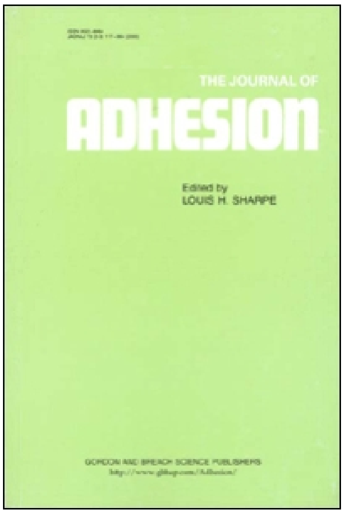

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Properties of Polyisoprene-Based Pressure Sensitive Adhesives Crosslinked by Electron Beam Irradiation

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Many pressure sensitive adhesives are based on partially-crosslinked blends of an elastomer and a tackifying resin. In this work, a model pressure sensitive adhesive system was studied based on anionically-polymerized polyisoprenes. The effects of the initial molecular weight of the polyisoprene and the degree of crosslinking on the adhesive properties were investigated. The adhesives were crosslinked by electron beam irradiation to achieve particular levels of gel content. The dependence of gel content on dose and molecular weight is in good agreement with statistical crosslinking theory. The molecular weight of the soluble fraction was always dominated by that of the initial elastomer. With regard to creep resistance, it was observed that high gel content could compensate for low molecular weight. This was not true of the peel behavior.

Keywords: PSA; polymer blends; elastomer; tackifier; molecular weight; properties; degree of crosslinking; gel content; peel behavior; creep resistance

INTRODUCTION

Pressure sensitive adhesives (PSAs) such as those used on tapes may be prepared from blends of elastomers and tackifying resins. Useful tackifying resins are oligomeric materials of high glass transition temperature (T_g) compared with the elastomer which are thermo-

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dynamically miscible with the elastomer. The blend of elastomer and tackifier, then, exhibits a higher T_g and lower plateau modulus than the elastomer itself. Such modification creates a material with sufficiently low modulus in the time scale of bond formation (of the order of 1 second) coupled with sufficient stiffness and/or energy dissipation at the bond breaking time scale (of the order of 0.01 second) to be a useful PSA [1, 2].

Such adhesives based on natural rubber (*cis*-polyisoprene) have been used since the beginnings of this industry. Typically, the rubber is milled or processed in a Banbury internal mixer to reduce its molecular weight and gel content as well as incorporate fillers and antioxidants. The adhesive mixture is then prepared in a hydrocarbon solvent, coated onto the tape backing, and dried. Often the adhesive will be partially crosslinked to improve its cohesive strength, especially for applications such as masking tape, where clean removability is desired.

It is well known in this industry that the construction of a PSA for a particular application involves balancing the adhesion, tack, and cohesive strength of the material [3]. Typically, increasing the tackifier loading increases the adhesion and tack while decreasing the cohesive strength. Increasing the elastomer molecular weight or the amount of crosslinking improves cohesive strength but often reduces adhesion and tack [4]. High crosslink density is especially detrimental to tack. The peel adhesion at low peeling rate seems to be more adversely affected by high cohesive strength than the adhesion at high removal rate [5].

Previous work by Fortry [6] investigated the effect of molecular weight on adhesive properties of adhesives prepared from anionically-polymerized polyisoprenes. No crosslinking was used in his work. Fortry found that the shear creep viscosity measured at long time (1000 minutes) followed the expected power law dependence on molecular weight with an exponent of 3.4. Fortry did not measure peel adhesion but did test probe tack. The tack was not strongly influenced by molecular weight as long as the molecular weight was not so low that cohesive splitting was observed in the tack test.

Similar work has been conducted on polyisobutylene-based pressure sensitive adhesives by Krenceski and Johnson [7]. The systems examined in that study consisted only of polyisobutylene of varying molecular weight with no tackifying resin. No crosslinking was used.

The resistance to shearing load was found to increase with increasing molecular weight (*i.e.*, creep viscosity increased), the tack was found to decrease as molecular weight increased and the peel force decreased with increasing molecular weight. A transition from cohesive to adhesive failure in peel was also observed as molecular weight increased.

In the present study, we sought to investigate the interaction between the initial molecular weight (MW) of the elastomer and the degree of crosslinking with respect to the effects on adhesion and cohesive strength. We wanted to determine if there was a preferred molecular weight for the starting material for optimum property balance.

We approached this problem by synthesizing polyisoprene by anionic polymerization methods with well-defined, narrow molecular weight distributions. These elastomers were then formulated into adhesives using a single rubber/tackifier ratio and electron beam cured to various gel fractions. The adhesive properties were then examined.

EXPERIMENTAL METHODS

The polyisoprene samples were prepared using *sec*-butyl lithium initiator in cyclohexane at 50°C. Greater than 98% yield was obtained. The molecular weight distributions were measured by size exclusion chromatography (SEC) using polyisoprene standards for calibration. The distribution of chain microstructure was determined by nuclear magnetic resonance (NMR) spectroscopy analyzing the proton spectrum. (The three highest molecular weight samples were prepared in the laboratory of Prof. Roderic P. Quirk at the University of Akron by his student, Jian Yin. The remaining samples were prepared by coauthor J. Ma). The results of the characterizations of the starting materials are shown in Table I.

For simplicity, we will use the abbreviation, D, for the Dalton, the unit of molecular weight which is equivalent to a gram/mole. We will use kD to mean kiloDaltons (10^3 Daltons) and MD to mean mega-Daltons (10^6 Daltons).

The adhesive solutions were prepared by blending the following ratios of components:

TABLE I Characterization of synthetic polyisoprene starting materials

M_n kD	M_w/M_n	Microstructure (mole%) *cis*-1,4	*trans*-1,4	3,4
61	1.03	81	15	4
108	1.07	75	19	6
237	1.07	79	16	5
438	1.03	76	18	6
823	1.03	79	16	5
1340	1.05	77	21	2

Component	**Parts by weight**
Polyisoprene	60
Arkon P90 Tackifier	40
Irganox 1010 antioxidant	1

The Arkon P90 is a hydrogenated tackifier, obtained from Arakawa Chemicals, with a glass transition temperature of 36°C, which is known to be miscible with polyisoprene and provides minimal interference with the radiation curing of the elastomer [8].

The solutions based on the polyisoprenes with molecular weights ranging from 61 kD to 438 kD were dissolved in toluene at 30% solids. The 823 kD adhesive was prepared at 17.1% solids and the 1.34 MD adhesive was prepared at 11.6% solids. The solids content was varied to achieve manageable coating viscosities.

The adhesive solutions were coated using a notched bar coater onto 25 μm thick biaxially oriented polyethylene terephthalate film which had been treated with a proprietary primer. The adhesives were dried in a forced air oven at 65°C for 5 minutes. Another piece of polyester which had been coated with a proprietary, non-contaminating release coating was applied to the adhesive surface to protect the samples during storage. The adhesive coating thicknesses were generally about 40 μm.

The statistical crosslinking theories of Saito [9] and Charlesby [10] predict the following relationship between gel fraction and dose for an initially monodisperse molecular weight distribution and negligible scission reactions:

$$1 - g = \exp(-2gxu) \tag{1}$$

where:

g: gel fraction
x: number of crosslinks per main chain structural unit
u: initial degree of polymerization (number of main chain structural units per molecule).

We will assume that x is proportional to the radiation dose, d, *i.e.*:

$$x = Kd$$

In the radiation literature, the crosslink yield is normally expressed in terms of a quantity called G_x, which is defined as the number of crosslinks produced per 100 eV of absorbed energy. The dose is normally measured in MRads where a Rad is defined as the absorption of 100 ergs of radiation energy per gram of material. Thus, G_x is proportional to K as defined here.

Literature values of G_x are available for polyisoprene [13] but, because of the possible effects of the tackifier and antioxidant, the crosslink yield was determined experimentally for the formulation used in this work. In the preliminary experiments, a commercially-available, anionically-polymerized polyisoprene was used because large quantities were available. This material, LIR50 from Arakawa Chemicals, was found by SEC analysis to have a number average molecular weight of 35 kD and a polydispersity of 1.1.

Adhesives prepared from this elastomer were irradiated at doses ranging from 20 to 40 MRads. A plot of $\ln(1-g)/g$ *vs.* u^*d was made and the slope used to determine the value of K. The intercept was indeed very close to zero, verifying that scission reactions are negligible. This value was then used to predict the doses needed to achieve the desired gel contents of 25, 50 and 75% in adhesives made from each of the prepared polyisoprenes. Coated adhesive samples were then prepared and irradiated at these calculated dose levels for each of the polyisoprene molecular weights.

In the first iteration with our own prepared polyisoprene adhesives, all the gel contents were found to be lower than the target values. Therefore, an effective K was calculated for each of the polyisoprene samples from the measured gel contents and the desired doses recalculated. New samples irradiated at these doses produced gel contents close to the target values. These are the samples which were then subjected to the complete testing, the results of which are reported here.

All of the gel content data from these various iterations are plotted according to Eq. (1) in Figure 1.

If the K value is converted to a G_x, we find a value of 0.68 for the LIR50 materials and an average value of 0.52 for the prepared polyisoprene adhesives. These may by compared with a literature value of 0.9 found for purified and degassed natural rubber with no additives [11, 12, 13]. These authors also found that the ratio of scissions to crosslinks was 0.05, supporting our assumption that scissions may be neglected.

There does seem to be variation in the slope of these curves for the different samples which implies variation in the K and G_x values. However, these may also be the result of slight errors in the molecular weight measurement or variations in the molecular weight distributions.

For gel content determination, tape samples were soaked in toluene for 24 hours, drained, and dried. The gel content was calculated as the

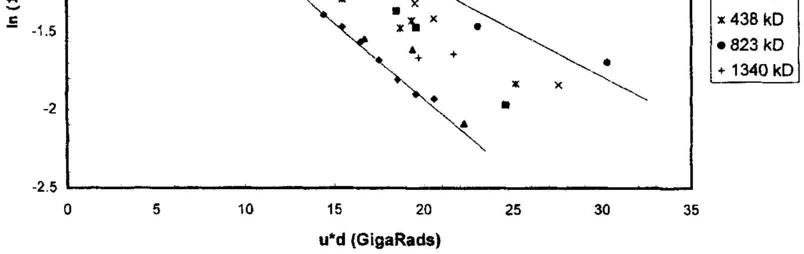

FIGURE 1 Experimental gel results for adhesive formulas plotted according to theoretical relation. All points for a given polymer should fall on a straight line extrapolating through the origin.

remaining insoluble adhesive mass divided by the initial mass of elastomer in the adhesive.

The glass transition temperature (T_g) of the adhesive was obtained by differential scanning calorimetry (DSC) using a Perkin–Elmer instrument scanning at 20°C/min. A sample of the adhesive was removed from the backing of the cured tape for these measurements.

The molecular weight distributions of the uncured adhesives and of the soluble portion of the adhesive after crosslinking were determined using SEC with the same column and solvent as the determination of the elastomer molecular weights. A one-inch diameter sample of the tape was cut with a circular die and soaked in 5 ml of tetrahydrofuran (THF). The extract solution was filtered with a 0.2 micron Teflon filter and injected into the SEC column. For the uncured adhesives, portions of the toluene solutions were dried and redissolved in THF. The calibration standard polyisoprenes were obtained form Polymer Laboratories and covered a range from 1.2 MD to 1.35 kD. The molecular weight distributions were normalized to give unit area under the curve. Therefore, the plotted curves represent the relative amount of the soluble portion at each molecular weight.

Two tests of the adhesive properties in addition to the gel and molecular weight characterization were used. The first was a measure of the peel force as a function of peeling speed for removal of the tape from a polished stainless steel test surface. The second was a measure of the creep resistance of the adhesive under a steady shearing load.

For the peel force *vs.* rate test, a 0.5 in wide sample of tape was applied to a polished stainless steel test panel and rolled down with two slow passes of a 2 kg roller with a 10 cm diameter and a 0.5 cm thick rubber covering. The tape was allowed to dwell on the panel for about 20 minutes. The panel was mounted in the lower grip of a Sintech universal testing machine. A leader on the tape strip was folded back and mounted in the upper grip so as to allow peeling of the tape in a 180° stripback mode. All of the speed points were obtained from a single sample. The sequence progressed from the fastest to the slowest speed.

The apparatus used for the shear creep compliance measurements was similar to that described by van Holde and Williams [14]. Two identical area tape samples are used, one on either side of a center block. The system is clamped together with sufficient pressure to prevent slippage of the backing or the liner on the blocks. A shearing load is applied to the center block by means of a weight and pulley mechanism. The applied shear stress was 3.54×10^4 dyne/cm^2. The creep displacement was measured with a capacitance probe transducer for a period of 100 minutes following the application of the load. The adhesive thickness was determined by making three measurements of the total samples thickness including the backing, adhesive, and release liner, averaging, and subtracting the average backing and liner thicknesses. All the creep compliance measurements were made at a temperature of 22°C. The change in the compliance from 32 minutes to 100 minutes was used to calculate an apparent creep viscosity in that time range to provide a scalar quantity for ready comparison of samples. For some of the very soft samples, the compliance exceeded the capacity of the instrument at earlier times. In those cases, the compliance change from the last two available time increments was used for the viscosity calculation.

Since it was desired to test the irradiated samples and, in fact, the identical samples to those used for adhesion testing, it was necessary to test adhesives which are quite thin (40 μm) for this type of testing. Errors in the knowledge of the adhesive thickness and variation across the sample limit the accuracy and precision of this measurement to something on the order of ±20% of the measured value of the compliance. These samples were also too thin to conduct dynamic mechanical tests in existing rheometers.

RESULTS AND DISCUSSION

Examples of the results of the SEC analysis of the uncured adhesives and the extractable portion of the cured adhesives are shown in Figures 2 and 3. The peak between 2 and 3 on the log MW axis is from the Arkon P90 tackifier. The higher molecular weight material is the polyisoprene. In each case the curves have been normalized to constant total area. Therefore, as the gel content increases, the relative amount of polyisoprene decreases compared with tackifier which is not incorporated into the gel. There is no evidence in any of these curves of the generation of polyisoprene fragments of lower molecular weight than the starting material upon irradiation, further verifying that

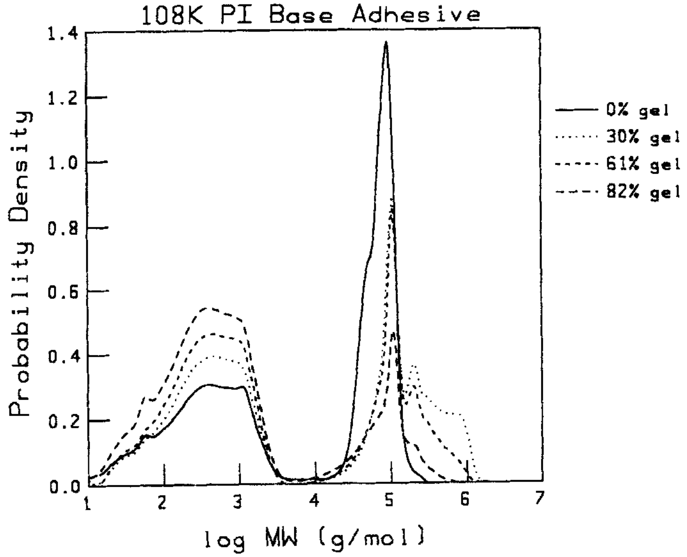

FIGURE 2 Molecular weight distribution of soluble fraction of adhesives based on 108 kD polyisoprene.

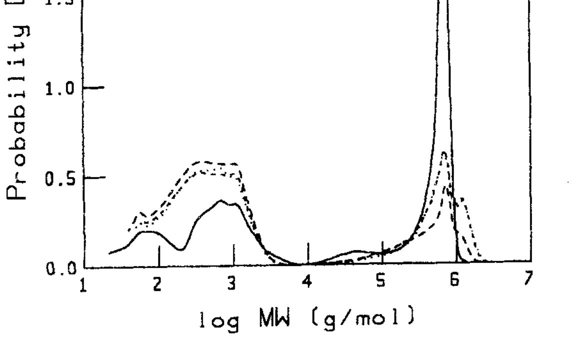

FIGURE 3 Molecular weight distribution of soluble fraction of adhesives based on 823 kD polyisoprene.

scission reactions are negligible. At low gel content, we do see new, higher molecular weight peaks being formed from the coupling of the starting material and later the disappearance of these peaks as they become incorporated into the gel. In all cases, the peak molecular weight in the soluble fraction is still dominated by the starting molecular weight. Thus, the differences among the samples persist even at high gel content.

These results are consistent with predictions of Flory [15] for molecular weight distributions of crosslinked monodisperse polymers. Of course, he predicts peaks only at integer multiples of the starting molecular weight and our curves are not so ideal but we do see the first multiple before the breadth of our initial distribution masks that effect. The predicted molecular weight distributions always have the highest weight fraction of material at the starting molecular weight, as we see here.

The results of the gel, DSC, peel, and creep measurements are summarized in Table II.

The creep compliance both at short times and at long times is governed by a combination of the initial molecular weight and the gel content. The compliance decreases and the viscosity increases as the molecular weight increases or the gel content increases. The effect of gel content becomes less important at the high molecular weights. These results are readily seen in Figure 4.

Three different failure modes were observed in the adhesion testing. Adhesive failure with no apparent change in the appearance of the stainless steel plate was favored by high molecular weight, high gel content, and high peel rate. Cohesive failure, leaving tacky adhesive both on the tape and on the panel, was favored by low molecular weight, low gel content, and low peel speed. When the molecular weight was low but the gel content was high and the peel speed was low, we observed a very thin residue on the stainless steel plate which often was of a bluish or brownish color and was non-tacky. These three failure modes have been indicated in Table II by the symbols *A*, *C*, and *R*, respectively.

The peel force *vs.* peel rate curves for the middle level of gel content are shown in Figure 5. For the 438 kD material, we see classical behavior known for uncrosslinked PSAs in which the peel force drops when the mode of failure changes from cohesive to adhesive. In others, we have an apparent change in the failure mode without any

TABLE II Summary of adhesive properties

MW *kD*	*Dose* *MRad*	*Gel* %	*DSC* T_g °*C*	*Peel force* (*N/cm*) *at speed of* 0.13	1.3	13 *cm/min*	130	*Creep compliance* ($10^{-6} cm^2/dyne$) *at time of* 0.1	1	10 *min*	100
61	17.2	21	−53.1	0.2 *C*	0.6 *C*	3.1 *C*	5.7 *C*	25	76	> 150	> 150
61	20.6	48	−52.9	0.5 *C*	1.4 *C*	4.3 *C*	6.9 *C*	13	32	70	112
61	27.4	79	−53.0	1.5 *R*	2.7 *R*	5.1 *R*	6.2 *R*	4.2	6.3	8.1	9.0
108	8.7	30	−52.8	1.1 *C*	2.5 *C*	5.8 *C*	8.9 *C*	4.4	11.6	33	98
108	10.5	61	−52.9	2.0 *C*	3.2 *C*	7.5 *C*	11.1 *C*	3.5	8.0	18	34
108	14.0	82	−52.8	2.1 *R*	4.3 *R*	7.1 *R*	8.4 *A*	3.4	5.6	8.3	11
237	4.9	27	−53.0	1.7 *C*	3.5 *C*	9.3 *C*	10.6 *A*	2.0	4.4	11.4	30
237	5.9	52	−53.0	2.3 *C*	4.4 *C*	9.8 *A*	11.4 *A*	1.8	3.6	8.0	17
237	7.9	75	−52.8	1.5 *R*	5.0 *R*	6.2 *A*	7.2 *A*	1.8	2.9	4.8	7.7
438	2.4	41	−53.7	2.0 *C*	5.0 *C*	10.3 *A*	11.5 *A*	1.9	2.5	4.1	7.5
438	2.9	57	−53.7	3.2 *C*	6.6 *C*	9.9 *A*	10.8 *A*	1.7	2.4	3.7	5.9
438	3.9	74	−53.7	3.5 *R*	6.1 *A*	8.1 *A*	10.6 *A*	2.1	2.9	4.2	5.8
823	1.6	29	−54.3	3.2 *C*	6.9 *A*	7.4 *A*	7.9 *A*	1.5	2.0	3.1	5.7
823	1.9	56	−54.0	3.4 *C*	6.4 *A*	7.0 *A*	8.7 *A*	1.2	1.6	2.6	4.9
823	2.5	69	−54.2	3.5 *R*	5.9 *A*	6.6 *A*	8.6 *A*	1.4	1.8	2.5	3.8
1340	0.7	19	−54.6	0.1 *A*	0.4 *A*	1.8 *A*	6.6 *A*	1.0	1.2	1.6	2.6
1340	0.8	40	−54.9	0.1 *A*	0.4 *A*	2.0 *A*	6.3 *A*	1.1	1.2	1.8	2.8
1340	1.1	66	−54.0	0.1 *A*	0.5 *A*	2.3 *A*	6.8 *A*	1.0	1.3	1.8	2.7

Note: *C*, *A*, and *R* indicate the failure mode. See text for explanation.

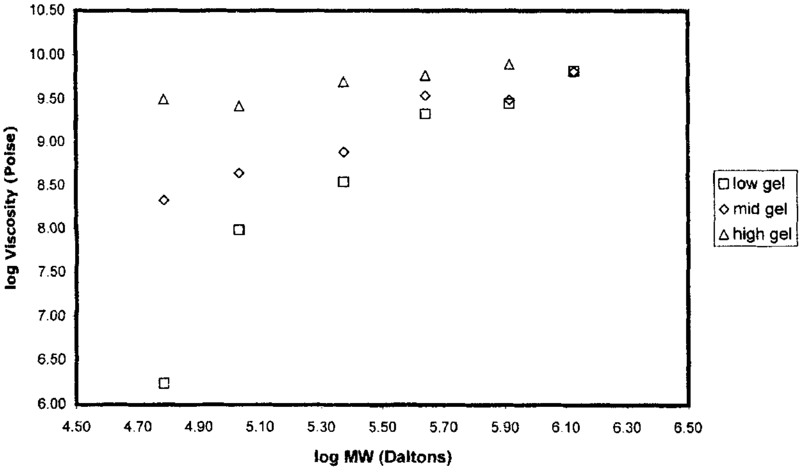

FIGURE 4 Effect of initial molecular weight on creep viscosity for various gel content ranges.

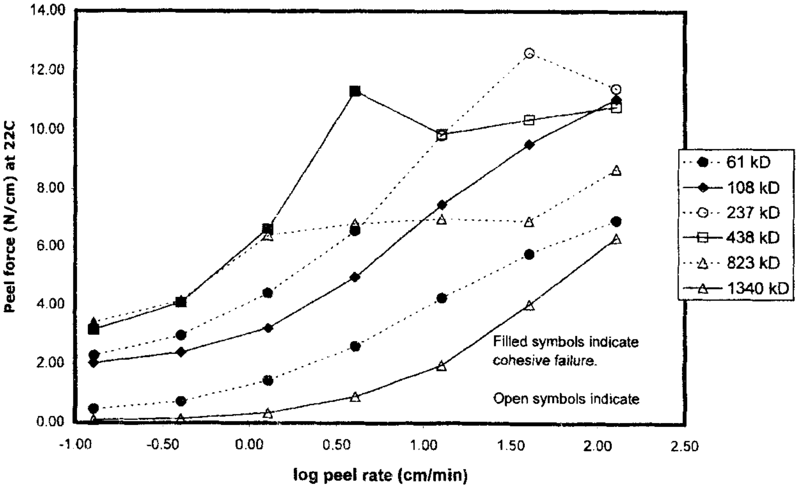

FIGURE 5 Peel force *vs*. peel rate curves at approximately 50% gel content for various initial molecular weights.

discontinuity in the peel force *vs*. rate function. Notice that the peel force goes through a maximum at a molecular weight of 438 kD for this middle level of gel content. The curve shown in Figure 6 demonstrates this feature.

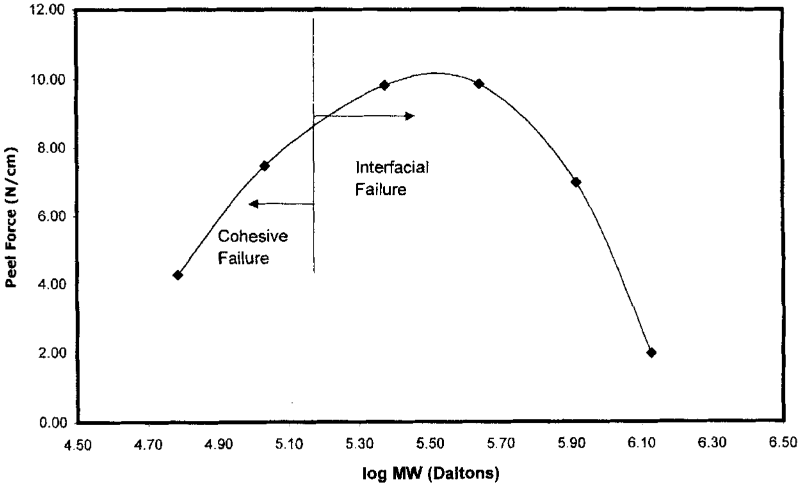

FIGURE 6 Maximum in peel force at constant peel rate and transition in failure mode for ~50% gel content as a function of initial molecular weight.

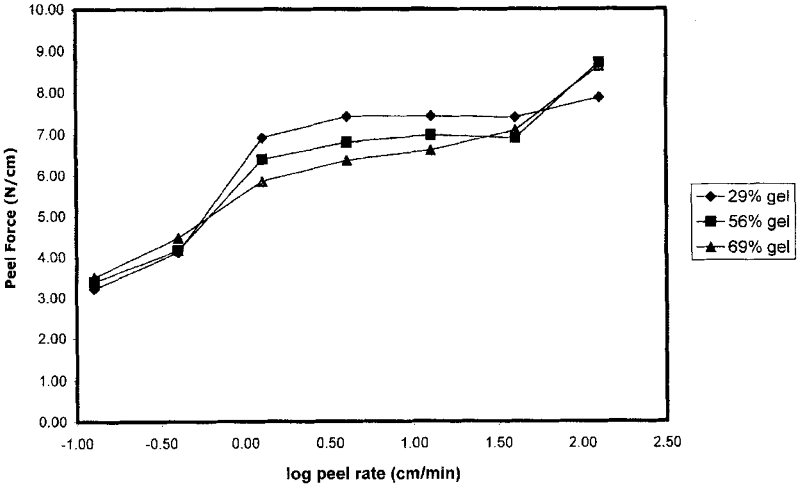

FIGURE 7 When failure mode is interfacial, peel force is only very weakly affected by gel content at any peel rate.

The peel response of the 1.34 MD material closely resembles the results observed in natural-rubber-based adhesives of similar formulation [5]. The 823 kD material seems to provide the flattest peel force *vs.*

peel rate response. The lower molecular weights exhibit generally lower peel forces coupled with the tendency for cohesive failure even at relatively high removal rates.

CONCLUSIONS

The molecular weight of the soluble portion of partially-crosslinked adhesives is always dominated by the initial molecular weight, even at high gel content. Creep resistance can be achieved either through molecular weight increases or gel content increases and, to a certain extent, one can compensate for low initial molecular weight with greater crosslinking as far as creep resistance is concerned. However, the peel behavior is strongly influenced by the initial elastomer molecular weight and further crosslinking does not provide performance equivalent to that obtained from higher molecular weight materials. The tendency to transfer adhesive or residue to the substrate is especially sensitive to the initial molecular weight, even at high gel content. The flatness of the peel force *vs.* peel rate response is optimal at intermediate molecular weights with very high molecular weight leading to poor adhesion at low rates.

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