HIGH SAFT EMUSION ACRYLIC TECHNOLOGY

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Introduction

Over the last few decades, emulsion acrylic pressure sensitive adhesives (PSA) have become popular in the industry due to their lower cost, superior environmental friendliness, lower operational hazards, higher solids, and higher coating speed. However, the use of emulsion acrylic PSA seems to be restricted to some less demanding applications, such as OPP packaging tape and paper/filmic labels, because of the inferior adhesion performance. There are continuing efforts in the industry to push the boundary of emulsion PSA technology, especially in the areas of water resistance, high cohesive strength, plasticizer/chemical resistance, and low surface energy (LSE) adhesion. For the high end specialty tape market, the dominant adhesive technologies seem to be confined to the solvent acrylic PSA, monomer syrup UV acrylic, and hot melt UV acrylic. Table 1 compares the pros and cons of the emulsion acrylic versus the above mentioned technologies. SAFT is the Shear Adhesion Failure Temperature. It is one of key test methods to define the temperature resistance of adhesives. Although emulsion PSA offers many advantages, it is clear that SAFT is the biggest performance gap. In this paper, we explore the effect of different crosslinking mechanisms and functional monomers on peel adhesion and SAFT. A new breakthrough high SAFT emulsion acrylic PSA was developed and benchmarked with market leading monomer syrup UV technology.

Table 1: Comparison of different acrylic PSA technologies

	shear	SAFT	VOC	odor	cost	%solids	coating speed
emulsion acrylic	--	--	+	+	+	+	+
solvent acrylic	+	+	-	-	-	-	-
hotmelt UV acrylic	-	-	+	+	-	++	++
monomer syrup UV acrylic	++	++	-	--	-	++	-

++: best, +: good, -: poor, --: worst

Experimental

Semi-batch emulsion polymerization was used in preparing the acrylic PSA for this study. Pre-emulsion was prepared by mixing water, surfactants, and monomers. The monomers contain 2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate, styrene, and acrylic acid. Several different crosslinking monomers, functional monomers and post-addition crosslinkers were introduced to study their effect on adhesion property and SAFT. After the pre-emulsion is prepared, water was charged to the reactor and heated to 78^{o}C with nitrogen purge. A small amount of pre-emulsion was added to reactor and thermal initiator, sodium persulfate, was charged to start the polymerization. Streams of pre-emulsion and initiator were flowed into

reactor over 3.5 hours and the reactor temperature is controlled at 85^{o}C. After the reaction, a post chaser of t-butyl hydrogen peroxide and sodium formaldehyde sulfoxylate to further reduce the residual monomers. After the reactor was cooled to room temperature, the pH was adjusted to close to 7.0 with ammonia. 1% wetting agent Aerosol OT-75 was added.

The samples were tested by coating onto 2-mil PET film, air dried at room temperature for 30 minutes and then further dried at 110^{o}C in an oven for 3 minutes with a dried adhesive coat weight of 50 g/m^{2}. The adhesive films were cut into 1-inch strips for peel adhesion testing on SS (stainless steel) panels with 15 minutes bond time, PL15 (SS), 24 hours bond time, PL24 (SS), and SAFT test. The SAFT test can be referenced to PSTC-17 method. It was run by reinforcing the PET film with aluminum tape to avoid tearing at high temperature. The adhesive film was adhered to a SS shear plate with 1"x1" contact area and then rolled twice using a 2kg weight roller. The SS panel was placed in SO-8 Shear Test Oven (by ChemInstruments) at 40^{o}C for 30 minutes. Then a 1-kg weight was hung on to the adhesive strip. The oven was programmed to hold at 40^{o}C for 20 minutes immediately after the weight was attached. Following the 20 minutes hold, the oven temperature increased at rate of 0.5^{o}C per minute. When the oven temperature reached 200^{o}C, the test was completed and the oven started to cool. When the 1-kg weight dropped due to the failure of the test strip on the SS panel, the temperature recorded as the SAFT value. If the test strip did not fail throughout the course of the temperature rise, the SAFT was recorded as 200+^{o}C.

Samples for DMA (Dynamic Mechanical Analysis) test were prepared in 2 different ways. One way was to cast 1-2 mm thick films in a silicone release liner tray and dry for 24 hours at room temperature, followed by 24 hours at 50^{o}C. The other way was to coat a film with dry thickness of about 50 g/m^{2} on a release liner using the method described above and then fold the film to the desirable thickness for the DMA. The DMA testing was run using a 8mm parallel plate geometry on a Anton Paar Physica MCR-301 rheometer. The run condition for the temperature sweep (-60^{o}C to 200^{o}C) is at 10 rad/s frequency with 3^{o}C/min ramp to 30^{o}C and 5^{o}C/min after.

Results and Discussions

The starting polymer contains 2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate, styrene, and acrylic acid with calculated Tg of -40^{o}C, a typical composition for PSA application. We started by investigating the effect of post addition of crosslinkers on SAFT and adhesion. The post crosslinkers studied include epoxy, polyisocyanate, polycarbodiimide, polyaziridine, and epoxy functional silane, which are commonly used in water borne acrylic system.

Effect of Epoxy Crosslinker

An epoxy crosslinker based on bisphenol A was added in 2 different levels of 1 and 2%. There is no change in SAFT under the testing conditions as shown in Table 2. The 15-minute adhesion

(PL15) decreases with increasing epoxy crosslinker. We aged the films at 50°C for 1 week and then tested again. There is slight increase in SAFT and decrease in peel adhesion, which is an indication of crosslinking. The failure mode for adhesion also changes from cohesive failure (c) to adhesive failure (a). The crosslinking between epoxy group and carboxyl group may require higher temperature.

Table 2: Effect of epoxy crosslinker

Epoxy (%)	0	1	2
PL15 (SS)	5.2 c	4.3 a	2.7 a
PL24 (SS)	4.9 c	5.3 c	5.2 c
SAFT (°C)	40	40	40
aged 1 week at 50°C			
PL15 (SS)	4.8 c	1.8 a	1.2 a
PL24 (SS)	4.8 c	3.3 a	2.2 a
SAFT (°C)	51	93	67

Peel adhesion unit: lbf/inch

Failure mode: a (adhesive), c (cohesive)

Effect of Polyisocyanate

A water dispersible aliphatic polyisocyanate was used in the study. The isocyanate group will react with the carboxyl group to form an amide and CO_2. Water in the system will compete for the reaction with the isocyanate. Table 3 shows the SAFT value increases to around 100°C with the addition of polyisocyanate crosslinker at 2 different levels. The peel adhesion decreases for the 2% level. Heat aging of the films at 50°C does not change the SAFT and peel adhesion much, which is an indication of no significant additional curing.

Table 3: Effect of polyisocyanate crosslinker

Polyisocyanate (%)	0	1	2
PL15 (SS)	5.2 c	4.2 a	2.1 a
PL24 (SS)	4.9 c	5.2 c	3.5 a
SAFT (°C)	40	105	105
aged 1 week at 50°C			
PL15 (SS)	4.8 c	3.0 a	2.0 a
PL24 (SS)	4.8 c	5.1 c	2.9 a
SAFT (°C)	51	129	105

Peel adhesion unit: lbf/inch

Effect of Polycarbodiimide

Polycarbodiimide is a popular crosslinker used in water-based coatings and adhesives. The crosslinking is based on the reaction of carbodiimide and carboxylic acid forming N-acyl urea. With addition of 2% and 4%, Table 4 shows there is a significant increase of SAFT and slight

adhesion reduction for 4%. The crosslinking reaction occurs at room temperature. The heat aging of films has little effect on the SAFT and adhesion.

Table 4: Effect of polycarbodiimide crosslinker

Polycarbodiimide (%)	0	2	4
PL15 (SS)	5.2 c	4.9 c	2.1 a
PL24 (SS)	4.9 c	5.3 c	3.8 a
SAFT (^{o}C)	40	146	170
aged 1 week at 50^{o}C			
PL15 (SS)	4.8 c	3.0 a	1.9 a
PL24 (SS)	4.8 c	5.2 c	3.9 a
SAFT (^{o}C)	51	147	174

Peel adhesion unit: lbf/inch

Effect of Polyaziridine

The tri-functional aziridine corsslinker can react with carboxyl functionality to form crosslinks at room temperature. It is used commonly in water based systems. With 3 different levels of addition, there are different degrees of reduction in peel adhesion as shown in Table 5. The SAFT increases for all 3 cases and appears to be at 90-100^{o}C regardless of the level.

Table 5: Effect of polyaziridine crosslinker

Polyaziridine (%)	0	0.15	0.25	0.5
PL15 (SS)	5.2 c	2.8 a	2.0 a	1.0 a
PL24 (SS)	4.9 c	4.0 c	2.6 a	1.6 a
SAFT (^{o}C)	40	89	101	88
aged 1 week at 50^{o}C				
PL15 (SS)	4.8 c	2.6 a	1.6 a	1.0 a
PL24 (SS)	4.8 c	5.0 c	2.9 a	1.5 a
SAFT (^{o}C)	51	97	110	88

Peel adhesion unit: lbf/inch

Effect of Epoxy Silane

Epoxy functional silane was added in 3 different levels to study its effect on SAFT. The methoxy silane group will hydrolyze and form silanol group for crosslinking. There are different degrees of peel reduction and increase in SAFT (Table 6). With the 50^{o}C heat aging of films for a week, there is further reduction of peel adhesion, which is an indication of continuing crosslinking. However, the effect on the SAFT seems unchanged.

Table 6: Effect of epoxy silane crosslinker

Epoxy silane (%)	0	0.3	0.5	1
PL15 (SS)	5.2 c	2.4 a	2.1 a	1.1 a
PL24 (SS)	4.9 c	4.5 c	3.7 a	2.5 a

SAFT (^{o}C)	40	136	103	98
aged 1 week at 50^{o}C				
PL15 (SS)	4.8 c	1.9 a	1.3 a	0.9 a
PL24 (SS)	4.8 c	3.2 a	2.5 a	1.5 a
SAFT (^{o}C)	51	105	97	84

Peel adhesion unit: lbf/inch

In addition to the post-addition crosslinker study, we have incorporated several crosslinking monomers in the polymerization to investigate their effect on peel adhesion and SAFT. They include N-methylol acrylamide (NMA), 3-(trimethoxysilyl)propyl methacrylate (TMSPM), 1,4-butanediol diacrylate (BDDA), and diacetone acrylamide (DAAM).

Effect of TMSPM

The trimethoxy silane group in TMSPM provides a possible mechanism for crosslinking during the film formation. As shown in Table 7, there is an increase in SAFT and decrease in peel adhesion. Heat aging at 50^{o}C didn't further change the adhesion and SAFT.

Table 7: Effect of TMSPM monomer

TMSPM (%)	0	0.25	0.5
PL15 (SS)	5.0 c	1.4 a	1.0 a
PL24 (SS)	4.7 c	2.4 a	1.4 a
SAFT (^{o}C)	40	106	114
aged 1 week at 50^{o}C			
PL15 (SS)		2.1 a	
PL24 (SS)		2.4 a	
SAFT (^{o}C)		95	

Peel adhesion unit: lbf/inch

Effect of NMA

NMA monomer provides a self-crosslinkable system with pendant hydroxymethyl group. With 2 different levels, there seems to be slight elevation in SAFT as shown Table 8 below. We aged the film of the sample containing 1% NMA at 50^{o}C for 1 week and re-tested the sample. There is a very significant increase in SAFT . It appears the crosslinking of hydroxymethyl group occurs at elevated temperature and has strong effect on SAFT.

Table 8: Effect of NMA monomer

NMA (%)	0	0.5	1
PL15 (SS)	5.0 c	2.1 a	2.4 a
PL24 (SS)	4.7 c	4.8 c	5.5 c
SAFT (^{o}C)	40	66	95
aged 1 week at 50^{o}C			
PL15 (SS)			2.2 a

PL24 (SS)			2.8 a
SAFT (^{o}C)			200+

Peel adhesion unit: lbf/inch

Effect of BDDA

BDDA is a di-functional acrylate monomer, which provides a unique way to form crosslinking inside polymer particles. With addition of 0.5% and 0.8%, there is an increase in SAFT and peel adhesion is reduced as shown in Table 9. Interestingly, the 24-hour peel shows cohesive failure mode with BDDA crosslinker. The crosslinking inside the particles may have caused the poor coalescence. This may result in low integrity of the films and lead to the cohesive failure.

Table 9: Effect of BDDA monomer

BDDA (%)	0	0.5	0.8
PL15 (SS)	5.0 c	1.6 a	1.1 a
PL24 (SS)	4.7 c	4.2 c	3.3 c
SAFT (^{o}C)	40	100	112

Peel adhesion unit: lbf/inch

Effect of DAAM

DAAM is a room temperature crosslinkable system with addition of ADH (adipic dihydrazide). The DAAM monomer was copolymerized into the polymer backbones. The carbonyl group of DAAM will react with dihydrazide to form crosslinking at room temperature after drying. Table 10 below shows addition of 3 different levels of DAAM decreases the peel adhesion and increases the SAFT. It appears to be an effective crosslinking monomer.

Table 10: Effect of DAAM monomer

DAAM (%)	0	0.5	0.75	1.5
PL15 (SS)	5.0 c	3.6 a	2.0 a	1.3 a
PL24 (SS)	4.7 c	4.3 a	3.5 a	2.3 a
SAFT (^{o}C)	40	95	137	200+

Peel adhesion unit: lbf/inch

Effect of Functional Monomers

From the above study, there are several alternative ways to increase the SAFT of emulsion acrylic PSA by introducing different crosslinking monomers. We also explored the introduction of hydroxyl (OH) functional monomer and several different types of nitrogen-containing (N) functional monomers. This was to investigate the effect of different functionalities on SAFT. Table 11 shows minimum effect on SAFT with different functional monomers except sample #6. It appears the combination of hydroxyl monomer and nitrogen-containing monomer 4 provides a very strong effect on SAFT. The presence of only nitrogen-containing monomer 4 (sample #7) and only hydroxyl monomer (sample #2) does not lead to the drastic increase in SAFT.

Table 11: Effect of functional monomers

	#1	#2	#3	#4	#5	#6	#7
OH monomer		x	x	x	x	x	
N monomer 1			x				
N monomer 2				x			
N monomer 3					x		
N monomer 4						x	x
PL15 (SS)	5.0 c	4.9 c	5.4 c	4.6 c	5.5 c	2.0 a	2.0 a
PL24 (SS)	4.7 c	4.8 c	5.0 c	4.4 c	4.7 c	3.7 a	4.1 c
SAFT (^{o}C)	40	53	48	40	55	200+	71

Peel adhesion unit: lbf/inch

DMA curves of sample #1 and 6 are compared in Figure 1. It is clear to see the increase of storage modulus (G') at elevated temperature for sample #6. This is an indication of crosslinking reaction, which has led to the increase in SAFT. The actual mechanism of crosslinking is being further investigated.

Prototype

Different crosslinking mechanisms can lead to different degrees of reduction in peel adhesion. It is interesting that their effect on SAFT is very different. Some have much stronger effect than the others. Fundamentally, there will be more to investigate in terms of structure/property to fully understand how different crosslinking mechanisms affect the SAFT. This study provides a valuable glimpse into their effect on SAFT. With this research work, we were able to develop a new prototype emulsion acrylic adhesive which has superior adhesion properties and SAFT. The new emulsion adhesive was benchmarked with a market tape product using monomer syrup UV acrylic technology as shown in Table 12. It is very exciting to see the new emulsion technology has comparable adhesion performance and SAFT vs. a leading market tape product using syrup UV. The DMA curves of the new emulsion technology and market tape product are also compared in Figure 2. The new emulsion shows narrower tan δ and comparable storage modulus (G').

Table 12: Comparison of performance for new emulsion vs. syrup UV acrylic PSA.

	new emulsion	syrup UV
15-min peel on SS, lbf/inch	3.3	3.5
24-hour peel on SS	4.7	4.3
1-week peel on SS	6.1	5.9
1-week peel 70^{o}C on SS	7.9	7.2
15-min peel on HDPE	1.5	1.9
24-hour peel on HDPE	2.4	2.2

25°C shear (1/2”x1/2”x500g), hrs	100+	100+
70°C shear (1”x1”x1kg), hrs	66+	66+
93°C shear (1”x1”x1kg), hrs	66+	66+
SAFT (°C)	200+	200+

The new emulsion was also tested for immersion in different fluids, including water, gasoline, MEK (methyl ethyl ketone), IPA (isopropyl alcohol), and 10W30 engine oil. It exhibits great performance and peel retention after immersion, which is very comparable to syrup UV PSA.

Conclusions

The SAFT performance of emulsion acrylic PSA can be controlled by varying different types of crosslinkers (internal and external) and different functional monomers. Epoxy crosslinking and hydroxymethyl crosslinking require extra heating to show effect on the SAFT. Polycarbodiimide, polyisocyanate, and DAAM provide a good crosslinking option for high SAFT. The incorporation of both hydroxyl and nitrogen-containing functional monomers also give significant increase in SAFT. The new prototype emulsion acrylic PSA shows comparable adhesion and SAFT performance to market leading technology. This opens the door for the emulsion adhesive to be used in high end specialty tape applications.

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Figure 1: DMA of sample #1 vs. sample #6

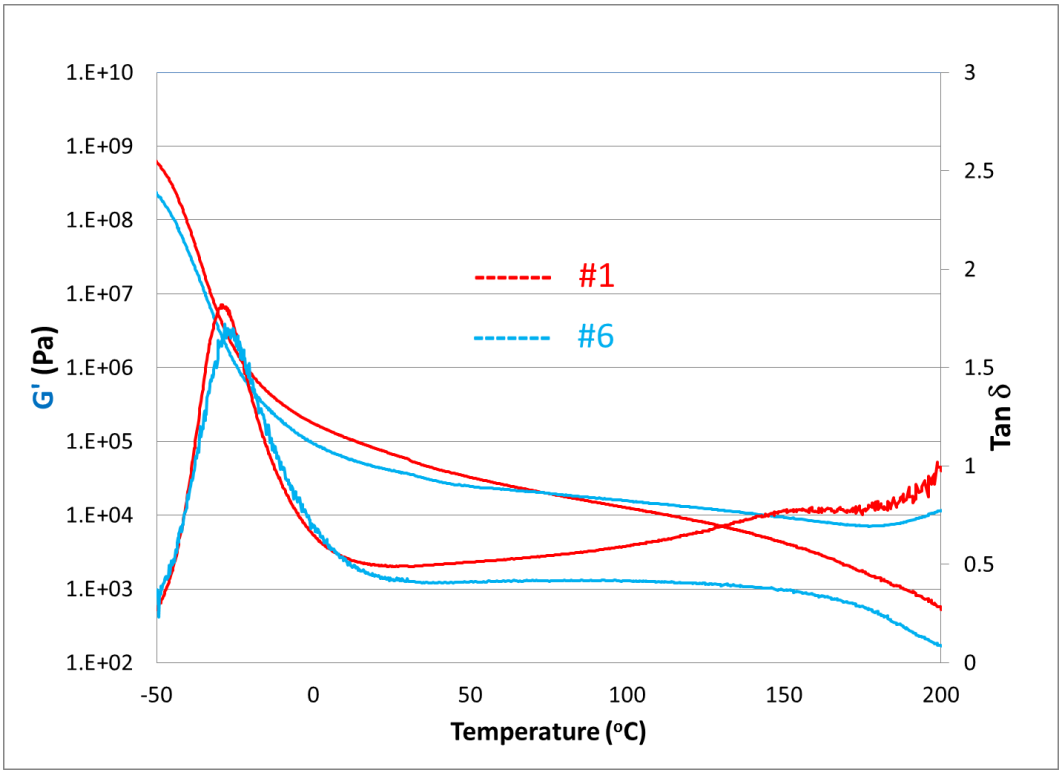

Figure 2: DMA of new emulsion vs. syrup UV acrylic PSA