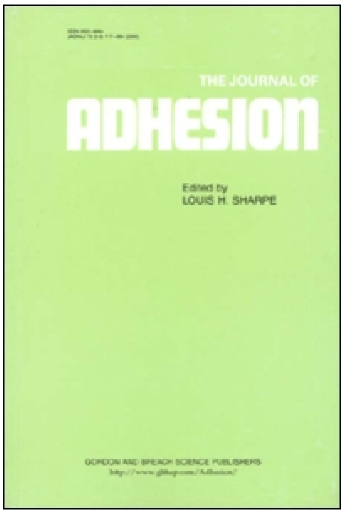

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Jan J. Spitzer[a]
[a] Dispersion R & D, Charlotte Technical Center, BASF Corporation, Charlotte, NC, USA

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The Maximum Peel Strength of Pressure-Sensitive Styrene-Butadiene Emulsion Polymers*

JAN J. SPITZER

BASF Corporation, Dispersion R & D, Charlotte Technical Center, 11501 Steele Creek Rd, Charlotte NC 28273, USA

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Peel strengths of five pressure-sensitive styrene-butadiene emulsion polymers, having different amounts of gel and different glass transition temperatures, have been determined as a function of temperature and peel rate. For each peel rate, the peel strength reaches a maximum at a particular temperature, and this maximum peel strength is associated with the change of the mode of failure from cohesive to adhesive. The maximum peel strength is found to be largely independent of the gel level and possibly of the glass transition temperature of the polymer within the domain of pressure-sensitive polymeric properties. The maximum peel strength appears to be dependent on the kind of substrates and the stabilization system of the emulsion polymers (surface free energy properties of the bonded interfaces).

KEY WORDS: Peel strength; pressure-sensitive adhesive; styrene-butadiene polymers; emulsion polymers; peel rate dependence; temperature dependence; gel; surface properties.

1. INTRODUCTION

One of the key application requirements of elastomeric pressure-sensitive adhesives is their peel strength. The basic understanding of the peel experiment has been described by a general equation of the form[1,2]

$$W_p = W_a(\phi + 1) \tag{1}$$

where W_p is the overall work of peeling, W_a is the thermodynamic work of adhesion and the function ϕ represents the bulk viscoelastic energy dissipation, dependent on peel rate, temperature and the extent of adhesive deformation. This equation has been used in the literature,[1–4] with the recognition that the function ϕ approaches zero in the limit of zero peel rate. However, in practical applications of usually only partially cross-linked adhesives, the mode of failure usually changes from adhesive to cohesive as the peel rate is lowered, which limits the usefulness of this equation for developmental purposes. Also, the dependence of the function ϕ on fundamental polymeric properties is not well known. Nevertheless, Equation (1) provides the basic understanding of how

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the work of adhesion determines the peeling energy as a multiplication factor, even though the work of adhesion is negligible in comparison with the viscoelastic dissipation term, ϕ.

Other approaches toward understanding peeling phenomena rely on correlations of the peeling force with other mechanical properties, *e.g.* with stress-strain relationships or with basic viscoelastic parameters,[5–7] and also with observations of fibrillar structures during peeling.[8] For adhesive developmental purposes, the peeling strength is usually directly correlated with physico-chemical properties (*e.g.* molecular weight distribution, glass transition temperature and polarity) of adhesive polymers and their blends with resins and plasticizers.[9–14]

In this paper, we report a new empirical observation that suggests that for a given pressure-sensitive polymer film and a given substrate to be bonded, the maximum peel strength attainable is largely independent of gel content and glass transition temperature of the polymer within the useful range of pressure-sensitive properties. The maximum peel strength appears to depend on the stabilization system of the emulsion polymer and on a given substrate to be bonded.

2. EXPERIMENTAL

2.1 Synthesis

Five functionalized styrene-butadiene emulsion polymers were synthesized by a continuous monomer addition process, utilizing small seed latex particles for particle size control. The level of chain transfer agent was suitably adjusted to obtain a range of polymers with pressure-sensitive properties. The resulting latexes had particle sizes of about 165 nm (Nicomp dynamic light scattering) and solids content of about 50%. The latexes were neutralized with concentrated ammonia, and the residual monomers and other volatiles were removed by a combination of steam and chemical stripping.

2.2 Polymer Characterization

2.2.1 The Methods

Glass transition temperature range, T_g. The T_g was obtained with a DuPont DSC 10 differential scanning calorimeter as a midpoint determination from 20°C/min runs.

Gel content. Gel content was determined gravimetrically as an insoluble portion of a well-dried film in toluene, using a cage of 325 mesh, and allowing the sol to dissolve for 48 hours. The molecular weight of the sol portion is essentially independent of the gel level, and is in the range of 10,000 to 14,000 g/mol.

Dynamical mechanical analysis. The values of storage modulus, G', and damping factor, $\tan\delta$, were obtained using the Rheometrics RDA-700 Analyzer with 4 mm radius aluminum shear plates in the frequency sweep mode. Preliminary runs established that the storage modulus is essentially independent of the strain up to 50%. Strains below 10% gave torque values outside the lower calibration limit.

TABLE I
Polymer characterization data and the maximum pell strength

Polymer	Gel Content			Glass Transition Temperature	
	high	medium	low	high	low
T_g (DSC) [°C]	−39	−41	−39	−39	−51
Gel [%]	41	26	15	47	47
$G' \times 10^{-5}$ [dyn/cm^2]*	7.5	4.3	1.9	18	12
tan δ	0.56	0.75	1.03	0.58	0.52
Maximum Peel Strength (lb/in)	~7	~7	~7	~4.5	~4.5
(kg/cm)	~1.2	~1.2	~1.2	~0.8	~0.8
@ 12 in/min (30 cm/min) T [°C] =	+5	−10	−8	20	−10
@ 1.2 in/min (3 cm/min) T [°C] =	−10	−25	−20	5	−15
@ 0.12 in/min (0.3 cm/min) T [°C] =	−30	−40	−30	−10	−30
Water-sensitivity	low	low	low	high	high

*Strain = 30%, frequency = 1.0 Hz, temperature = 30°C

Water sensitivity. Water sensitivity was judged qualitatively by placing a drop of water for 0.5 hr on a well-dried polymer film, placed against a black background, and observing the degree of whitening.

2.2.2 *Polymer Samples*

The characterization parameters are given in Table I. The first three polymers under the heading "Gel Content" have the same stabilization system (itaconic acid and *n*-hexyl sulfosuccinate) and the same glass transition temperature, the only difference being their gel content. The gel content of these polymers is referred to as low, medium and high, cf. Figures 1–3. The remaining two polymers under the heading "Glass Transition Temperature" have a different stabilization system (itaconic acid and acrylamide) from the first three polymers, which is reflected in their much higher water sensitivity. These two polymers have about the same gel content but different glass transition temperature ranges, referred to as low and high, cf. Figures 4 and 5.

The pressure-sensitive films of these polymers were additionally characterized by DMA measurements of storage modulus G' and damping factor tan δ. The expected trends of these viscoelastic parameters with the amount of gel in the pressure-sensitive films are also shown in Table I.

2.3 Peel Strength Measurements

The samples for peel strength measurements were prepared by direct coating of thickened latexes onto 1 mil polyester film with an automatic bar coating machine. A pressure-sensitive adhesive film of about 20 micrometers was obtained upon drying the

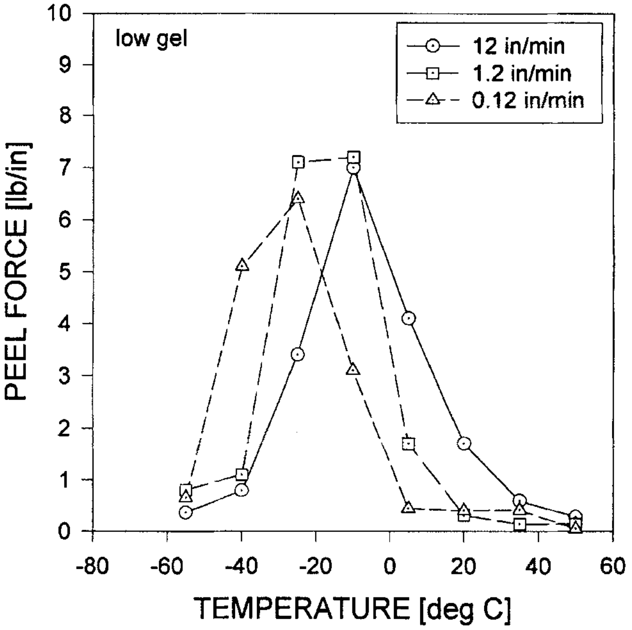

FIGURE 1 Dependence of peel strength on temperature for the low gel polymer.

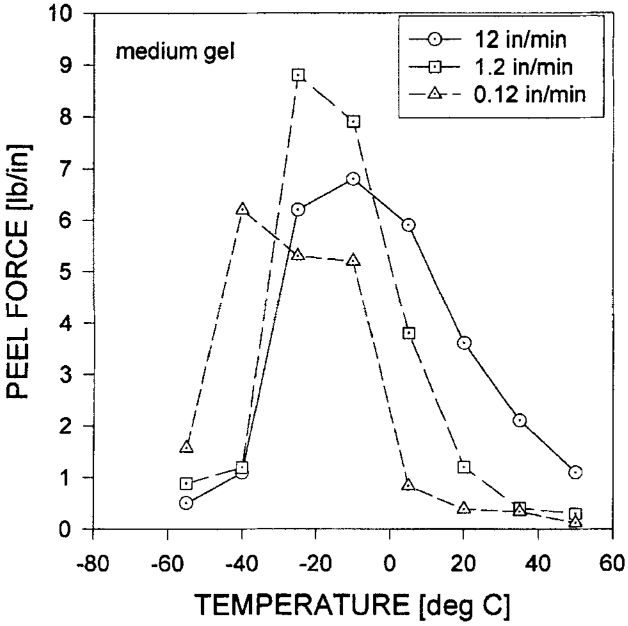

FIGURE 2 Dependence of peel strength on temperature for the medium gel polymer.

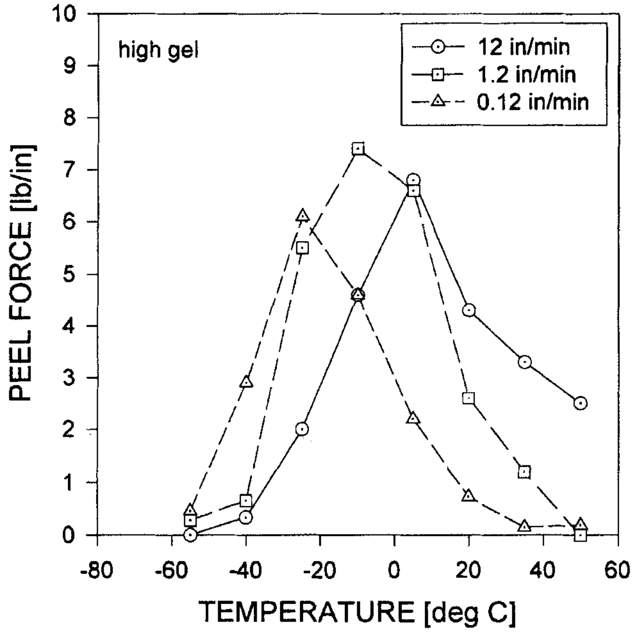

FIGURE 3 Dependence of peel strength on temperature for the high gel polymer.

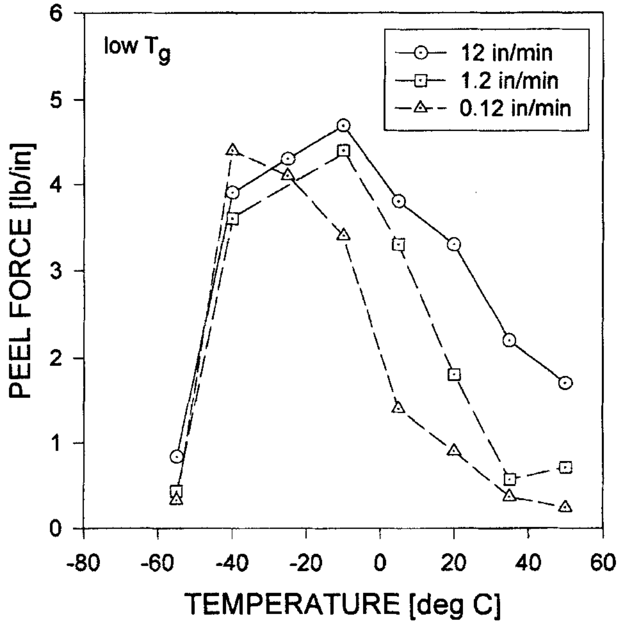

FIGURE 4 Dependence of peel strength on temperature for the low T_g polymer.

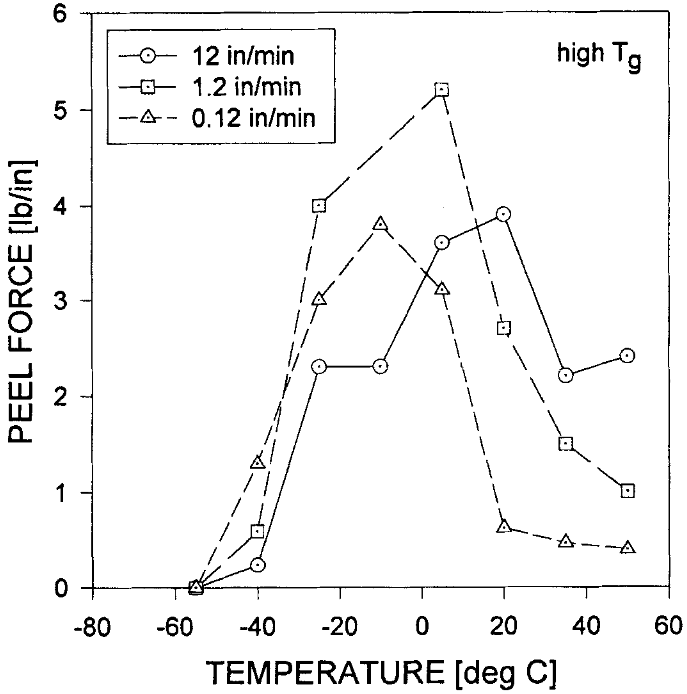

FIGURE 5 Dependence of peel strength on temperature for the high T_g polymer.

wet film at 90°C for three minutes. These films were conditioned at 23°C and 50% R.H. for about 24 hours. Then one-inch (2.5 cm) strips were fastened to cleaned stainless plates with a 4.5 lb (2 kg) roller, and the 180° peel strength determined using the Sintech tensile machine equipped with a constant temperature chamber. The measurements were performed as soon as the temperature reached the set temperature, the total residence time of the adhesive on the substrate being about one hour. Each measurement was done three times, the standard deviations varying from 3 to 20%. In the regions of temperatures and peel rates where the mode of failure changed, the errors were generally higher. The data were obtained over a temperature range of − 55 to 50°C and at cross-head peel rates of 0.12, 1.2, and 12 in/min (0.30, 3.0 and 30 cm/min).

3. RESULTS AND DISCUSSION

3.1 The Dependence on Peel Rate and on Temperature

The results of the peel measurements are summarized in Figures 1–3 for the constant glass transition series (variable gel content) and in Figures 4 and 5 for the constant gel samples (variable glass transition temperature). It is seen that for each peel rate there is a maximum in the peel force, such that the lower the peel rate the lower the temperature at which this maximum occurs, as qualitatively expected from time-temperature superposition considerations.

The mode of failure was cohesive at the high temperature range, and adhesive (determined visually) with or without slip-stick at the low temperature range. In the intermediate temperature range the mode of failure changed from cohesive to adhesive with decreasing temperature. These observations on mode of failure are in accordance with the generally-recognized three regions of the peeling behaviour:[1,3]

a) Predominantly viscous deformation at high temperatures or slow pulling rates, when the cohesive strength of the adhesive is lower than the adhesion to either the backing or the substrate,
b) Predominantly elastic deformation retarded by viscous flow, when the adhesive's cohesive strength is higher than the adhesion to the substrate (if the adhesion to the backing is the highest),
c) Mixture of elastic deformation and a glassy adhesive response at low temperatures or high rates of peel, leading to debonding either at the substrate or at the backing, with oscillatory force variations (slip-stick).

3.2 The Maximum Peel Strength

A qualitative examination of Figures 2–3 shows that the temperature of maximum peel strength depends on the gel level of the polymer at the same glass transition temperature. A comparison of Figures 4 and 5 shows that the temperature of maximum peel strength depends on the glass temperature of the adhesive at constant gel level. These temperatures of maximum peel are summarized in Table I for all three peel rates.

Further examination of the data reveals that the *actual values of the maximum peel strength are largely independent of the gel content (Figs. 1–3) and of glass transition temperature (Figs. 4 and 5).* Thus, the slightly functionalized, constant glass transition temperature polymers have maximum peel strength of about 7 lb/in (1.2 kg/cm) regardless of the gel content, whereas the highly functionalized, constant gel polymers have maximum peel strength of about 4.5 lb/in (0.8 kg/cm), regardless of the glass transition temperature. These findings are summarized in Table I.

As these two sets of polymers differ predominantly in their stabilization systems (copolymerized hydrophilic monomers, and surfactants), it seems reasonable to suggest that the difference between the maximum peel strengths for these two sets of polymers is due to their stabilization systems (and, hence, to their surface properties). However, more data are needed to determine the extent to which the constancy of the maximum peel strength is maintained, as, at higher gel levels than those reported here (above 50%), the storage modulus becomes too large for pressure-sensitive bonding. At such high gel levels the maximum peel strength is likely to decrease because of significantly lower viscous flow energy dissipation and too slow a wetting-out of the substrate (Dahlquist criterion). Similarly, in the region of extremely low molecular weights (no gel and low molecular weight), the viscous energy dissipation is expected to decrease and, hence, also the maximum peel strength.

The new empirical correlation can be expressed by a general statement of the form: *max. peel strength = constant = FUNCTION (peel rate, temperature),* in which the peel rate and temperature are not independent, and probably related by the time-temperature superposition principle. In other words, for any peel rate there is a unique temperature at which the peel strength reaches a maximum, when the cohesive and adhesive strengths of the bond become about equal (the bond fails adhesively or cohesively with an equal chance). In this sense, the observation of maximum peel strengths can be re-stated using Equation (1) as

$$W_{p(\max)} = W_{a/c}(\phi_{\max} + 1)$$

where the maximum energy of peeling, $W_{p(\max)}$, is related to the maximum viscous energy dissipation, $\phi_{\max}$, by a multiplication factor, $W_{a/c}$ (meaning either the thermodynamic work of adhesion, W_a, or cohesion, W_c). In practice, if these two surface thermodynamic terms were numerically close, there would be no observable discontinuity in the maximum peel strength; however, if the thermodynamic work of cohesion and adhesion was substantially different, then there will be a discontinuity in the observed maximum peel strength, manifested by an apparent poor reproducibility of the peel strength measurement. Such apparently poor reproducibility might be caused by any small perturbations (*e.g.*, cleanliness of the substrates, coatweight, acceleration of the tensile machine at the start of peeling), which will then determine the observed mode of failure.

In general, it would be useful to study the region of the cohesive/adhesive mode of failure transition in more detail for a number of different pressure-sensitive adhesives and substrates, as this region is important both theoretically and practically.

4. CONCLUSIONS

An examination of the dependencies of peel strength on peel rate and temperature suggests that the maximum peel strength (characterized by a unique temperature for a given peel rate) is largely independent of gel level and glass transition temperature of the adhesive within the range of useful pressure-sensitive properties.

The maximum peel strength could be used as a basic characteristic of an adhesive/substrate bond. The maximum peel strength can be shifted into a useful range of application peel rates and temperatures by adjusting the glass transition temperature and the gel level of the adhesive by compounding or by polymerization synthesis.

It is suggested that the peel strength region where the mode of failure changes from cohesive to adhesive be further investigated, both from experimental and theoretical standpoints.

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References

1. A. N. Gent and J. Schultz, *J. Adhesion*, **3**, 281 (1972).
2. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc. A.*, **332**, 385 (1973).
3. D. W. Aubrey, in *Adhesion 8*, K. W. Allen Ed. (Elsevier, London, 1984), p. 19.
4. A. Zosel, *Coll. Polym. Sci.*, **263**, 541 (1985).

5. W. C. Dale, M. D. Paster and J. K. Haynes, *J. Adhesion*, **31**, 1 (1989).
6. E. P. Chang, *J. Adhesion*, **34**, 189 (1991).
7. M. F. Tse and K. O. McElrath, *Adhesives Age*, **31**, 32 (September 1988).
8. Y. Urahama, *J. Adhesion*, **31**, 47 (1989).
9. K. C. Seghal and M. A. Sherwin, in *Proc. PSTC First World Congress 1992*, (Pressure Sensitive Tape Council, Chicago, 1992), p. 85.
10. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 807 (1985).
11. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 815 (1985).
12. J. B. Class and S. G. Chu, *J. Appl. Polym. Sci.*, **30**, 825 (1985).
13. S. Naruse, H.-J. Kim, T. Tsukatani, M. Kajiyama, A. Takemura and H. Mizumachi, *J. Adhesion*, **47**, 165 (1994).
14. D. W. Aubrey and M. Sherriff, *J. Polym. Sci.: Polym. Chem. Ed.*, **18**, 2598 (1980).