EFFECT OF CROSSLINKING CHEMISTRY ON PEEL PROPERTIES IN ACRYLIC EMULSION PSA's

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I. Introduction

Applications utilizing removable adhesives require tailoring of peel performance to promote specific levels of initial adhesion and tack and yield removability after long-term aging conditions. Various crosslinking chemistries are employed to modify the peel resistance of these adhesives. Crosslinking reduces peel bond by inhibiting bond formation through the increase of storage modulus at the bonding frequency and reducing the ability of the adhesive to dissipate energy during the debond process.

Acrylic emulsions utilize two categories of crosslinking to promote removability, interparticle and intraparticle crosslinking. Intraparticle crosslinking is when the crosslinking is limited to within the individual particle, while interparticle crosslinking is crosslinking that occurs between neighboring particles. During the drying process of an acrylic emulsion, film formation of the particles occurs. Interparticle crosslinking chemistries are chemistries that react during and after the film formation process, leading to crosslinking between polymer chains within neighboring particles. Examples of well-known interparticle crosslinking chemistries for acrylic emulsions are azirdine, dispersible and blocked isocyanates, metal chelates, and carbodiimides. Intraparticle crosslinking chemistries mostly consist of different configurations of di- or tri-functional reactive monomers, such as bisacrylamide or trimethylolpropane triacrylate.

Along with good removability, another important characteristic for removable adhesives is anchorage to the facestock film. If anchorage to the facestock is insufficient, transfer failure of the adhesive to the substrate can be exhibited. This issue of facestock anchorage can be aggravated in coating systems utilizing transfer coating of the adhesive.

The objective of the present work is to gain insight into the effect of the chain length and level of intraparticle crosslinking on peel performance and rheology of the resulting adhesives. Intermolecular crosslinking is also explored to determine the effect on anchorage. From this study, two model adhesives will be exhibited.

II. Experimental

II.1. Latex and Film Preparation

All of the pressure sensitive adhesives (PSA) were synthesized using semi-batch emulsion polymerization method. A 2 liter jacketed reactor with a fluid circulation bath was

equipped with an agitator, condenser, and thermocouple. To the reactor was charged seed latex to control particle size and sodium persulfate oxidizing agent. In a separate vessel, water and surfactant were added with the monomer and mixed to form a preemulsion. The bulk monomer mix consisted of a ratio acrylonitrile, butyl acrylate, and 2-ethylhexyl acrylate with a Tg -23.5°C (max tan(δ)). The main surfactant was based on a non-migratory surfactant. The reactor was heated to 85°C and the preemulsion and additional sodium persulfate catalyst feed were fed over 3 hours reacting at 82 - 85°C. After reaction, the reactor was held at 85°C for 1 hour, followed by post catalyzation with t-butyl hydrogen peroxide and sodium formaldehyde sulfoxylate. Following post catalyzation, the reactor was cooled to room temperature and pH adjusted to 8.5. 0.75% dioctyl sodium sulfosuccinate was added as a wetting agent for the purpose of transfer coating.

One mil dry coatweight was coated to silicone release liner and dried at 110°C for 1 minute. Afterward, the adhesive liner was laminated to polymeric plasticized vinyl facestock. Peel resistance was tested using PSTC 101 at 180°C on stainless steel substrate at listed dwell times.

II.2. Rheological Characterization

Samples for rheological characterization were prepared by casting 1 – 2mm thick monolithic samples in a silicone release liner tray and drying for 24 hours at 50°C. Rheological testing was run using an 8mm parallel plate geometry using a Anton Paar Physica MCR-301 rheometer. Dynamic mechanical thermal analysis was run at 10 rad/s at 3°C/min ramp to 30°C, at which the rate was accelerated to 5°C/min. Frequency sweep was run at 1% strain from 0.01 rad/s to 100 rad/s. 1% was determined to be within the linear viscoelastic range for the adhesives by running amplitude sweeps before analysis.

II.3. Anchorage Testing

Anchorage testing was conducted by a finger rub technique, in which rubbing shear is applied to the adhesive and the ease of removal is determined. The test is run blind with 2 individuals running the test. Anchorage was judged with a 1 to 5 scale, with 1 being poor anchorage or easily removed adhesive while 5 denoted film deformation before adhesive removal.

III. Results and Discussion

III.1 Intraparticle Crosslinking Chain Length

A variety of configurations of multifunctional reactive monomers can be utilized to promote intraparticle crosslinking. In this study, the chain length of the intraparticle crosslinking was varied to determine the effect on the peel performance and rheology of the resulting

adhesives. A series of di-functional reactive monomers was used to vary the chain length between connected polymer chains. The short chain crosslinking species allowed for 2 atoms between polymer chains. The long chain allowed for 16 atoms between connected chains. The medium chain crosslinking was 8 and 10 atom length. The short chain was added at 0.23% of the monomer composition listed in section II.1. The other crosslinking levels were adjusted to achieve stoichiometric equivalence to the short chain level to take into account the varying molecular weights between the crosslinking chemistries. A blank adhesive was synthesized for comparison.
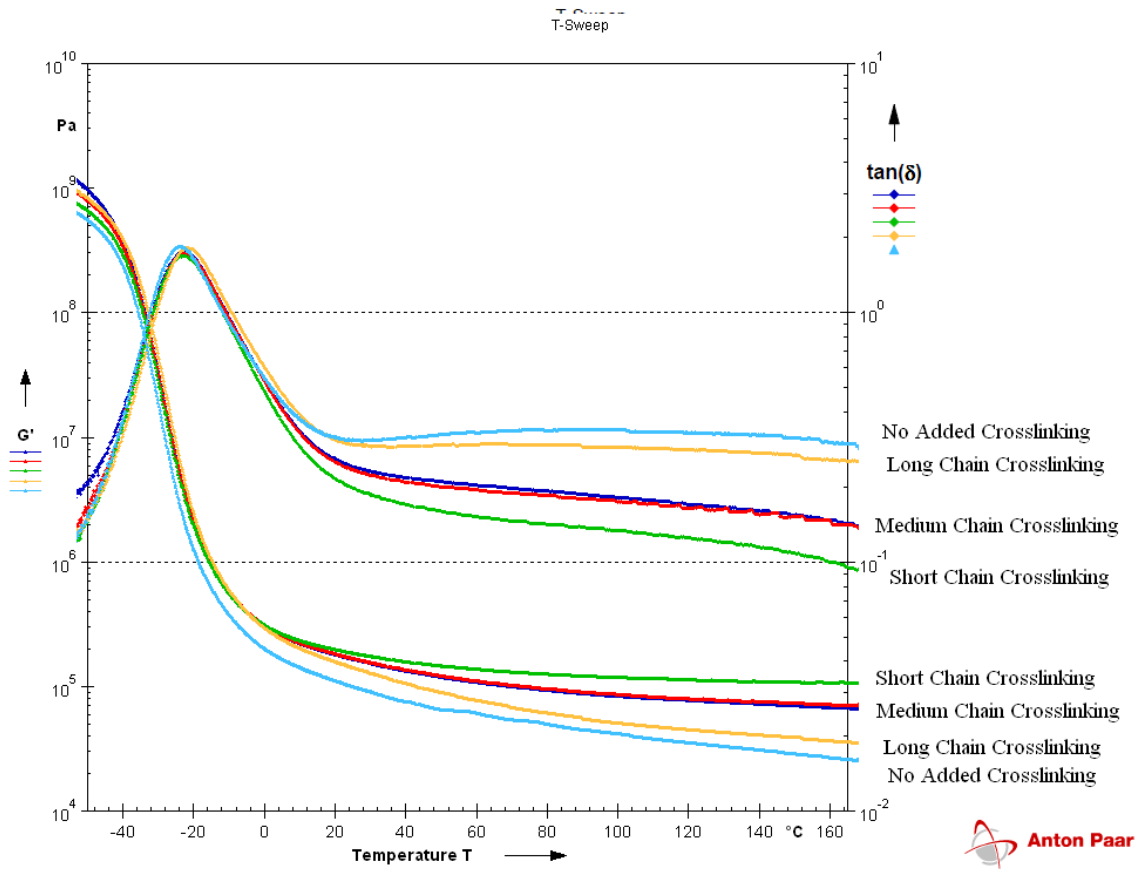
The peel performance of the resulting adhesives showed that, as the chain length of the crosslinking decreases, there is a reduction in initial peel and long-term 7 day at 70°C aged peel (Table 1). The short chain crosslinking chemistry reduced the initial peel to 50% of the blank. The aged peel of the short chain crosslinking chemistry was reduced to 38% compared to the blank. The medium chain crosslinking chemistry performed nearly identical and reduced the initial peel to 78% of the blank and 53% of the aged peel of the blank.   The long chain crosslinking chemistry had perceivably no effect on peel reduction.

Rheological characterization of the adhesives exhibited that as the crosslinking chain length decreased; there was an increase in the plateau storage modulus, inhibiting the adhesive substrate bonding[1] (Figure 1). This inhibition of bond formation also applied to facestock anchorage. As the peel level decreased, there was a corresponding lower anchorage to the facestock film (Table 4). There was also a reduction in the max tan delta, but the temperature at which this occurred was mostly unaffected.

Table 1 Peel Performance of Crosslinking Chemistries

Crosslinking	180° Peel, Stainless Steel		
Chemistry	15-Minute	24-Hour	7-Day 70°C
No Added Crosslinking	1.1	1.6	3.1
Long chain crosslinking chemistry	1.1	1.9	3.0
medium chain crosslinking agent 10 atom	0.8	1.5	1.8
medium chain crosslinking agent 8 atom	0.8	1.5	2.1
Short chain crosslinking chemistry	0.5	0.9	1.1
Interparticle crosslinking agent	0.6	1.1	2.0

Figure 1 Dynamic Mechanical Thermal Analysis of Crosslinking Chemistries

III.2 Intraparticle Crosslinking Level

It is understood that increasing the crosslinking amount will reduce peel, but the objective of this study is to compare high levels of a long chain crosslinking to lower levels of a short chain crosslinking[3]. A ladder study of short chain crosslinking chemistry at 0.5 times the original level and 1.5 times the original level were synthesized. Long chain crosslinking chemistry samples were also run at 1.5, 2.0, and 3.0 times the original level. Peel performance was run on the resulting adhesives. Frequency sweep of the adhesives was run as well to characterize the rheology.

The long chain crosslinking chemistry demonstrated that as the level of crosslinking increased, there was minimal effect on the initial peel (Table 2). The aged peel was reduced to 79% of the original value with 2.0 times the amount of long chain crosslinking chemistry and 43% with 3 times the original amount. The peel performance can be related to the ratio of the loss modulus at the debond frequency to the storage modulus at bonding frequency[2]. What was found with the rheological characterization of the levels of long chain crosslinking chemistry

was that the storage and loss modulus were relatively unaffected in the 1.0 to 100 rad/s region, while the storage modulus was raised in the 1.0 to .01 region (Figure 2). This would result in less effect on the initial peel, but reduction in the long-term bond formation. A similar effect was seen with short chain crosslinking chemistry, but there was a reduction in the initial peel as the level increased (Table 3). There was also a corresponding increase in the storage modulus across the whole region of the frequency sweep, but the storage modulus increase was more exaggerated in the low frequency region (Figure 3).

Table 2 Peel Performance of Long chain crosslinking chemistry Ladder Study

Crosslinking Chemistry	Level, Compared to Study 1	180° Peel, Stainless Steel		
		15-Minute	24-Hour	7-Day 70°C
Long chain crosslinking chemistry	1.0	1.1	1.9	3.0
	1.5	1.0	1.3	2.9
	2.0	1.1	1.3	2.4
	3.0	0.8	1.0	1.3

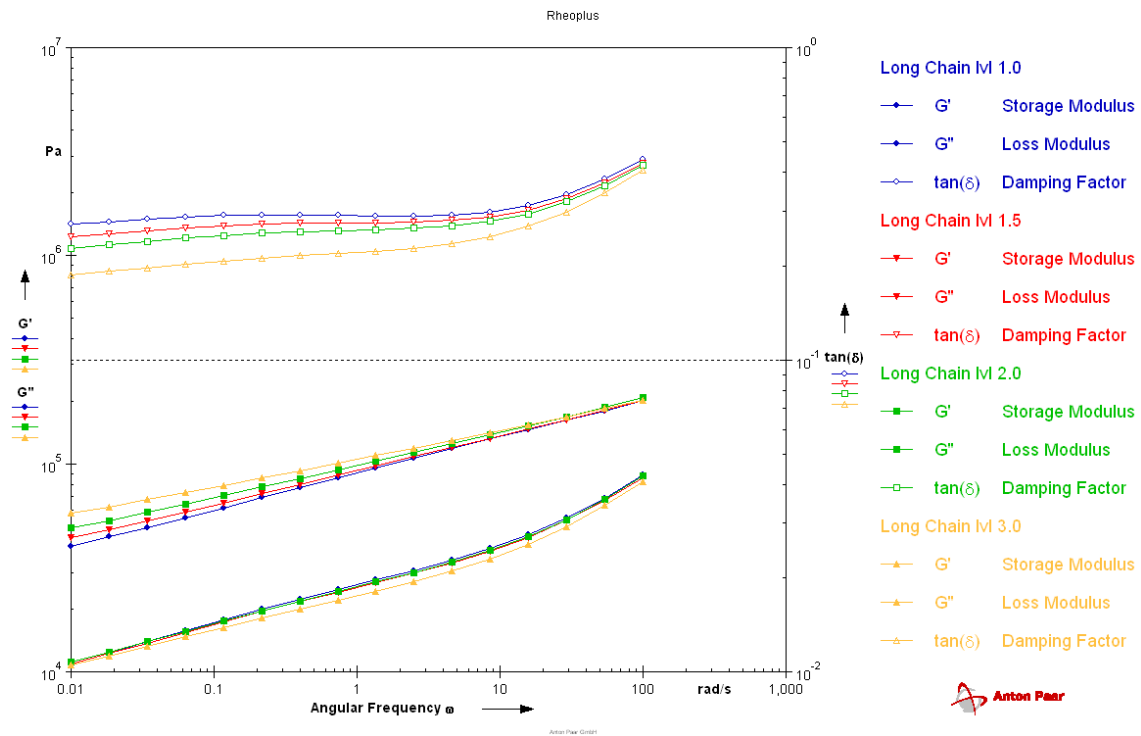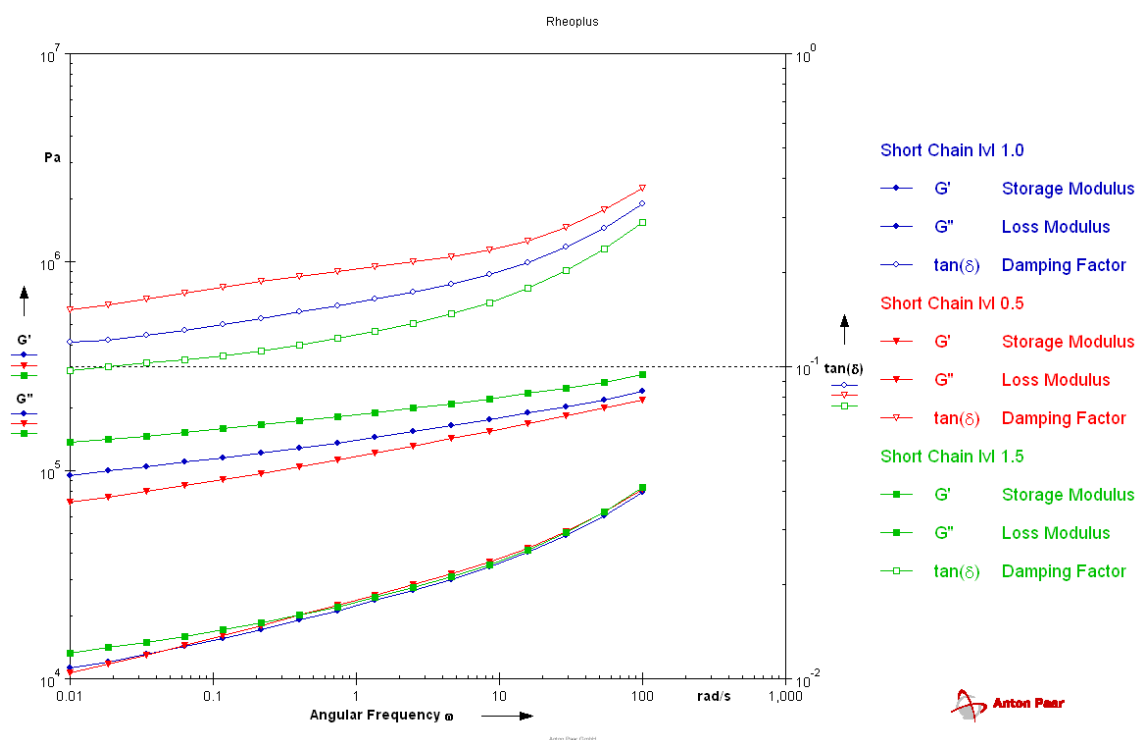**Figure 2** Frequency Sweep of Long chain crosslinking chemistry Ladder Study

Table 3 Peel Performance of Short Chain Crosslinking Chemistry Ladder Study

Crosslinking Chemistry	Level, Compared to Study 1	180° Peel, Stainless Steel		
		15-Minute	24-Hour	7-Day 70°C
Short chain crosslinking chemistry	0.5	0.8	1.3	2.2
	1.0	0.5	0.9	1.1
	1.5	0.4	0.4	0.7

Figure 3 Frequency Sweep of Short Chain Crosslinking Chemistry Ladder Study

III.3 Interparticle Crosslinking

The adhesives in the previous studies demonstrated corresponding low levels of anchorage as the peel was reduced. This was due to the crosslinking occurring during synthesis, and thus does not allow for facestock bond formation during transfer coating. In this study, an ambient cure crosslinking system was utilized to impart interparticle crosslinking. This interparticle crssolinking agent is a delayed cured system that takes place during and after film drying. In this study, the interparticle crosslinking agent was reacted into the same adhesive system as the previous studies, at the same molar ratio of crosslinking as the initial study.

The initial peel was reduced to 53% of the blank and ultimate peel was reduced to 64% of the blank (Table 1). The adhesives with the interparticle crosslinking agent had significantly improved anchorage, causing film deformation before removal of the adhesive. The anchorage was even improved over the polymer containing no crosslinking agent. The level the interparticle crosslinking agent was increased to 1.5 times the original level, but an increase in peel was exhibited. This may be attributed to complexities of the film formation – crosslinking process. The interparticle crosslinking agent requires diffusion of species to allow the crosslinking to take place. If the interparticle crosslinking agent does not achieve homogenous, complete crosslinking, it is believed that viscous domains of polymer can dissipate energy during the debond process, thus increasing peel resistance.

Table 4 Anchorage Testing Comparison

Crosslinking Chemistry	Anchorage 1-Poor, 5-Excellent
No Added Crosslinking	4.0
Long chain crosslinking chemistry	3.5
Medium chain crosslinking agent 10 atom	2.5
Medium chain crosslinking agent 8 atom	2.5
Short chain crosslinking chemistry	1.5
Interparticle crosslinking agent	4.5

III.4 Model Systems, Hybrid Approach

Out of these studies, we found that the initial and aged peel could be refined by the crosslinking chain length and level of intraparticle crosslinking and the anchorage could be significantly improved by introduction of interparticle crosslinking. From these studies, two model adhesives were made with a hybrid approach. The peel performance was expanded to include glass and HDPE (Table 5). Adhesive 1 demonstrated a similar peel performance to the study 1 short chain crosslinking chemistry adhesive, but with significantly improved anchorage. Adhesive 2 demonstrated higher tack and higher initial peel with a flattened peel profile and good anchorage to the film facestock.

Table 5 Performance Testing of Model Systems

	Model 1	Model 2
180° Peel, Stainless Steel		
15-Minute	0.9	0.7
24-Hour	1.0	0.7
7-Day 70°C	2.0	1.3
180° Peel, Glass		
15-Minute	0.6	0.3
24-Hour	0.7	0.5
7-Day 70°C	1.5	0.8
180° Peel, HDPE		
15-Minute	0.4	0.2
24-Hour	0.5	0.2
7-Day 70°C	0.6	0.2
Anchorage	4.5	4.5

IV. Conclusions

Optimizing peel performance in acrylic emulsion removable adhesives requires a multifacetated approach with crosslinking. The crosslinking's chain length and level can be varied to promote deadened peel with a flat peel profile. Introduction of interparticle crosslinking that allows for crosslinking during the film formation aids in adhesion to the facestock film. Through application of these findings, removable acrylic emulsions can be formulated to achieve a variety of peel performance profiles with improved anchorage.

Acknowledgement

Literature

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