

# Fundamental Structure-Property Relationships of PSAs Using Rheological Characterization

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## Introduction

Pressure sensitive adhesive performance relies heavily on the viscoelastic behavior where in the end-use application a polymer may experience large degrees of deformations that occur over at least 4 orders of magnitude in strain deformation rate. Many studies have attempted to relate dynamic mechanical rheology and tensile testing to adhesive properties with very limited success. In the past, rheology studies have been limited to the linear regime and therefore have failed to characterize phenomena that only onset at much larger deformations (greater than 100% strain). Although tensile testing can capture responses at high deformations, the deformation rate is limited to many orders of magnitude lower than what is experienced during typical peel and tack conditions. In addition, the practicality of conventional tensile testing of PSAs is limited by the ability to handle freestanding films of these low- $T_g$  materials without causing premature deformation. There is an extremely limited database that bridges polymer composition and polymerization processes to actual deformations that are experienced in real world pressure sensitive adhesive testing.

While surface energy (compositional effects and chemical potential) contributes to work of adhesion ( $W_A = 2\gamma + G_p$  Equation 1), this term alone can usually not explain differences in adhesion between polymers of varied compositions.<sup>1</sup>

$$W_A = 2\gamma + G_p$$

**Equation 1**

Where  $G_p$  is a term accounting for the energy dissipated in deforming the polymer, which is likely to be significant especially at high deformation rates.<sup>2,3</sup> From this it becomes clear that work of adhesion, and measured peel forces, are the result of both interfacial and rheological effects. Therefore the plastic dissipation term must come into consideration, and indeed Falsafi and Tirrell have shown that this is the main mechanism contributing to adhesion of acrylic pressure sensitive adhesives.<sup>4</sup>

This paper aims to develop structure-property relationships using different analytical and rheological tools. Here we explore the effect of soft monomer and styrene content on PSA performance via a full factorial design of experiments (DOE). Initial dynamic mechanical analysis (DMA) and extensional rheology results will also be discussed in terms of their correlation to PSA performance, or lack thereof.

## Experimental

### Sample Preparation

Water-borne PSAs were prepared by standard emulsion polymerization techniques with either no styrene, or a small percentage of styrene. The PSA emulsions were drawn down with a 12-mil Bird bar

to target 8-mil dry films. The drawdowns were dried for 5 minutes at 80 °C. Peels were measured at 90 degrees after 20 minute dwell time, at a rate of 12 in/min. Shear configuration was 1 inch x 1 inch with a 1 kg weight. For Dynamic Mechanical Analysis (DMA) and extensional rheology, the polymer emulsions were poured or pipetted into ChemWare Petri dishes. The films were allowed to dry in a convection hood at ambient temperature for 1-2 weeks. The films were then flipped and placed back in the Petri dishes with the bottom surfaces exposed. The dishes were placed back in the convection hood for an additional 1-2 weeks for further drying. Then, the samples were placed in a mild oven (ca. 50 °C) for approximately 8 h to complete the drying process. The dry films were placed under vacuum at ambient temperature until the time of the analysis.

### Dynamic Mechanical Analysis (DMA)

The samples were tested on a Rheometrics Mechanical Spectrometer (RMS-800) using 8 mm diameter aluminum disposable plate fixtures. A dynamic temperature ramp mode was used for testing the sample from -80 °C to 180 °C and back to -80 °C at a rate of 3 deg/min, using an applied frequency of 6.28 rad/s. The AutoStrain option was employed for testing with the initial strain set at 0.005-0.1% upon heating and 0.2-0.5% upon cooling, and a maximum strain limit of 5%, to ensure the test conditions remained in the linear viscoelastic regime. The fixtures were zeroed at the initial test temperature of -80 °C. The instrument was then heated to room temperature. The thickness of the sample was measured using the instrument micrometer after loading the sample between the parallel plates. The instrument and sample were then cooled to -80 °C with a slightly positive normal force on the sample to maintain good contact with the plates. Testing was started after approximately 15 minutes of equilibration at -80 °C.

### Extensional Rheology

The dried films were run on an ARES-G2 Rheometer from TA Instruments using the extensional viscosity fixture (EVF) at 25 °C. The width and thickness of the sample were measured by a micrometer and input to the test program. The solid density was estimated at 1.08 g/cm<sup>3</sup> for the BA polymers and 0.908 g/cm<sup>3</sup> for the EHA polymers. Melt densities of 1.0 g/cm<sup>3</sup> and 0.9 g/cm<sup>3</sup> were used for BA and EHA polymers, respectively. The sample was loaded into the oven and the run immediately started, using a 120 second delay before test option to achieve thermal equilibration. The ARES-G2 has a forced air oven, and all experiments were conducted under a nitrogen gas atmosphere. The extensional viscosity is measured at the desired rates of 0.1, 1, and 10 s<sup>-1</sup>, and the data was taken in a logarithmic sampling mode with 200 points.

## Results and Discussion

A series of polymers was synthesized with the following variables: soft monomer (BA vs. EHA) and styrene content. Peel, shear, and tack were tested and are summarized in Table 1.

**Table 1: PSA Properties**

| Soft Monomer | Styrene | Sample ID | SS Peel (N/in) | HDPE Peel (N/in) | SS Tack (N) | HDPE Tack (N) | Shear (hr) |
|--------------|---------|-----------|----------------|------------------|-------------|---------------|------------|
| BA           | No      | SRZ 5892  | 4.7            | 5.2              | 6.7         | 5.8           | 12         |
| BA           | Yes     | SRZ 5891  | 5.2            | 4.0              | 5.8         | 4.3           | 131        |
| EHA          | No      | SRZ 5893  | 0.5            | 0.8              | 1.5         | 1.7           | 1.3        |
| EHA          | Yes     | SRZ 5894  | 1.3            | 1.9              | 3.4         | 3.6           | 360        |

All peel failures were adhesive, while all shears were cohesive. The testing results were modeled in JMP software using both main effects and two-factor interactions. Significant effects are shown in Table 2 **Error! Reference source not found.**. The choice of soft monomer (BA vs. EHA) had a significant effect on the properties of the resulting PSA, which is not surprising given that those monomers represented a large fraction of the overall polymer composition. However, it is not expected that with all other variables held constant, an EHA polymer would have lower performance in terms of both peel and shear than a BA polymer. Take for example SRZ 5892 (BA-based) compared with SRZ 5893 (EHA-based). SRZ 5893 had both lower peel (to both substrates) as well as lower shear than SRZ 5892. Another example is SRZ 5891 (BA-based) vs. SRZ 5894 (EHA-based). In this case the EHA polymer still has lower peel than the BA one, but also higher shear (although on the same order of magnitude). The difference between these two pairs of polymers may be attributable to the styrene present in 5891 and 5894.

The lower peel values of the EHA-based polymers than the BA-based polymers at the same synthetic conditions are believed to be due to the more crosslinked nature of the EHA polymers. Figure 1 compares the temperature dependent  $G'$  and  $\tan \delta$  for SRZ 5892 (BA based) and SRZ 5893 (EHA based) upon cooling. It is obvious that the EHA polymer shows a much higher and flatter  $G'$  along with a much smaller  $\tan \delta$  signal in the rubbery plateau regime, suggesting a more crosslinked polymer architecture. The same trend was observed for SRZ 5891 versus SRZ 5894 (Figure 2), although the difference is not as large, presumably because styrene incorporation washes out the effect of bulk monomer composition.

**Table 2: Significant Effects from Linear Regression Modeling of PSA Testing**

| <b>Response</b> | <b>R<sup>2</sup></b> | <b>Significant Effects</b>                      | <b>Prob&gt;  t </b>           |
|-----------------|----------------------|---|-------------------------------|
| SS Peel         | 0.98                 | Soft Monomer<br>Soft Monomer*Styrene            | <0.0001<br>0.0111             |
| HDPE Peel       | 0.93                 | Soft Monomer<br>Soft Monomer*Styrene            | <0.0001<br><0.0001            |
| SS Tack         | 0.89                 | Soft Monomer<br>Soft Monomer*Styrene            | <0.0001<br><0.0001            |
| HDPE Tack       | 0.74                 | Soft Monomer<br>Soft Monomer* Styrene           | 0.0017<br><0.0001             |
| Shear           | 0.94                 | Soft Monomer<br>Styrene<br>Soft Monomer*Styrene | <0.0001<br><0.0001<br><0.0001 |

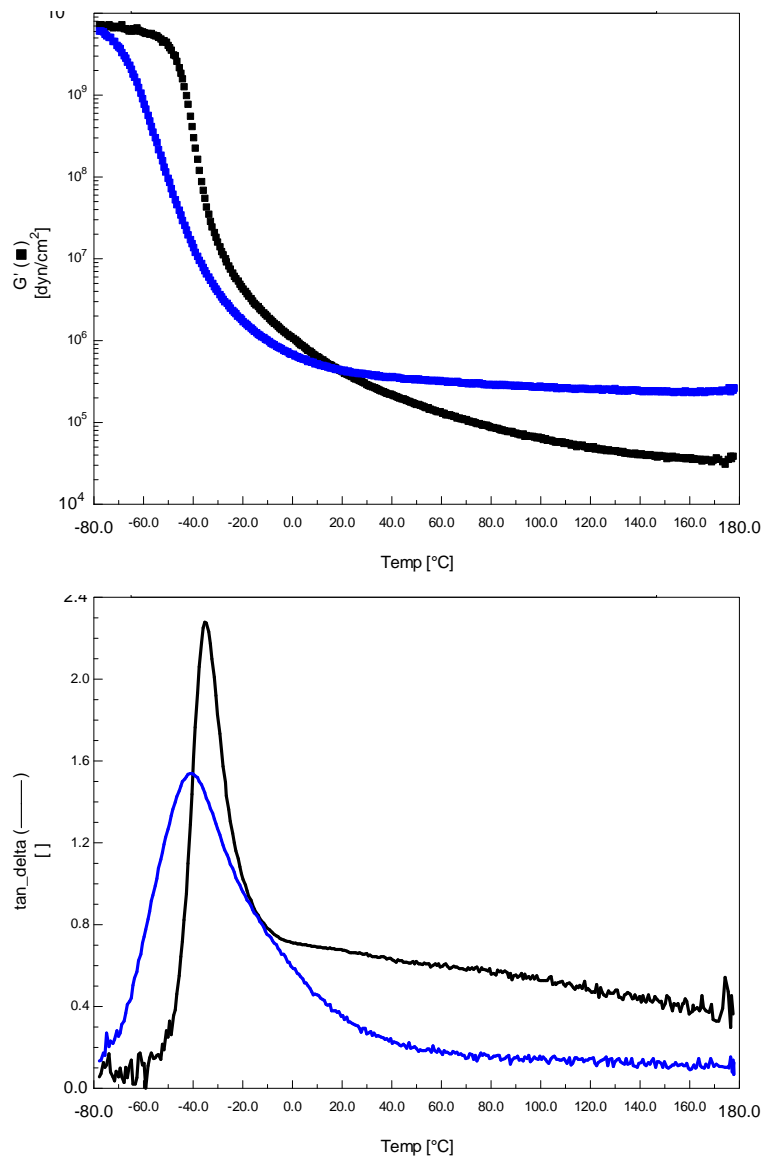
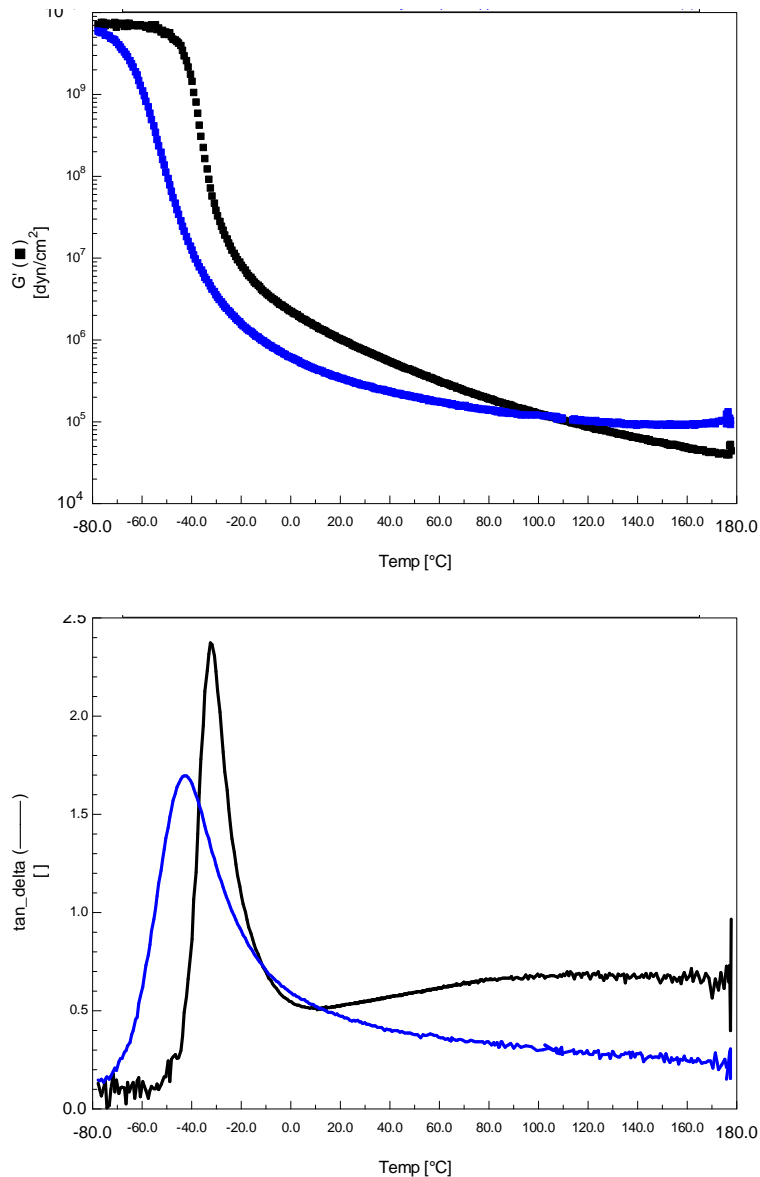


Figure 1. Overlay of  $G'$  (top) and  $\tan \delta$  (bottom) versus temperature for SRZ 5892 (black) and SRZ 5893 (blue).



**Figure 2. Overlay of  $G'$  (top) and  $\tan \delta$  (bottom) versus temperature for SRZ 5891 (black) and SRZ 5894 (blue).**

Styrene seemed to have a more pronounced effect on the performance of EHA-based polymers than on BA-based ones. With BA-based polymers, peel and tack remained roughly the same or slightly decreased when styrene was incorporated (SRZ 5892 vs. 5891). In these polymers, the shear also increased by about one order of magnitude. This is thought to be a significant change in shear. However, when styrene was introduced into EHA-based backbones, the peel and tack increased (see SRZ 5893 vs. 5894), while the shear also increased by two orders of magnitude. This is an unusual result, as an increase in either peel or shear typically comes at the expense of the other property.

The effect of styrene incorporation on shear improvement of PSAs is attributed to an increase in standing monomer during polymerizations containing styrene, which can lead to less backbiting and hydrogen abstraction and hence more linear polymers with fewer and longer branches. This is consistent with the trends observed from DMA, with incorporating styrene leading to more linear and less crosslinked architecture for BA and EHA, respectively. Figure 3 compares the DMA results for BA polymers with or without a small amount of styrene. SRZ 5892 (no styrene) shows both a flatter  $G'$  and  $\tan \delta$  at high temperature than SRZ 5891 (with styrene), suggesting a more branched or less linear structure without incorporation of styrene. Analogously, for EHA (Figure 4), the plateau modulus for SRZ 5893 (no styrene) is higher than that for SRZ 5894 (with styrene), along with a lower  $\tan \delta$  signal, suggesting a more crosslinked architecture without addition of styrene.

We hypothesize that the opposite trends in peel and shear for BA vs. EHA after incorporation of styrene are due to their different types of molecular architecture. The BA-based polymers in this study appear to be branched, showing  $\tan \delta$  with a slope above  $T_g$ , while the EHA-based polymers appear to be crosslinked, showing nearly flat  $\tan \delta$  in the same temperature range. While incorporating styrene results in a more linear/less crosslinked architecture and improves shear, the effect on peel could be quite different. The unusual increase in peel with the addition of styrene for EHA may be due to the more crosslinked nature of the polymer without styrene: as styrene is added, the degree of crosslinking decreases, bringing a soft thermoplastic elastomer that behaves similar to a rubber closer to a lightly crosslinked PSA.<sup>5</sup>

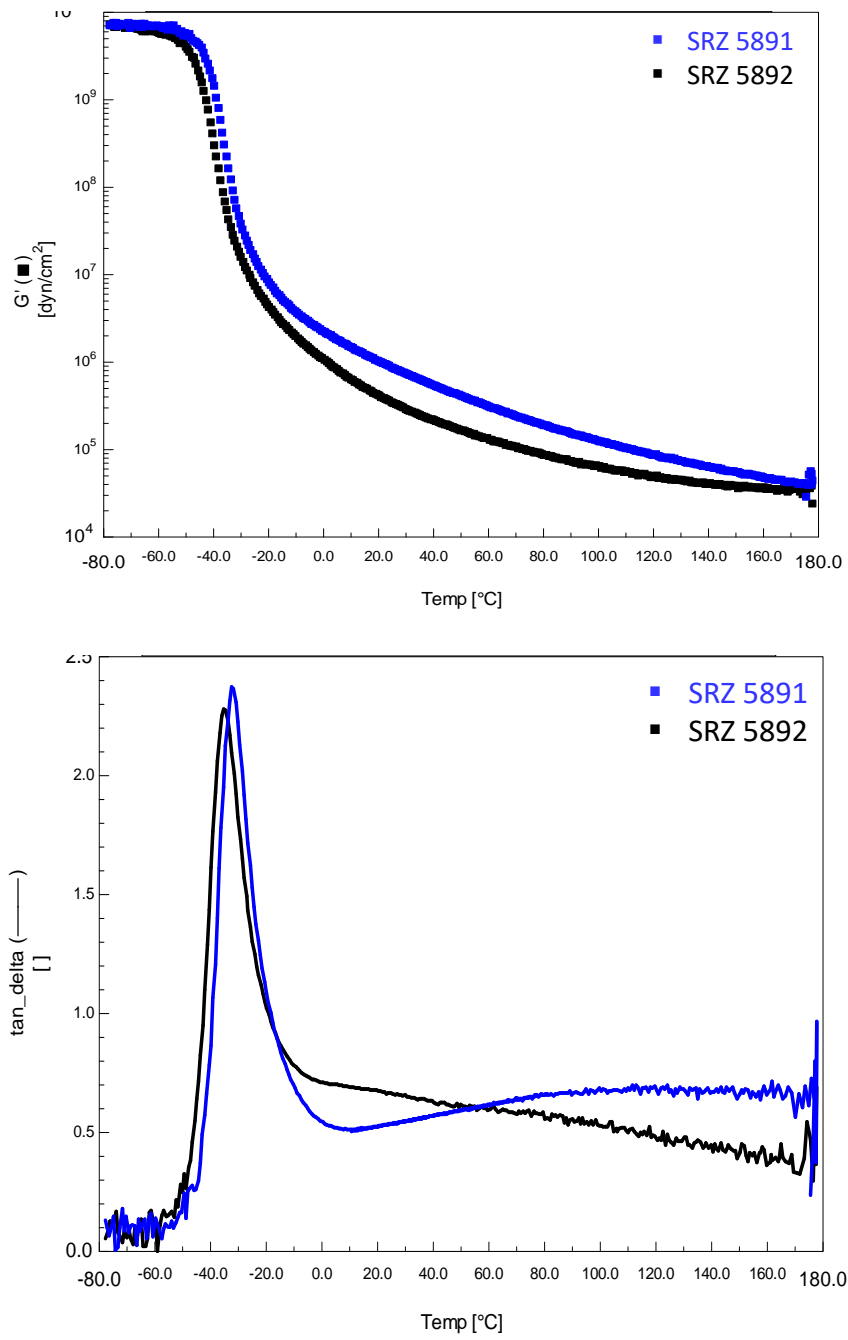
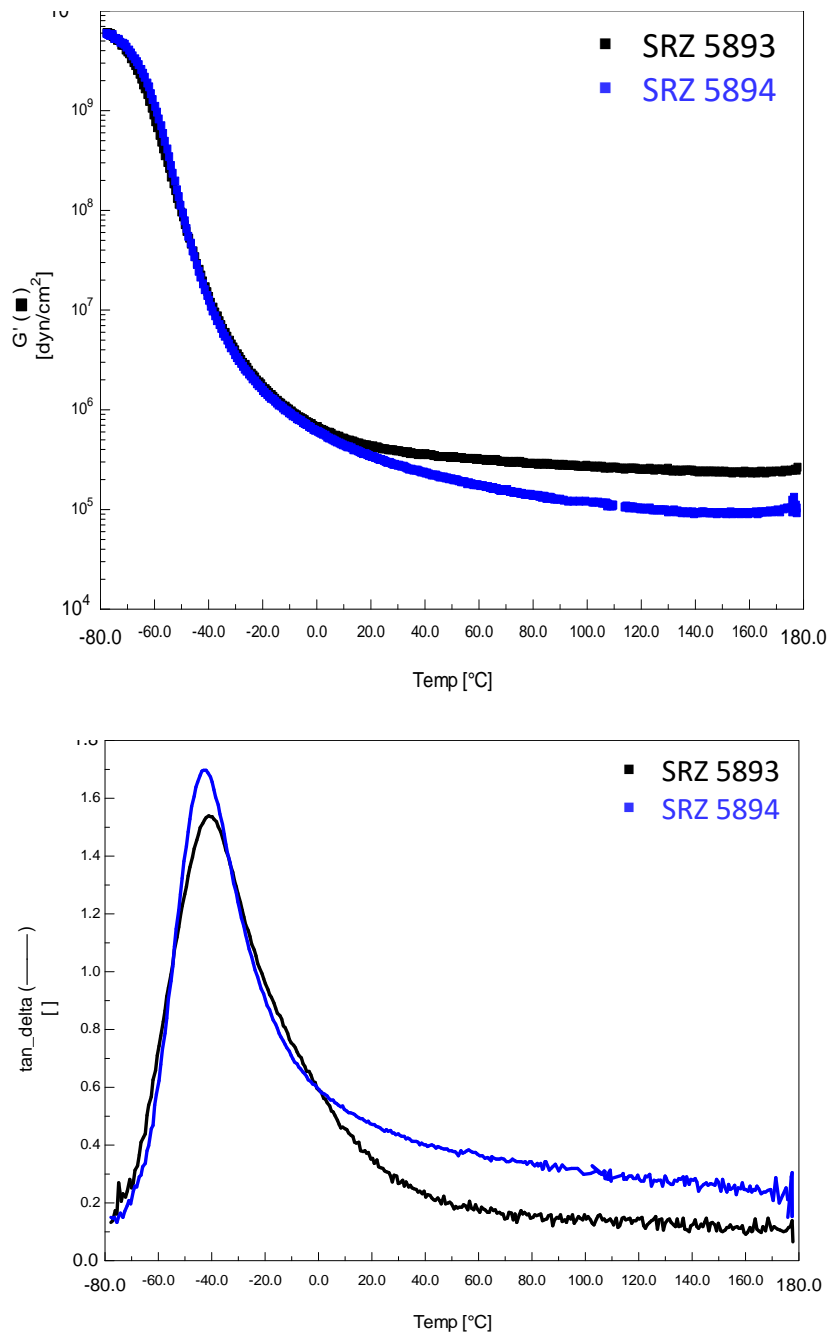


Figure 3. Overlay of  $G'$  (top) and  $\tan \delta$  (bottom) versus temperature for SRZ 5892 (black) and SRZ 5891 (blue).

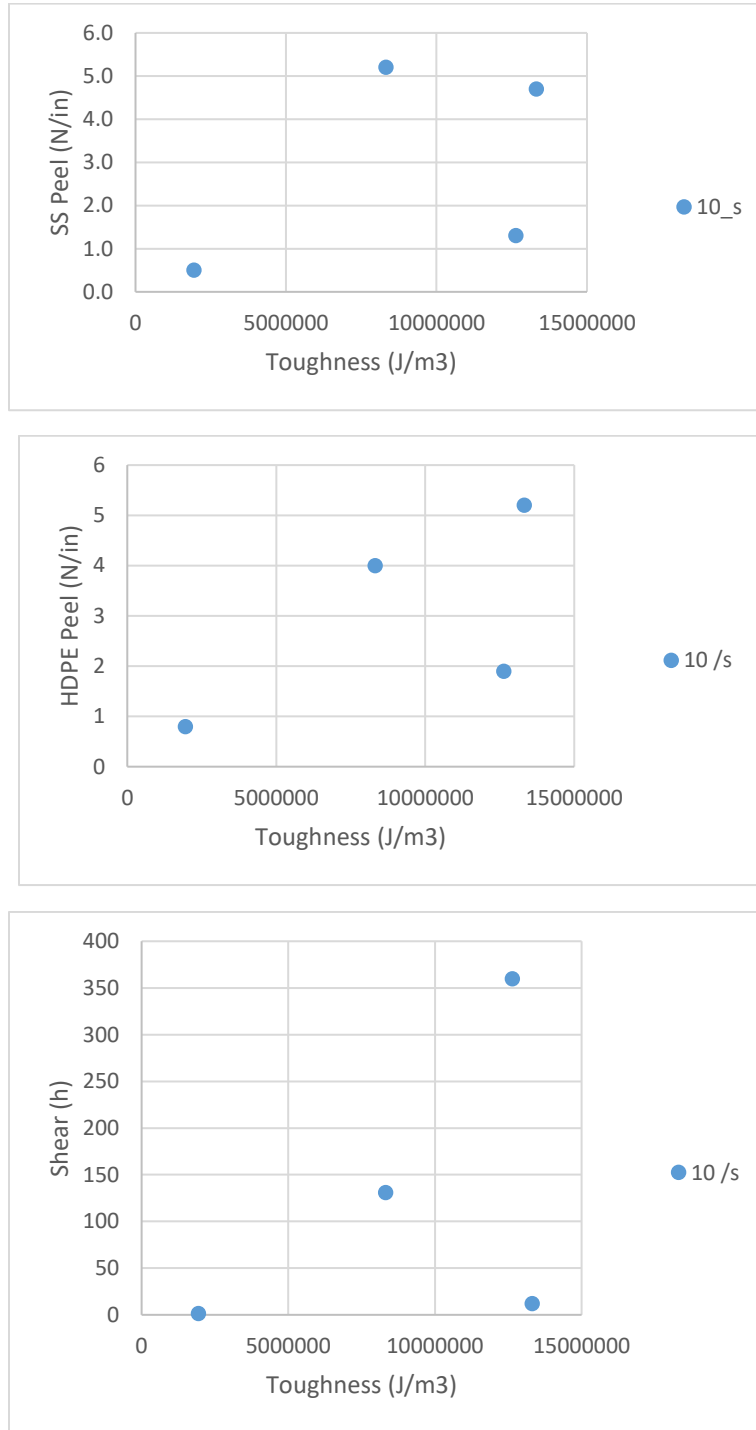




**Figure 4. Overlay of  $G'$  (top) and  $\tan \delta$  (bottom) versus temperature for SRZ 5893 (black) and SRZ 5894 (blue).**

It is noteworthy that the stronger effect of styrene incorporation for EHA is not illustrated from the DMA results. This is in part due to the lack of quantitative understanding in degree of branching or crosslinking from the  $\tan \delta$  signal. Other techniques such as <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy may provide better quantification on degree of branching. Additionally, other techniques such as extensional rheology may provide insight as well. Early attempts to correlate PSA performance

with polymer toughness, obtained from extensional rheology experiments, were inconclusive (Figure 5). More work is needed to refine the experimental conditions for this test.



**Figure 5: Correlation of PSA Properties with Toughness from Extensional Rheology Measurements (Top: SS Peel; Center: HDPE Peel; Bottom: Shear)**

In this study, the DMA results did not correlate well with the PSA performance of the polymers studied. This is not surprising given that DMA measurements are taken at very small deformations, while PSA behavior such as peel and shear is measured at very high deformations. Additionally, the internal failure mechanism (on a molecular level) may be different for various polymers, depending on the molecular weight, linearity (both length and number of branches), and other factors such as hydrogen bonding or ionic interactions. For example, a lower molecular weight polymer with short branches or a linear structure will undergo a disentangling (flow) mechanism during shear failure, while a highly branched or lightly crosslinked polymer will likely undergo chain scission during shear testing. These variables can be difficult to control when varying PSA composition and process conditions, and make DMA a less-than-ideal tool for predicting PSA behavior.

## Conclusions

In this fundamental exploration of PSA composition and architecture, the effects of bulk monomer (EHA vs. BA) and styrene incorporation were investigated. EHA polymers had lower peel and shear, but this shear deficit was overcome by incorporation of styrene. The effect of styrene incorporation was more pronounced in EHA polymers than in BA. Inclusion of styrene increased shear in both BA and EHA backbones, but also increased peel and tack in EHA polymers. DMA shows that with styrene incorporation, the resulting polymer chains are less crosslinked (for EHA) or more linear (for BA). However, DMA does not correlate with PSA testing (peel and shear) due to the differences in extent and speed of deformation between these two tests. Extensional Rheology may be a potential tool to correlate polymer mechanical properties (i.e. toughness) with PSA behavior, but further optimization of the test conditions is necessary.

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