Therefore, HSP values can be used to identify solvents and solvent solutions that are similar to a target solution.

Hansen Solubility Parameters are a beneficial concept to reduce the use of toxic solvents in a myriad of research applications, including membrane processing, cosmetics, and assessing the solubility properties of safer biomass-derived solvents compared to toxic petro-derived solvents. The creation of polymeric membranes typically involve dissolution of a polymer in a solvent, the homogenous solution is subsequently cast as a flat film and the membrane is formed by evaporation of the solvent fraction [15]. The solvents typically used in this process, such as dimethylformamide, dimethylacetimide, 1,4-dioxane and tetrahydrofuran, are toxic (i.e., hazardous to human health) [15]. Using the HSP values of the membrane material cellulose acetate (CA), researchers searched for small distances between the HSP values of CA and the safer solvents. Safer solvents and solvent combinations that would dissolve the polymer were successfully predicted [15]. Within the cosmetic industry, petrolatum (i.e. petroleum jelly) is the main component in many lotions and ointments such as Vaseline. However, petrolatum is frequently contaminated with carcinogenic polycyclic aromatic compounds [16]. A study investigated a mixture of an ethyl-cellulose (EC) polymer and an oil and/or surfactant as a safer alternative to petrolatum [16]. The more closely the HSP values of the EC polymer matched of those to the oil/surfactant, the better the two were shown to mix [16]. In an effort to reduce greenhouse gas emissions and the use of fossil fuels, bio-based solvents made from biomass feed stock have been in increasing demand [17]. One study investigated whether the bio-based solvents glycerol acetals and ketals provided similar solubility to the petro-based solvents glycol ethers and aniline [17]. The concept of HSP was used to identify similarities in solubility properties of solvents by their location in HSP space [17]. In these and other cases, the use of HSP provides predictive power that improves beyond a "guess and check" method, enabling the rational search for new chemical combinations.

Beyond satisfying solubility criteria, alternative solvents for contact adhesives must satisfy additional physical, economic, and safety criteria. The primary physical requirements for the new solvents are that they possess a fast to medium evaporation rate, stable solubility at low temperatures, low to medium odor, and are colorless. The solvent component must evaporate quickly without adversely affecting the ultimate bond strength in order to reduce the time between spraying and bonding. The relative evaporation rate (RER) is a chemical's evaporation rate normalized to the evaporation rate of diethyl ether. The RER values range from 200–1000 for solvents used in contact adhesives. The solvents also need to have stability at low temperatures to enable pumping of the chemical formulation throughout the plant. The odor should not be pungent and be sufficiently mild so that it is not overly offensive to workers. The color should be clear to allow dyeing of the adhesive so that workers can visualize the adhesive coverage of the substrate. From a commercial perspective, these solvents should be readily available in sufficient quantities and have a low cost per kg in order to be economically feasible.

In terms of safety and environmentally friendly criteria, the new solvents should not be listed as a hazardous air pollutant (HAP) and avoid excessive VOC emissions. A chemical qualifies as a HAP if it is known to cause cancer or other serious health impacts such as reproductive mutations [18]. The need for low to no HAPs within contact adhesives has triggered research for alternative solvents to HAPs. U.S. Army surveys found 33% of Army HAP emissions were due to emissions from adhesives under the A-A-1936A specification [19]. In 2014, the Army Research Laboratory performed a study to evaluate HAP-free or low-HAP contact adhesives that meets the A-A-1936A specification [20]. The elimination of HAPs was considered the cheaper and more efficient alternative to emission control devices [19]. While none of the adhesive candidates studied met all the requirements under this certain specification, 3M's Scotch-Weld 94 CA high strength adhesive matched performance metrics; however, further modifications would be needed to satisfy the open time specification [20].

New government regulations are limiting the emissions of VOCs. Many states such as California, Massachusetts, Maine, and Virginia have adopted a 250 g/L limit on VOCs (per EPA Method 24) within a contact adhesive product. Any product exceeding this VOC threshold cannot be sold in these jurisdictions. There are a limited number of solvents that are considered VOC-exempt, which restricts the ability to reformulate adhesives. In order to meet this 250 g/L specification, some companies have introduced water-based contact adhesive products [21]. Although these water-based contact adhesives satisfy safety and environmental requirements their performance is lacking [21]. These

water-based adhesives compare poorly to solvent-based systems with regards to reduced peel strength, adhesion to a more limited set of substrates, and excessively lengthy dry time (approximately 20 min whereas solvent-based systems' dry time is approximately 6 min) [21]. Due to this compromised performance, there is a need for new solvent-based contact adhesives that satisfy performance but meet the 250 g/L VOC content limit to satisfy health and environmental concerns.

Here, we establish a rational methodology to find solvent combinations for contact adhesives that meet the technical and economic requirements of contact adhesives but eliminate HAPs and can meet VOC emission limits. A database of safer chemicals is generated and input to the software package *Hansen Solubility Parameters in Practice* (HSPiP). Safer solvent blends are identified that possess HSP parameters similar to commercial contact adhesive formulations containing toluene and hexane. These novel solvent blends are tested for their solubility, evaporation rate, spray application and bond strength and their performance compared to their commercial formulation counterparts.

2. Experimental

2.1. Materials

Rubber, resin, and antioxidant components of interest were obtained from ITW Polymer Sealants (Rockland, MA) to form two control formulations. Control formulation 1 contains polychloroprene rubber and resin 1, a hydrocarbon resin, while control formulation 2 contains styrene-isoprene-styrene (SIS) tri-block copolymers and resin 2, a phenolic resin. The solvents toluene, hexane, and acetone were provided by ITW. Reagent grade methyl acetate, parachlorobenzotrifluoride (PCBTF) ($C_7H_4ClF_3$) (see Supplementary information for the chemical structure) [22], cyclohexene, methyl cyclohexane and cyclohexane were used as purchased from Fisher Scientific. Bond characterization was performed on standard consumer particleboard substrates and high pressure decorative laminates (HPDL).

2.2. Polymer sphere calculation

Solubility spheres in HSP space were determined for each of the polychloroprene rubber, resin 1, SIS rubber, and resin 2 components. Each solid component was mixed with twenty-seven different solvents and solvent combinations (Table S1 in Supplementary information section) that covered a broad area within HSP space. Approximately 10 mL of solvents and 1 g of the solid component were added in a 20 mL glass scintillation vial. After a dwell time of 24 h at ambient temperature with no mechanical agitation, the dissolution of the solid component was assessed. Within the HSPiP software, a value of 1 is input for a solvent that dissolved the rubber or resin within 24 h, while a value of 0 is input for a solvent if the polymer was insoluble. From this experimental data, the HSPiP software calculates the center and radius of the best-fit sphere.

2.3. Identifying safer solvents

In order to identify alternative safer solvent solutions, the software HSPiP was used. The HSP values of the two solutions of toluene, hexane, and acetone were found through the software. The HSP values were target values against which the HSPiP solvent optimizer searched a customized database. This database, composed of approximately 2000 safer chemicals, was generated based on metrics related to reduced toxicity, environmental, or flammability hazards. The list of chemicals best matched to the target values was narrowed to 18 based on price (less than $11.03/kg), relative evaporation rate (100 and greater), and phase (liquid only) constraints. The pairwise and triwise functions in the optimizer were used to calculate solvent combinations that are closely positioned to the HSP target values. The closest positioned solvent combinations were plotted on the polymer solubility spheres to

ensure that each solvent solution is likely to dissolve the given rubber or resin.

2.4. Solubility testing for safer solvents

The solvent blends that were identified as likely to dissolve the rubber and resin were experimentally tested for solubility. Ten milliliters of the solvent solution was placed in a 20 mL scintillation vial. Vials containing 5.33:1 of solvent solution to polychloroprene rubber and resin 1 and 1.84:1 of the solvent solution to SIS rubber and resin 2 were created. The vials were shaken at 90 rpm on a platform shaker (New Brunswick Scientific C1). Every 30 min the vials were shaken vigorously by hand for 30 s to disperse agglomerated components, then returned to the platform shaker. The time at which each component completely dissolved was noted.

2.5. Evaporation testing

The evaporation time was quantified for solvent blends in which the rubber and resin fully dissolved. A balance (model PI-214, Denver Instruments) recorded the sample mass as a function of time. A solvent blend specimen of approximately 0.1 g of initial mass was measured until the mass reached a plateau value.

2.6. Adhesive mixing and rheology

Formulations were scaled to 1 gallon (3.785 L) for rheology and spray testing. The adhesive was prepared by the addition of the required ratios of rubber, resin, and antioxidants to a mixing container, after which the solvent was added. The containers were sealed and mixed by continuous rolling overnight. If the adhesive appeared non-homogenous after mixing, it was further mixed via mechanical shearing at 3800–7600 rpm using a high shear mixer (Ross), after which solvent was added to replace the lost solvent. The containers were re-mixed by roll mixing to form a homogenous dispersion. The viscosity of the adhesive was then measured at 25 °C using a Brookfield viscometer to determine the adhesive was suitable for spray application.

2.7. Spray testing

Spray application of the adhesives was tested. Oil Red B4 liquid was added to the adhesive to visualize the adhesive spray pattern. The adhesive was loaded into a Binks 2100 gun and SG2 plus pot. A series of nozzle and pot pressure adjustments were made to generate similar patterns of coverage between the baseline formulations and the new solutions.

2.8. Mechanical testing

The adhesive was tested for its ease of application, the duration of the open time and its edge lift strength. Six 4.125 in. × 6 in. (0.1 m × 0.15 m) particle boards and twelve 4.125 in. × 3.125 in. (0.1 m × 0.08 m) plastic laminates were sprayed over an exposed area of six particle boards. The open time of the baseline formulations occurs after 10 min. Three laminates were bonded to the particle board at this 10 min time; subsequent specimens of three laminates were bonded 15 min, 30 min and 60 min after this point. A J-roller was used to secure the bond to the test samples immediately after they were bonded. The HPDL laminate uplift strength was tested on a universal testing machine (Instron-5567). In this test, the edge of the laminate was pulled upwards at a given crosshead speed while the particleboard substrate remained stationary. The test continued until there was a failure in the adhesive or in the laminate. The crosshead speed was set to 21.6 mm/s (5 in./min) and the peak load was measured. This test was performed on specimens bonded after 1 day and 7 days.

Table 1
Summary of solvent blend solubility properties (SIS = SIS, CR = polychloroprene, HF = HAP-free, LV = low VOC).

Formulation	Solvent 1		Solvent 2		Solvent 3		∂D	∂P	∂H
	Name	vol%	Name	vol%	Name	vol%			
SIS-control	Toluene	10–30%	Hexane	5–50%	Acetone	15–45%	16.3	4	3
SIS-HF1	Methyl Acetate	50%	Cyclohexene	35%	Methyl Cyclohexane	15%	16.2	4	4.7
SIS-HF2	Methyl Acetate	55%	Cyclohexene	45%	–	–	16.3	4.4	5.1
SIS-HF3	Methyl Acetate	20%	Cyclohexane	50%	Acetone	30%	16.15	4.6	3.7
SIS-HF-LV	Methyl Acetate	63%	Cyclohexane	20%	PCBTF	17%	16.1	5.2	5.3
CR-control	Toluene	10–31%	Hexane	23–59%	Acetone	17–45%	16.0	3.8	2.6
CR-HF1	Methyl Acetate	50%	Cyclohexene	35%	Methyl Cyclohexane	15%	16.2	4	4.7
CR-HF2	Methyl Acetate	55%	Cyclohexene	45%	–	–	16.3	4.4	5.1
CR-HF3	Acetone	52%	Cyclohexane	48%	–	–	16.1	5.4	3.7

3. Results

3.1. Identifying safer solvents

In order to identify solvent blends safer than those used in two commercial contact adhesives, the use of HSP and polymer solubility concepts were implemented via the software HSPiP. The new solvent blends should not be a hazard to human health or the environment while meeting the technical requirement of dissolving both types of rubber and resin while remaining affordable. Five distinct solvent blends were identified that balance the competing requirements for each type of adhesive. A summary of these solutions and their HSP values are provided in Table 1. The HSP values represent the bond energy from the dispersion, polarity and hydrogen bond forces respectively; the solutes and solvents possess greater compatibility when these values are more closely aligned (i.e., the concept of "like dissolves like"). The similarity of the HSP values shown in Table 1 indicate that these novel solutions are likely to be compatible with the rubber and resin. The satisfaction of requirements and anticipated cost is seen in Table 2. Two solvent solutions were found (XX-HF1, XX-HF2) to dissolve the solid components for both the polychloroprene (CR) and the SIS rubbers (SIS) adhesives and which are HAP-free (HF); however, the cost is high relative to commercial products. Two other formulations (CR-HF3 and SIS-HF3) were found to be HAP-free as well as having a low cost (the target price being between $1.26/kg and $1.43/kg). For these two formulations, CR-HF3 is only suitable to dissolve solids for the polychloroprene-based adhesive, while SIS-HF3 is suitable for the SIS adhesive. Lastly, a fifth solution (SIS-HF-LV) was found for the SIS adhesive; it is HAP-free and meets a low VOC (LV) requirement of 250 g/L VOC content. In summary, all solvent blends are HAP-free, SIS-HF-LV meets the VOC standard, and CR-HF3 and SIS-HF3 meet the price target.

The HSP values for each formulation listed in Tables 1 and 2 were graphed with the polymer spheres in the HSPiP software. Any solvent blend that is positioned within the bounds of both the rubber and resin spheres is considered likely to dissolve both the rubber and the resin. A junction point represents the calculated optimal location for a solvent

Table 2
Summary of solvent blend HAPs and VOC content and estimated cost.

Formulation	HAPs free?	VOC content (g/L)	Cost ($/kg)
SIS-control	No	373	0.90
SIS-HF1	Yes	424	1.83
SIS-HF2	Yes	409	1.96
SIS-HF3	Yes	413	1.30
SIS-HF-LV	Yes	242	1.58
CR-control	No	607	0.86
CR-HF1	Yes	636	1.82
CR-HF2	Yes	631	1.96
CR-HF3	Yes	687	1.23

to dissolve both the rubber and the resin within the overlap region of the two spheres. These graphs are shown in Fig. 1. Each solvent blend is positioned well within the bounds of the spheres and are closely located to the junction point estimated by the software to be an optimal composition.

3.2. Solubility testing

The solvent blends in Table 1 were tested to experimentally verify their ability to dissolve the polymer and resin components. The solvent blend was combined with either rubber or resin and observed for dissolution. Table 3 shows the dissolution time for each of the rubbers and resin in the solvent mixtures.

The solubility of a solute in a solvent solution is related to the solvent's location in comparison to the solute sphere in HSP space. The closer the solvent is towards the center of the sphere or the junction point, the better the solubility becomes. For example, CR-HF3 is closest of all solvent blends to the optimal junction point in Fig. 1a. This results in a half-hour reduction in the dissolution time for polychloroprene rubber relative to the other solutions. Overall the dissolution times in Table 3 are similar to the control solutions and do not exceed the original solution times by more than 0.5 h. Though there is a slight increase in dissolution times for some solutions, solvent-based contact adhesive manufactures typically mix the solvent and polymers overnight (i.e., in excess of 12 h). As long as the solvent dissolves the polymers within 24 h, it's considered a good candidate. All solvent blends dissolved the rubber and resin in adequate time, therefore were all considered viable candidates.

3.3. Evaporation testing

A rapid evaporation rate is essential to reduce the dry time of the adhesive, after which bonding can occur. Moreover, if the evaporation rate is not rapid and too much solvent remains, the strength of the bond may be lessened. Lifting or bubbling of the substrate can also result from trapped solvents. The relative evaporation rates (RERs) of the chemicals being used (Table 1) are all above 100 with the exception of PCBTF, which has an RER of 21.8, indicating that its evaporation rate is relatively slow. Evaporation of neat solvent mixtures was measured to ensure that the new solvent blends evaporated quickly to allow rapid bonding after spray-up. The data from these evaporation tests was normalized by the initial solvent mass and is shown in Fig. 2.

Fig. 2 shows both control solutions evaporating within 5 min (300 s), which was the target range for the new solutions. SIS-HF1, CR-HF1, SIS-HF2, CR-HF2, SIS-HF3 and CR-HF3 all evaporated at a rate equal to or more rapid than the control solutions (Fig. 2). SIS-HF-LV, by contrast, evaporates in approximately 20 min (1200 s). SIS-HF-LV contains 17% PCBTF; this PCBTF component of SIS-HF-LV evaporates more slowly and could in theory extend the period of time between the spray application and the beginning of the open time. However, after 10 min, 90% of the solvent mixture had evaporated, which could be
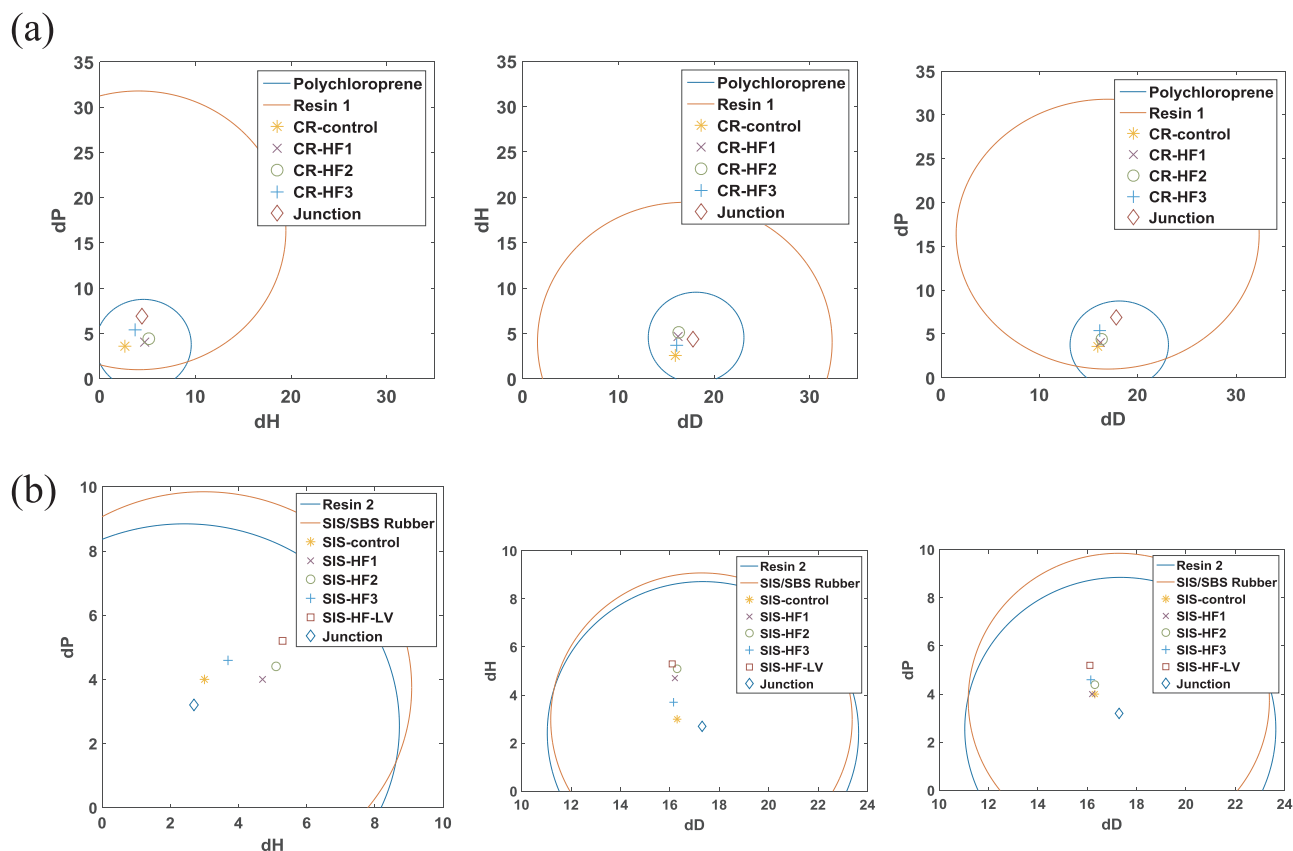
Fig. 1. HSP values of HAP-free and low VOC formulations superimposed on 2D projections of 3D HSP solubility sphere for polymer and resin. (a) Polychloroprene formulation (b) SIS formulations.

Table 3
Solubility results of solvent solutions for polychloroprene, SIS, and resins.

Formulation	Rubber (CR or SIS) (h)	Resin (1 or 2) (h)
SIS-control	1.35	0.35
SIS-HF1	1.18	0.35
SIS-HF2	0.98	0.32
SIS-HF3	1.57	0.72
SIS-HF-LV	1.37	0.70
CR-control	5.07	0.05
CR-HF1	5.07	0.05
CR-HF2	5.07	0.05
CR-HF3	4.37	0.08

Table 4
Viscosity of the SIS adhesive and the polychloroprene adhesive formulations.

Test day	Formulation	Brookfield viscosity	Viscosity (Pa-s)
Round 1	SIS-Control	32	0.16
	SIS-HF1	48	0.24
	SIS-HF2	50	0.25
	CR-Control	35	0.175
	CR-HF1	88	0.44
	CR-HF2	97	0.485
Round 2	SIS-Control 2	37	0.185
	SIS-HF3	72	0.36
	SIS-HF-LV	61	0.305
	CR-Control 2	37	0.185
	CR-HF3	52	0.260

sufficient to initiate the open time.

3.4. Spray testing

The viscosity of the adhesive is an important property to ensure that it would not clog the nozzle during spray application. Table 4 shows the viscosity measurements. The viscosity for the two target solutions was tested for each round of testing, which were performed on different days.

In round 1, formulations SIS-HF1, CR-HF1 and SIS-HF2, CR-HF2 have viscosities that are 50%, 151%, 56%, and 177% higher than the target solutions, respectively. The difference in the viscosities is likely related to the difference in the solids loading fraction. The commercial adhesive ratio of solvent to rubber, resin and additives is based on weight; hence, the new solvent mixtures, which are more dense than the control composition, results in a lower volume of solvent added to the adhesive to maintain the same weight ratio. In round 2, CR-HF3,
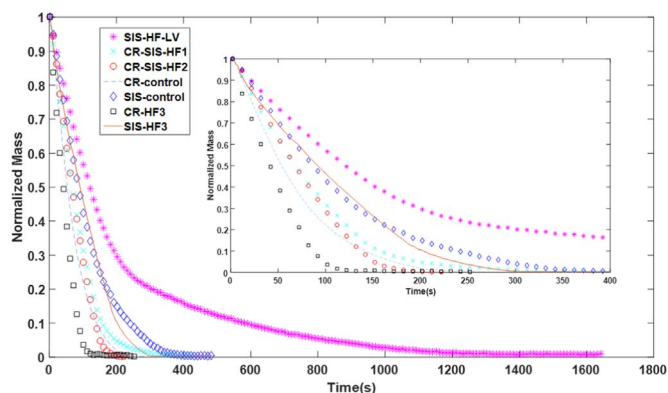

Fig. 2. The change in normalized mass of solvent blends vs. the time. Inset graph expands the first 400 s of evaporation data.

Fig. 3. Image of SIS adhesive spray pattern: optimized for solubility (left) and optimized for cost and low VOC (right).

SIS-HF3, and SIS-HF-LV were created to match the solids loading fractions of the controls. While these adhesives were prepared on a volume basis to lower the viscosity, the viscosities of the new blends remained greater than that of the control. The viscosity of CR-HF3, SIS-HF3, and SIS-HF-LV are 40%, 94%, and 65% greater than the baselines, respectively. Despite the observed viscosity increases, the viscosities were sufficiently low for spray gun application of the adhesive.

The spray patterns of each adhesive were assessed by spraying the formulations through a spray gun onto a kraft paper substrate. The spray gun can be adjusted in order to produce the same spray patterns over a range of viscosities. For the polychloroprene adhesive the spray gun was set to 100 psi ($689,500 \text{ N/m}^2$) of air pressure (in the nozzle of the hose) and 13 psi ($89,630 \text{ N/m}^2$) of pot pressure (inside the canister containing the adhesive). For the SIS adhesive the air pressure was set to 40 psi ($275,800 \text{ N/m}^2$) and the pot pressure was set to 6 psi ($41,370 \text{ N/m}^2$). The resulting spray patterns are shown in Fig. 3 for the SIS-based adhesive and Fig. 4 for the polychloroprene based adhesives.

As can be seen in the images on the left in Figs. 3 and 4, the spray patterns appear qualitatively similar between the three different
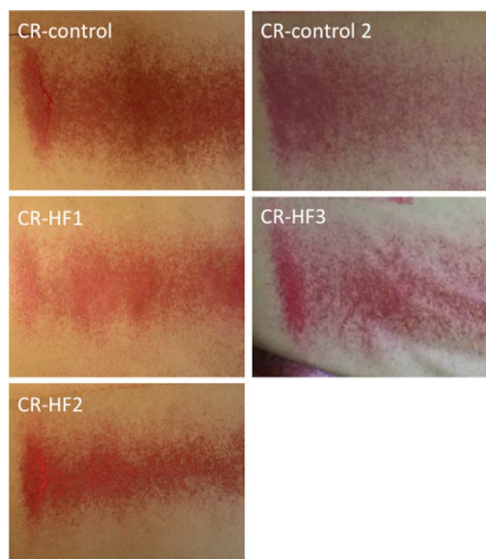

Fig. 4. Polychloroprene adhesive spray pattern: optimized for solubility (left) and optimized for cost (right).

adhesives. The SIS-based adhesive shown in Fig. 3 on the left maintained the same spray pattern under the same translation rate of the spray gun for the control and two HAP-free formulations. The polychloroprene-based control adhesive shown in Fig. 4 on the left sprayed on easily whereas the adhesives for CR-HF1 and CR-HF2 had to be applied with a slower translation rate in order to obtain the same spray pattern; this slower translation rate was attributed the higher viscosities of CR-HF1 and CR-HF2. If the formulation is corrected to consider volume fraction instead of weight, this problem is anticipated to be reduced. In Fig. 3 on the right the control and SIS-HF-LV both display similar spray patterns whereas SIS-HF3 has a more speckled look. This speckled pattern could be due to the faster evaporation rate of SIS-HF3 relative to the other two formulations. When the adhesive exits the spray gun nozzle it is rapidly hit with air accelerating the evaporation rate of an already fast evaporating solvent. As soon as the adhesive leaves the nozzle of the spray gun the solvent starts evaporating and the rapid movement of the air disperses the solvent into the environment. This rapid solvent loss thickens the adhesive making it difficult for the spray gun to spray a continuous and homogenous pattern. The result would produce the speckled pattern that is seen in SIS-HF3 instead of the smooth web pattern that is observed in the control and SIS-HF-LV. Fig. 4 on the right shows the control solution and CR-HF3 displayed similar spray patterns with little to no adjustment of the spray nozzle.

3.5. Bond strength testing

The primary function of a contact adhesive is to provide a secure bond. In order to make sure that the contact adhesive has adequate strength, the bonded laminates are tested by the edge lift test. After 24 h the specimens that were bonded 10 min after spraying (i.e., at the start of the open time) were tested for strength. The peak load was measured. The results are shown in Fig. 5.

Based on typical commercial formulations, the SIS adhesive peak load is typically expected to be between 222 and 334 N (50–75 lbf) and the polychloroprene adhesive peak load is expected to be between 267
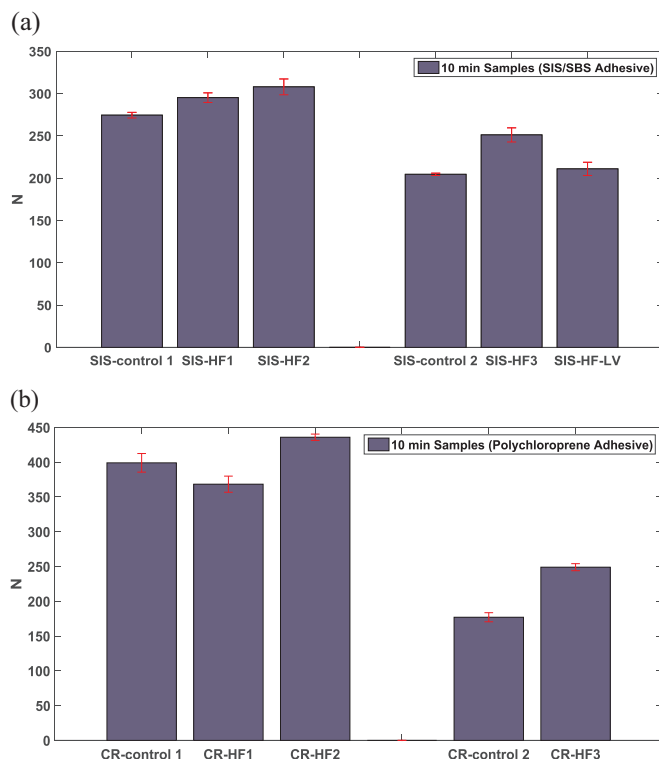

Fig. 5. 24 h cleavage results with a 10 min open time. (a) SIS adhesive. (b) Polychloroprene adhesive.
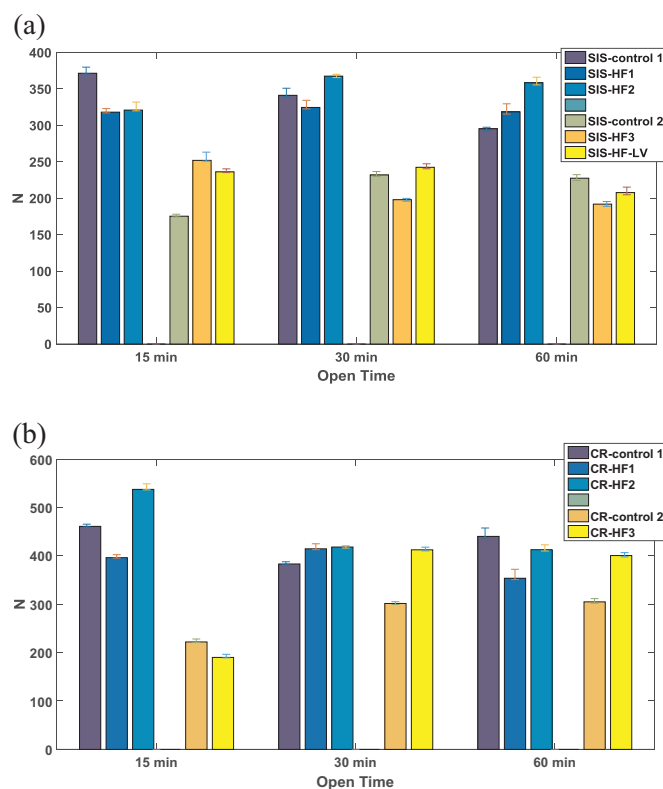
Fig. 6. 7 day strength results for specimens bonded 30, and 60 min after spraying: (a) SIS adhesive, (b) polychloroprene adhesive.

and 445 N (60–100 lbf). Fig. 5a and b show all adhesives falling within the given expectations for round 1 of testing. Most of the solutions, including the controls, tested in round 2 fall below the given expectations (Fig. 5a and b). A possible reason for these lower results is that the pressure applied to the laminates – which is applied by a human operator – was likely decreased in round 2 of testing. While this manual pressure application is known to introduce variation into the testing, it is representative of adhesive bonding in the field, and is a standard method used in industry to assess the bond strength. Additional potential sources of variation between batches include the solution viscosities, which can affect the spray pattern and the deposited amount, and the temperature and humidity, which vary substantially between seasons. Even though the strength of the formulations in round 2 fell below the typical range, the HAP-free and lower VOC adhesive formulations still exhibited 3–40% greater strength than the control laminates. The data shows that the open time for each adhesive occurs within ten minutes, matching the quick time of the commercial formulations. The edge lift test is performed for specimens seven days after being bonded to make sure that the strength is maintained throughout the open time. If the load decreases significantly from the 30 min to 60 min (1800 s–3600 s) specimen, then that indicates that the open time is reduced. Specimens that were bonded after 15 min, 30 min, and 60 min from the time that the specimens were sprayed were tested for strength. The results are shown in Fig. 6.

The SIS adhesive has a peak load range between 222 and 334 N and the polychloroprene adhesive has a peak load range between 267 and 445 N. The first round of adhesive tested fall within the given range. Some are 2–21% higher than the upper limit of the range which is not considered a problem for industrial applications. These adhesives were able to maintain strength through the full 60 min of open time. While the second round of adhesives tested fell below the typical range, the controls were also lower. As previously mentioned, this decrease in strength could be due to the difference in the amount of bonding pressure applied to the laminates, solution viscosities, and the lab

environment. In Fig. 6a, the bond strength of SIS-HF3 is reduced with longer open times. However, this drop is not significant enough to indicate a loss of open time. SIS-HF-LV maintains a constant strength throughout the 60 min. Fig. 6b shows CR-HF3 performing adequately compared to the control and maintaining its strength throughout the time period. Overall, all of the adhesives tested exhibited adequate strength throughout an open time duration of one hour.

4. Conclusion

This project aimed to address the pressing need to reduce the use of toxic solvents hazardous to human health used in contact adhesives. The concept of Hansen Solubility parameters was used to search a database to find comparable replacement solvent blends with low toxicity issues.

Five solvent blends that do not contain hazardous air pollutants (HAP) were identified. Two of these blends (CR-HF1, SIS-HF1, CR-HF2 and SIS-HF2) were optimized for solubility of the rubber and resin solid components. The next two blends (CR-HF3 and SIS-HF3) trade optimal solubility in order to achieve desirable low prices. The fifth blend (SIS-HF-LV) contains no HAPs and has a VOC content under 250 g/L. All five solvent blends were demonstrated to dissolve the given rubber and resin, evaporated sufficiently quickly to initiate the open time, and strength tests confirmed that all five formulations possess strengths equal to or greater than commercial formulations and retain a 1 h open time.

Therefore, the solvent solutions identified are shown to be functionally equivalent to the target commercial formulations. SIS-HF-LV has a low VOC content which allows it to be sold in states that have a VOC limit of 250 g/L, thereby providing an alternative to water-based suspensions that have substantially slower evaporation rates and poorer performance. Using these solvent solutions to replace toluene and hexane will provide consumers and industrial users the ability to use a quality contact adhesive while avoiding detrimental health and environmental impacts.

Acknowledgements

Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ijadhadh.2017.06.022.

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