GREATLY ENHANCED PRESSURE SENSITIVE ADHESIVE PERFORMANCE THROUGH CONTROLLED RADICAL POLYMERIZATION IN EMULSION

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Abstract

The synthesis of high performance emulsion acrylic pressure sensitive adhesives is reported. Emulsion acrylic polymers were prepared with controlled molecular weight, architecture and placement of reactive functional groups utilizing RAFT control and polymerizable surfactant. A synergistic effect through combining controlled polymerization and polymerizable surfactant on adhesion performance of emulsion PSA performance was observed. The greatly enhanced adhesive performance of these novel emulsion acrylic polymers provides water-borne PSA options for the replacement of traditionally used hydrocarbon solvent-based PSA in many high performance applications.

Introduction

The emergence of controlled radical polymerization (CRP) chemistry over the past 25 years has provided much greater access to both molecular size control and block copolymer synthesis within commercial polymer systems than ever before. Of the several CRP techniques to have emerged, Reversible Addition Fragmentation chain Transfer (RAFT) polymerization is one that delivers excellent molecular weight control with simplicity, over a broad range of (meth)acrylic and vinyl monomers and under a diverse range of conditions.[1]

RAFT controlled synthesis of acrylic solvent grade PSA's has provided improved molecular weight and monomer distribution control, enabling higher product solids while maintaining low viscosity for solvent-borne adhesive, coupled with improved adhesion performance.[2] Also noticed during the RAFT controlled acrylic solvent PSA adhesive development was the emergence of a characteristic or signature rheology profile in the cured adhesive, especially when reactive groups are confined to near polymer chain ends[2, 3] (telechelic functionality), as shown in Figure 1 below.

Controlled radical polymerization via RAFT provides a simple means to prepare adhesive precursor polymers with reactive functionality confined to chain ends. Upon cross-linking, these telechelic precursor polymers form gel networks that deliver enhanced adhesive performance in the form of very high static shear resistance without the typically observed loss in peel adhesion or pressure sensitive tack.[2, 4] As can be seen in Figure 1., moving from non-RAFT control to RAFT control with random incorporation of functional monomer, and then further to RAFT control coupled with functional monomer placement at polymer chain ends in a solvent-borne system, drives the emergence of a second peak (a relaxation) in the tangent delta response of the DMA curve. It is the emergence of this new relaxation, coupled with maintenance of a high storage modulus (G') that has been associated with the high adhesion performance offered by cross-linked, RAFT controlled telechelic polyacrylate PSA, whether derived from solvent or emulsion systems.[2, 4]

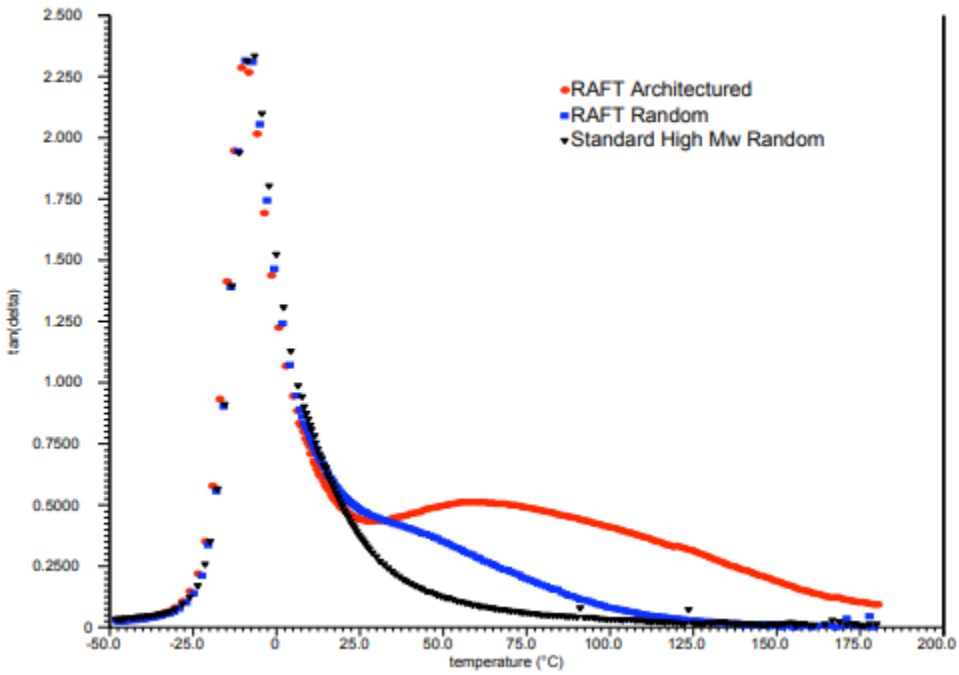

Figure 1. Tan delta as a function of temperature for acrylic copolymers a with fixed level of functionality but varying architecture

Figure 2 shows the basic reaction steps for controlled radical polymerization via RAFT leading to the preparation of block copolymers.[2] Using, for example, a symmetrical dithiocarbonate RAFT agent like DBTTC enables controlled monomer addition to both ends of a propagating polymer chain simultaneously. In this way, feeding monomer A first provides the opportunity to confine reactive functional groups (where monomer A is a functional monomer) to chain ends (telechelic polymers), enhancing rheological response, toughness[3] and adhesion improvement.[2, 4]

Solvent-borne acrylic PSAs typically offer the highest range of performance in heat, chemical, and water resistance. They can also have a balance of cohesion and adhesion properties superior to that of waterborne PSAs.[5, 6] However, increasing sustainability and regulatory requirements are demanding a shift from solvent-borne technologies.Therefore, developing new waterborne PSAs with properties that rival the performance characteristics of their solvent-borne counterparts but with lower volatile organic compounds (VOCs) that can be coated quickly and economically[6] is a continuing challenge. In this publication, the successful translation of RAFT polymerization in solvent systems to yield high performance emulsion PSA is presented.

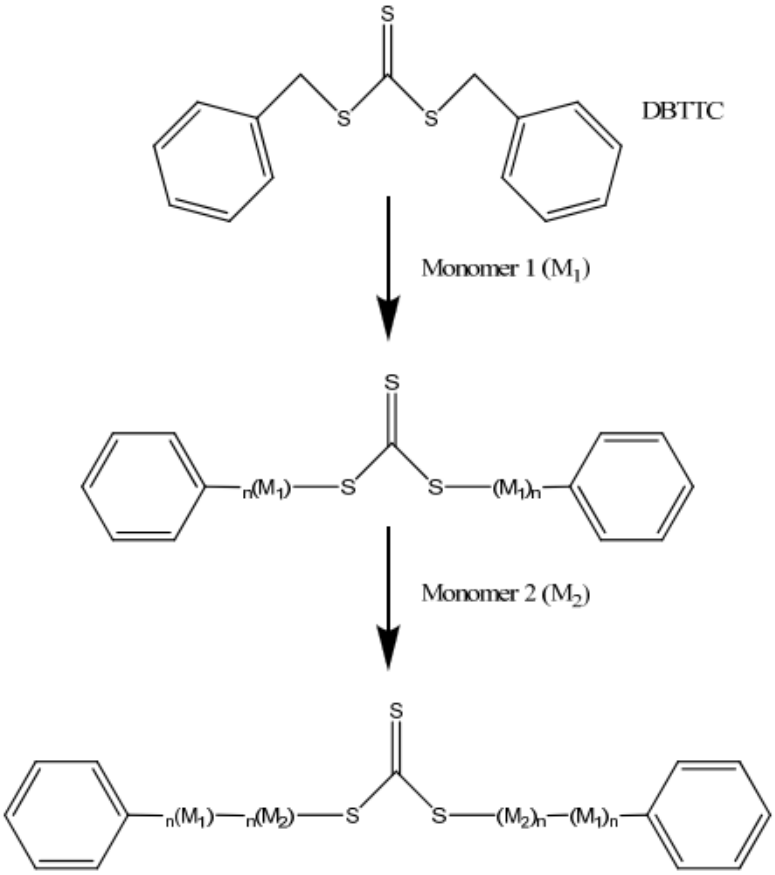

Figure 2. Chemical structure of dibenzyl trithiocarbonate (DBTTC) and polymers after a single monomer addition followed by a subsequent monomer addition.

Experimental

Materials

Synthesis of RAFT controlled emulsion polymers

Emulsion and solvent-borne polymers were synthesized with target glass transition temperatures (Tg) of -20° C. using predominantly n-butyl acrylate and t-butyl acrylate monomers. Emulsion RAFT mediated polymerizations were conducted via mini-emulsion polymerization using a pre-made RAFT macromer dissolved in the monomer phase together with a small amount of hydrophobe. The RAFT macromer was prepared via a solvent polymerization process. The formulation and manufacturing process is described in US patent 10,287,464 B2.[4]. The functional RAFT macromer was used to prepare the RAFT emulsion PSA samples via a miniemulsion process.[4]

The RAFT emulsion PSA polymer formulations and the associated miniemulsion preparation steps, together with the subsequent polymerization steps are also provided in US patent 10,287,464 B2.[4] Emulsion RAFT polymers stabilized by conventional and reactive surfactants were prepared in identical fashion and details are provided in US patent 10,287,464 B2.[4]

Synthesis of RAFT controlled solvent-borne polymers
The solvent-borne RAFT mediated polymerizations were conducted according to the technique described in US patent 2011/0118372 A1.[7]

Characterization of adhesive films
Polymer films (derived from both emulsions or solvent-borne solutions) were prepared by drawing down the cross linker-containing systems using wire-wound draw-down bars directly to 2 mil polyethylene terephthalate (PET) film. The wet adhesive films were dried and cured in a convection oven at 120° C. for 5 minutes before laminating to silicone coated glassine release paper. Dry adhesive coat weights of 18 - 22 gsm were targeted for adhesion performance testing and coatweight target was achieved through selection of wire-wound draw-down bars with an appropriate wound wire diameter.

Adhesive coat weight of prepared laminates was measured by weighing a 100 mm x100 mm section of adhesive coated PET. The weight of a 100 mm x100 mm uncoated sample of PET was subtracted and the result multiplied by 100 to obtain a coat weight estimate in gsm.

180° peel adhesion after 15 mins and 24 hours dwell to stainless steel was measured by applying a 1 inch wide strip of test laminate to a stainless steel panel with a 4.5 pound roller with 1 pass in each direction. Samples were conditioned and tested under the standard testing conditions of 21-23°C and 45 - 55% relative humidity. After 15 minutes and 24 hours dwell, the average peel force was measured over at least 20 mm of test strip three times.

Static shear was measured by adhering a 1 inch by 1 inch area of a looped test strip to a stainless steel panel and rolling with a 5 pound roller with one pass in each direction. After conditioning the adhered test loops for 24 hrs, a 1000 g weight was hung and the time to failure was recorded. Samples were conditioned and tested under the standard testing conditions of 21- 23°C and 45 - 55% relative humidity.

Characterization of emulsion and solvent-borne polymers
The molecular weights of the THF soluble polymer fractions were measured using a Agilent Technologies 1200 Series GPC outfitted with a refractive index detector and calibrated using polystyrene standards.

Dynamic mechanical analysis (DMA) was performed on a TA Instrument AR-2000 rheometer using parallel plate clamps. 1.5 mm thick samples were placed in the clamp and annealed at 50 ºC for 10 minutes to ensure good adhesion. The samples were then cooled to -80 ºC for 10 minutes and ramped at 3 ºC per minute up to 180 ºC. During the temperature ramp the sample was oscillated at a frequency of 10 rad/s. Thermal locations in the peaks of the tangent delta curves obtained during the DMA temperature sweeps were reported as the T_g values.

Results

The physical properties (including 180 peel to stainless steel and static shear) of the RAFT solvent-borne polymer and the RAFT emulsion polymer are presented in Table 1.

Table 1. Molecular weight, glass transition temperature and adhesion performance of RAFT emulsion (using conventional surfactant) and solvent-borne PSA

Sample Description	Mn (X1000 g/mol)	PDI	Tg (°C)	180 deg. Peel to SS (lb/inch)				Static Shear (1"x1"x 1kg) (mins)
				15 min Peel to SS (lb/inch)	Failure Mode	24 hr Peel to SS (lb/inch)	Failure Mode	
Cross-linked RAFT Emulsion Polymer (prepared using conventional surfactant)	159.9	1.8	-21.7	1.9	clean	1.18	clean	402
				1.5	clean	0.68	clean	350
				1.53	clean	0.45	clean	812
Cross-linked RAFT Solvent Polymer (prepared using solvent polymerization process)	176.2	1.8	-21.4	1.84	clean	7.79	cohesive	>10000
				2.46	clean	7.33	cohesive	>10000

The RAFT emulsion using conventional surfactant yielded a polymer that had good molecular weight control, as indicated by the low polydispersity of 1.8. The molecular weight control matched that of the solvent-borne PSA, which also returned a polydispersity of 1.8. Molecular weights were also very similar, as evidenced by the molecular weight number averages of 159.9 and 176.2 Kg/mol for the emulsion and solvent-borne polymers respectively.

The very similar monomer compositions also lead to very similar glass transition temperatures (-21.7 and -21.4 C for the emulsion and solvent-borne polymers respectively) as can be seen from dried film DMA temperature sweeps presented in Figure 3. In addition, the DMA temperature sweep overlay highlights the very similar rheology profile overall, most notably the characteristic relaxation evident in the tangent delta curves at around 75 °C for these cross-linked, telechelic RAFT polymers. Furthermore, shear storage modulus (G') for both polymers followed a similar temperature profile, with both cross-linked adhesive systems delivering shear storage modulus of around 10 kPa at 150 °C.

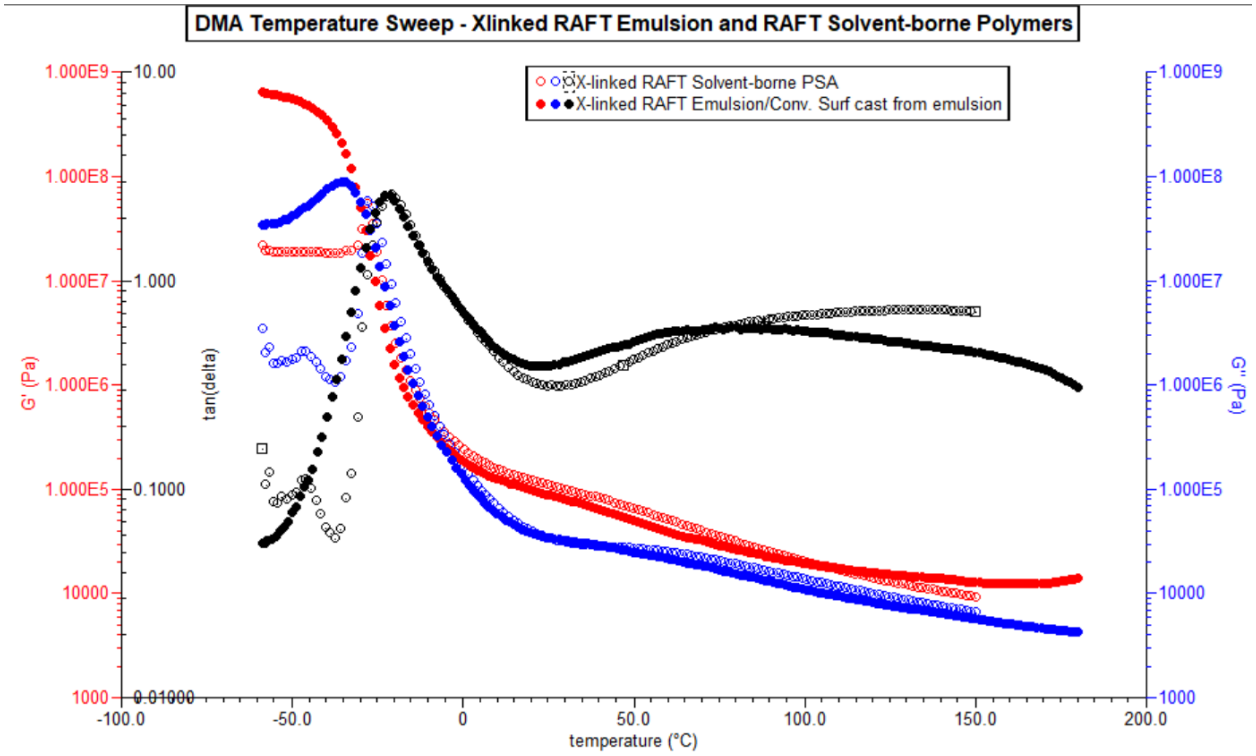

Figure 3. DMA temperature sweeps of crosslinked polymer via RAFT emulsion polymerization using conventional surfactant cast from water and the RAFT controlled solvent-borne polymer, cast from solvent

Surprisingly, adhesion performance was very different. As can be seen from Table 1, the RAFT emulsion using conventional surfactant returned 180 degree peel and static shear test results that were both much inferior to the solvent-borne equivalent. In an effort to explore the origin of the performance differences, the polymer dispersed within the RAFT emulsion stabilized using conventional surfactant was isolated by destabilizing the emulsion through addition of methanol. After vigorous mixing of the emulsion with methanol and filtering the polymer precipitate to isolate the polymer, the polymer was washed a further three times with methanol before dissolving the isolated polymer in ethyl acetate. After adding a stoichiometric equivalent of aziridine, the polymer was cast as a film to release liner using a wire wound bar and dried and cured at 120 ºC for 5 mins to leave a film thickness of approx 18 gsm. The dried film was then laminated with 2 mil PET and later tested for adhesive properties after conditioning under standard testing conditions for 24 hours. Table 2 and Figures 4 and 5 include the adhesion performance data for the solvent cast cross-linked adhesive film derived from the RAFT emulsion prepared with conventional surfactant compared with the performance obtained from the solvent-borne PSA and the performance obtained with emulsion cast, RAFT emulsion prepared with conventional surfactant.

Table 2. Adhesion performance of RAFT emulsion (using conventional surfactant) via films directly cast from emulsion, and after polymer isolation and casting from solvent vs adhesion performance obtained via solvent polymerized PSA

Sample Description	Continous Phase for Film Casting	180 deg. Peel to SS (lb/inch)				Static Shear (1"x1"x 1kg) (mins)
		15 min Peel to SS (lb/inch)	Failure Mode	24 hr Peel to SS (lb/inch)	Failure Mode	
Cross-linked RAFT Emulsion Polymer (prepared using conventional surfactant)	Water (from original emulsion)	1.9	clean	1.18	clean	402
		1.5	clean	0.68	clean	350
		1.53	clean	0.45	clean	812
Cross-linked RAFT Solvent Polymer (prepared using solvent polymerization process)	Solvent (ethyl acetate)	1.84	clean	7.79	cohesive	>10000
		2.46	clean	7.33	cohesive	>10000
Cross-linked RAFT Emulsion Polymer (prepared using conventional surfactant)	Solvent (ethyl acetate)	1.66	clean	6.32	cohesive	>10,000
		1.84	clean	6.57	cohesive	>10,000
		1.34	clean	6.47	cohesive	>10,000

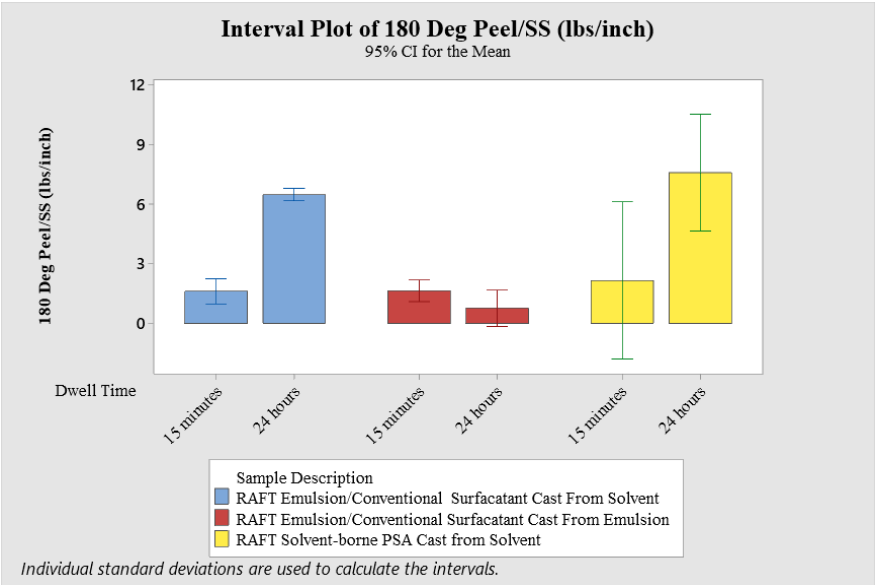

Figure 4. Peel adhesion performance of RAFT emulsion (using conventional surfactant) via films directly cast from emulsion, and after polymer isolation and casting from solvent vs adhesion performance obtained via solvent polymerized PSA

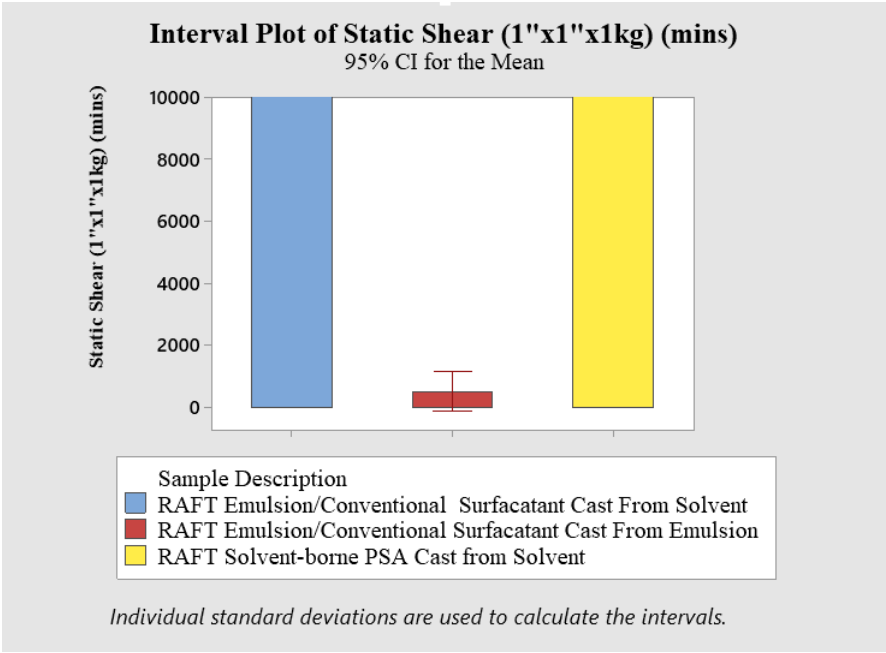

Figure 5. Static Shear adhesion performance of RAFT emulsion (using conventional surfactant) via films directly cast from emulsion, and after polymer isolation and casting from solvent vs adhesion performance obtained via solvent polymerized PSA

Clearly, isolating the emulsion polymer prepared via conventional surfactant and casting it (with cross-linker added) from a solvent solution results in a high performance adhesive after drying and curing while Figure 6 confirms that the rheological response is unchanged as a result of polymer isolation process and subsequent casting from both water and solvent. Indeed, the peel and static shear outcomes rise to the levels provided by the RAFT solvent-borne analogue. Such an outcome is not surprising given the similarity of the polymer architecture, the molecular weight distribution and the rheology profiles of the cross-linked RAFT emulsion and solvent-borne adhesives. The explanation lies in the nature of the surfactant employed during the polymerization process as described by Zhang et al[8] and as exploited in the patent protected commercial manufacture of emulsion PSA by Avery Dennison.[4]

Zhang et al[8] showed the adhesion performance of emulsion pressure sensitive adhesives can be severely degraded by the migration of conventional surfactants to the surfaces of emulsion-cast PSA films. Furthermore, they concluded that polymerizable surfactant can be bound during emulsion polymerization reactions to the adhesive in such a way that its migration to film surfaces during drying and film formation is inhibited, preventing degradation of adhesive performance.

In effect, un-bound (migrateable), conventional surfactants can migrate to adhesive film interfaces to form a weak boundary layer, reducing the work of adhesion potential and reducing the opportunity to exploit the more dissipative/higher performance potential offered by the more

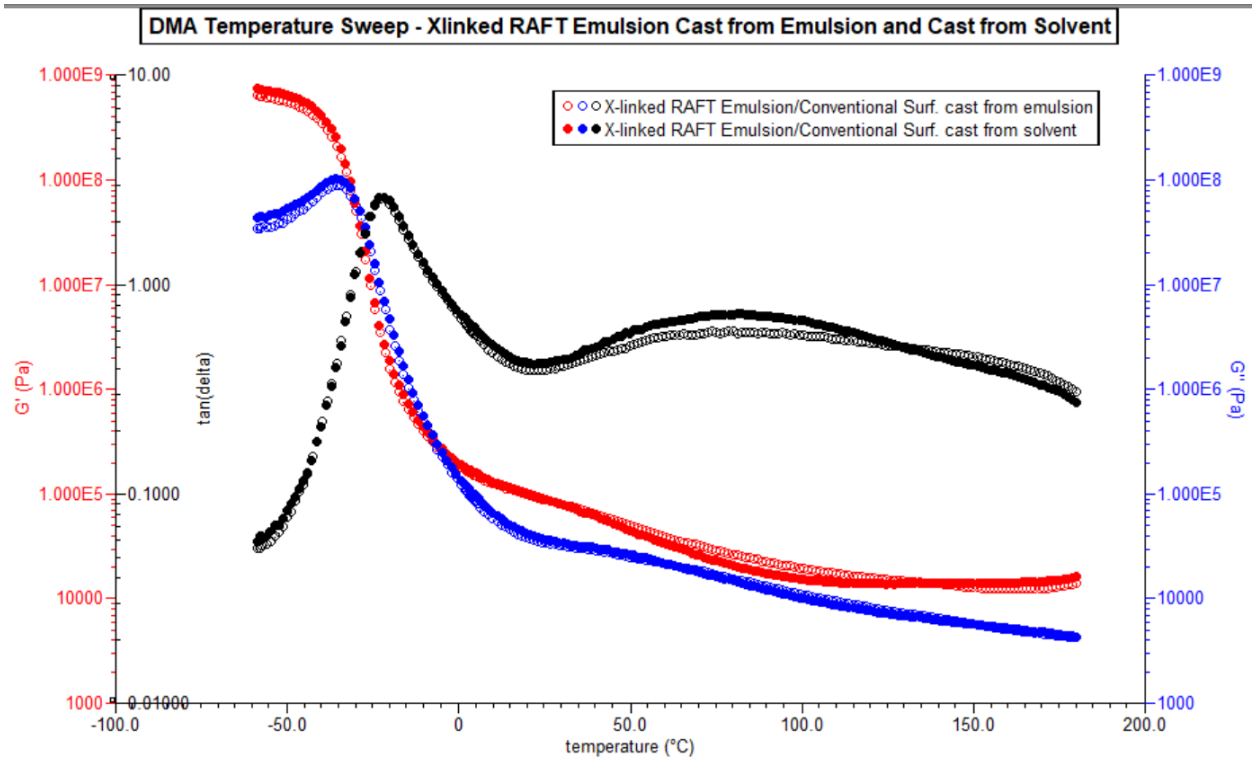

Figure 6. DMA temperature sweeps of crosslinked polymer via RAFT emulsion polymerization using conventional surfactant cast from water and cast from solvent

dissipative adhesive as a result of the RAFT controlled derived cross-linked architecture. Figure 7 provides a diagrammatic representation of the surfactant distributions suggested for emulsion polymers derived via conventional and polymerizable/reactive surfactants[9].

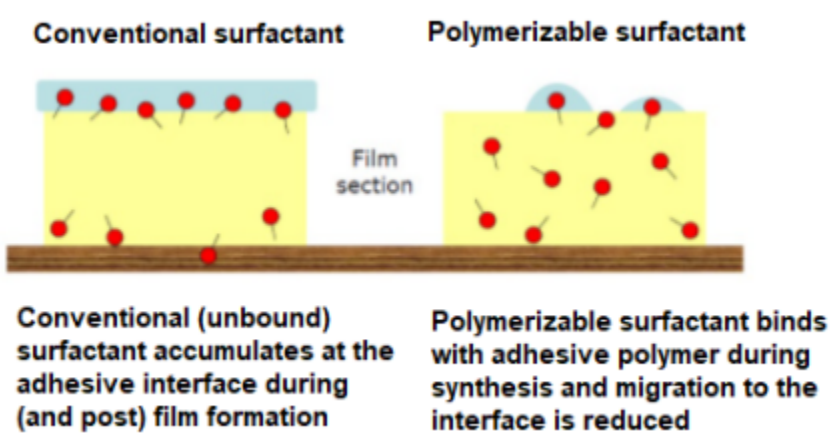

Figure 7. Surfactant accumulation at adhesive interfaces (conventional vs polymerizable type)[9]

The synthesis of the RAFT controlled emulsion PSA was repeated but using a polymerizable surfactant as described in US Patent 10,287,464 B2[4]. The molecular weight, glass transition

temperature and adhesion performance outcomes compared with the previous two polymers (RAFT emulsion PSA prepared with conventional surfactant and RAFT controlled solvent-borne PSA) are presented in Table 3.

Table 3. Molecular weight, glass transition temperature and cross-linked adhesion performance of RAFT emulsion (using conventional surfactant), RAFT emulsion (using polymerizable surfactant) and solvent-borne PSA

Sample Description	Mn (X1000 g/mol)	PDI	Tg (°C)	Continous Phase for Casting Film for Adhesion Testing	180 deg. Peel to SS (lb/inch)				Static Shear (1"x1" x 1kg) (mins)
					15 min Peel to SS (lb/inch)	Failure Mode	24 hr Peel to SS (lb/inch)	Failure Mode	
Cross-linked RAFT Emulsion Polymer (prepared using conventional surfactant)	159.9	1.8	-21.7	Water (from original emulsion)	1.9	clean	1.18	clean	402
					1.5	clean	0.68	clean	350
					1.53	clean	0.45	clean	812
Cross-linked RAFT Emulsion Polymer (prepared using conventional surfactant)	159.9	1.8	-21.7	Solvent (ethyl acetate)	1.66	clean	6.32	cohesive	>10,000
					1.84	clean	6.57	cohesive	>10,000
					1.34	clean	6.47	cohesive	>10,000
Cross-linked RAFT Solvent Polymer (prepared using solvent polymerization process)	176.2	1.8	-21.4	Solvent (ethyl acetate)	1.84	clean	7.79	cohesive	>10000
					2.46	clean	7.33	cohesive	>10000
Cross-linked RAFT Emulsion Polymer (prepared using polymerizable surfactant)	164.8	1.6	-21.7	Water (from original emulsion)	1.49	clean	3.98	clean	>10000
					1.19	clean	5.51	clean	>10000
					1.66	clean	5.79	clean	>10000

Table 3 confirms the very similar glass transition temperatures observed, together with the similar molecular weights and polydispersities for the polymers prepared for this study. The raw 180 degree peel angle adhesion and static shear data is also presented in Table 3 and again in graphical form in Figure 8. As suspected the, the cross-linked RAFT emulsion made from polymerizable surfactant provides high peel and high static shear from the emulsion cast adhesive film, confirming the suspected synergistic effect of polymerizable surfactant and RAFT control in this adhesive system.

Conversely, the cross-linked, RAFT emulsion polymer prepared via conventional surfactant, returned low peel and relatively low static shear. As discussed earlier, it is possible to obtain high performance (high peel adhesion and high static shear) from the emulsion polymer made using conventional surfactant but the polymer must be isolated from the emulsion, washed free of conventional surfactant, dissolved in solvent with added x-linker and a new film cast from solvent. The same polymer and performance data obtained after isolating the conventional emulsion polymer and casting a new cross-linked film from solvent is presented again in Table 3 and Figure 8 for comparison.

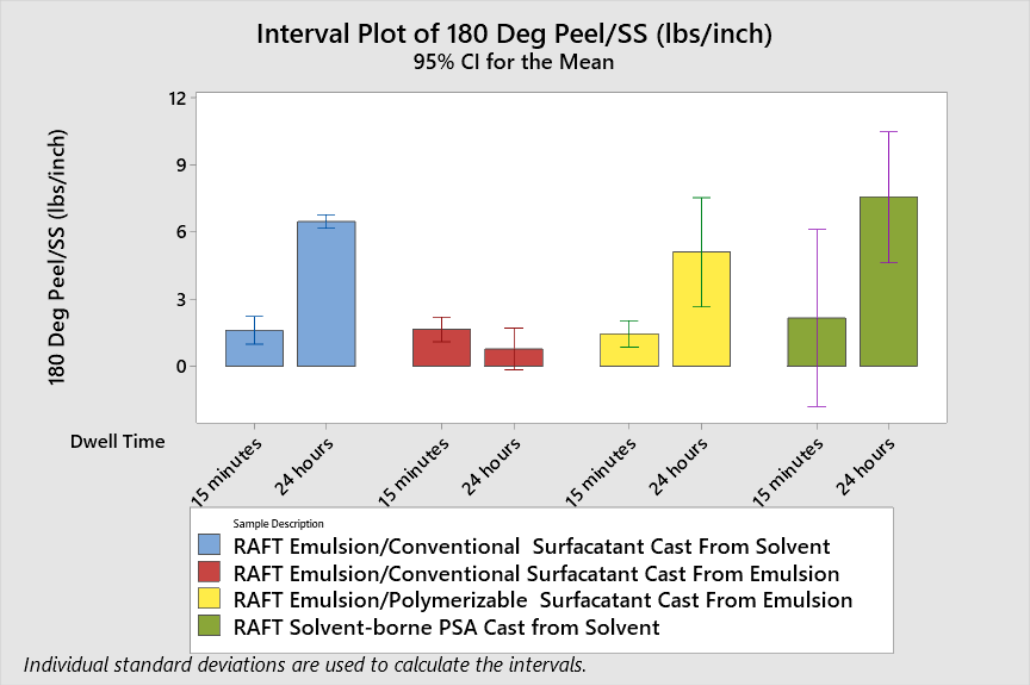

Figure 8. Peel adhesion performance of RAFT emulsion (using conventional surfactant) via films directly cast from emulsion, and after polymer isolation and casting from solvent vs adhesion performance obtained via solvent polymerized PSA and RAFT emulsion prepared via polymerizable surfactant for cross-linked film cast directly from the emulsion.

Figure 9 compares the DMA temperature sweep for the cross-linked emulsions (prepared via conventional and polymerizable surfactants) and the cross-linked solvent-sample. The similarity in the DMA response is very high. The close alignment of the molecular weight distributions and the cross-linked PSA dynamic mechanical response (DMA curves) confirms that similar architecture control was achieved during each polymerization. The rheological response of each cross-linked adhesive closely matches the characteristic response expected from cross-linked, telechelic PSA ie. relatively high shear storage modulus above room temperature and the characteristic shape of the tangent delta curve over the same temperature range. The molecular weight distributions, the dynamic mechanical response curves and the performance comparisons confirm the hypothesis that it is possible to closely replicate RAFT solvent-borne PSA adhesion performance from emulsions using RAFT control when the surfactant chosen to stabilize the emulsion is of the polymerizable type. When correctly formulated, polymerized and cross-linked, RAFT controlled emulsion PSA utilizing polymerizable surfactants can deliver adhesion performance levels much higher than their conventional surfactant derived analogues and with adhesion levels comparable with their high-performance RAFT-controlled solvent-borne analogues.

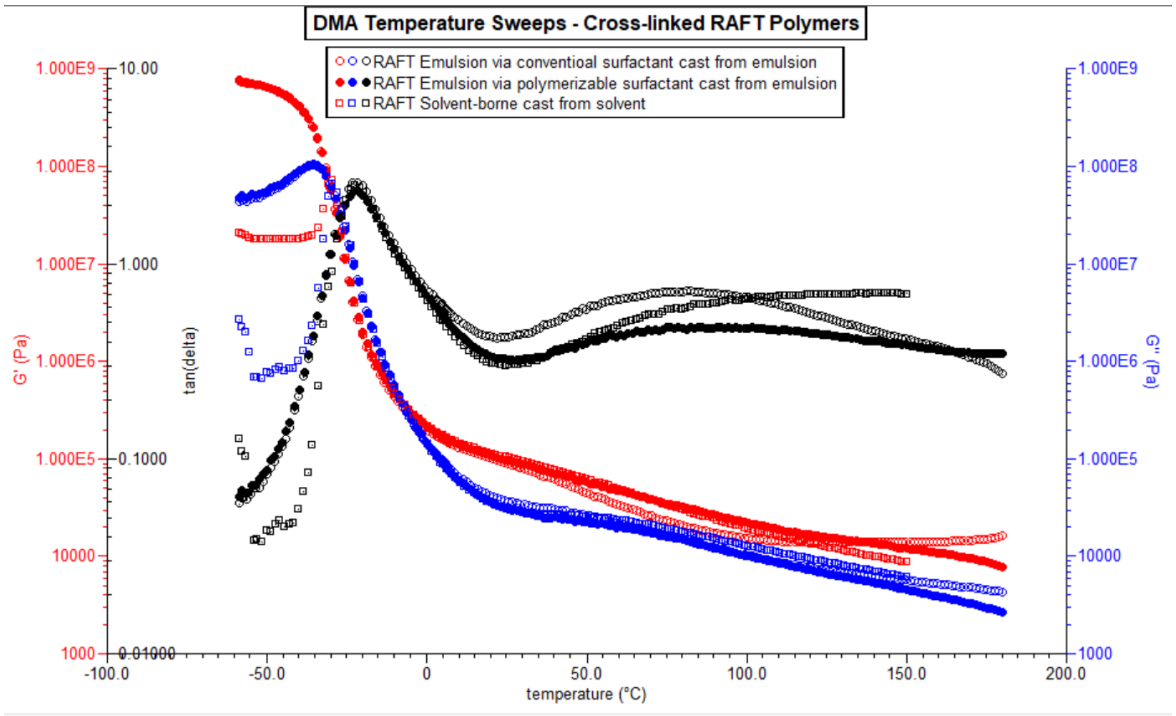

Figure 9. DMA temperature sweeps of crosslinked polymer via RAFT emulsion polymerization using conventional surfactant, via RAFT emulsion polymerization using polymerizable surfactant and via RAFT solvent polymerization

Conclusions

A high-performance, RAFT controlled, telechelic acrylic pressure sensitive polymer was prepared using solvent polymerization. Two RAFT controlled, telechelic emulsion polymer examples were prepared with composition and architecture similar to the solvent-borne polymer yielding very similar molecular number average molecular weight and very similar molecular weight distributions (PDI) but where the first emulsion was prepared using a conventional surfactant and where the second was prepared with a polymerizable surfactant. After cross-linking the adhesives and casting adhesive films, adhesion performance testing revealed that the RAFT controlled, telechelic solvent-borne polymer and the RAFT-controlled telechelic emulsion utilizing polymerizable shared similar high adhesive performance. By contrast the RAFT controlled, telechelic emulsion polymer prepared using conventional surfactant returned much lower peel adhesion and static shear resistance. When the polymer from the emulsion adhesive prepared via conventional surfactant was isolated, dissolved in solvent, and a cross-linked film cast from solvent was prepared, the peel adhesion and static shear resistance was dramatically increased, in-line with withe the solvent-borne analogue.

It is concluded that emulsion polymers prepared with telechelic placement of reactive functional groups can yield high peel adhesion and high static shear strength (rivaling performance of similarly controlled solvent-borne polymers) when cross-linked films are cast directly from the emulsion and when polymer architecture control for the emulsion is combined with emulsion stabilization through the use of polymerizable surfactants. A synergistic effect is observed enabling higher adhesive performance when the more dissipative cross-linked network formed

through telechelic functionality is combined with polymerizable surfactant technology to inhibit or reduce the detrimental effect of surfactant accumulation at the interface.

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The author would like to thank Avery Dennison for its continuing commitment to excellence in the field of pressure sensitive materials, and in particular, its continuing commitment to emulsion psa development. The author thanks the entire team at the Polymer and Coatings Center of Excellence at Mill Hall, and in particular, Chuck Williams, Jimmy Carson, Jim Akeley, Mike Leisner and Dan Hartinger for their thoughtful discussions throughout.

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