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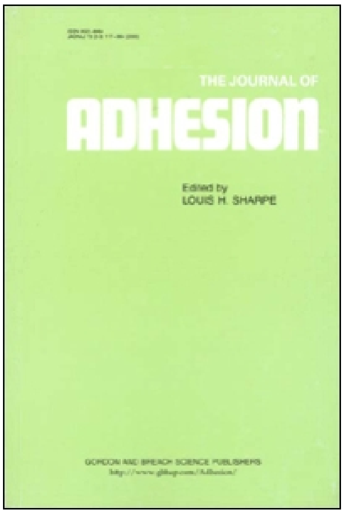

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Effect of Cross-Linking on Tack and Peel Strength of Polymers

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To cite this Article Zosel, A.(1991) 'Effect of Cross-Linking on Tack and Peel Strength of Polymers', The Journal of Adhesion, 34: 1, 201 — 209

To link to this Article: DOI: 10.1080/00218469108026514

URL: http://dx.doi.org/10.1080/00218469108026514

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J. Adhesion, 1991, Vol. 34, pp. 201–209
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Printed in the United Kingdom

Effect of Cross-Linking on Tack and Peel Strength of Polymers

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(Received October 18, 1990; in final form December 17, 1990)

In this work the influence of cross-linking on the adhesive fracture energy and the peel strength is studied choosing polydimethylsiloxane (PDMS) as a model polymer. A series of samples was prepared by electron-beam irradiation which covers the whole range from a viscoelastic liquid to a cross-linked rubber. The mechanical behaviour of these PDMS samples was characterized by mechanical spectroscopy. Tack measurements with an instrument described elsewhere^5 and peel measurements show that the adhesive fracture energy after short contact times as a measure of tack and the peel strength have a pronounced maximum in the range above the gel point, where the PDMS consists of a very loose and imperfect network and a high fraction of soluble polymer. In this range debonding is connected with the formation of fibrillar structures within the polymer.

KEY WORDS adhesive fracture energy; peel strength; dynamic shear modulus; cross-linking; gel point; fibrillar structure.

1 INTRODUCTION

Polymers to be used as pressure-sensitive adhesives have to meet requirements with respect to bond formation and bond separation, which are contradictory to some extent. Bond formation requires a sufficiently high segmental mobility in order to obtain contact in molecular dimensions between adhesive and adherend during the possibly very short contact time. During the separation phase, the adhesive has to store and to dissipate an amount of deformation energy as high as possible before fracture occurs. When a polymer passes from the uncross-linked to the cross-linked state, its ability to come into intimate contact with the adherend by elastic deformation and viscous flow is reduced, whilst its cohesive strength is enhanced. It can thus be imagined that the material should pass through an optimum in the balance between good deformability and high strength in this transition from uncross-linked to rubberlike behaviour. It is the objective of this study to verify this assumption by investigating a series of model polymers with different and well-known degrees of cross-linking.

2 SAMPLES

Polydimethylsiloxane (PDMS) was chosen as a model polymer. It can easily be cross-linked by electron-beam irradiation and has a very low glass transition temperature (T_g) of about −125°C. As all measurements in this work were carried out at 23°C, *i.e.* about 150°C above T_g, their results are expected to be essentially independent from influences of the glass transition range. A polydimethylsiloxane sample with a mean molecular mass of 1.5×10^5 g/mole was chosen for these investigations, which is a highly viscous liquid with a zero-shear viscosity of 4.1×10^2 Pa·s at 23°C. Polydimethylsiloxane has an entanglement network with a mean molecular mass between entanglements, M_e, in the range from 8 to 14×10^3 g/mole, according to the literature.[1,2] This temporary network is superimposed by a permanent network in the radiation cross-linked samples.

Samples with a thickness of 1 mm were irradiated at room temperature under N_2 atmosphere with electrons from a 2 MeV Van de Graaff accelerator. The radiation dose, defined as the ratio of absorbed energy and mass of the exposed sample, ranged from 10 to 1000 kGy.[1] The effect of the radiation can be studied by swelling measurements in a liquid which is a good solvent for the uncross-linked polymer. The swelling ratio Q, *i.e.* the weight of the swollen sample divided by the weight of the dried sample, and the weight fraction, s, of the soluble polymer are summarized in Table I for various radiation doses. Ethyl acetate served as the swelling agent.

According to Charlesby and Pinner,[3,4] the quantity $s+s^{1/2}$ should be linearly dependent on the reciprocal radiation dose, D^{-1}, for polymers with an initially random distribution of the molecular mass, *i.e.*

$$s+s^{1/2}=A+\frac{B}{D} \tag{1}$$

The soluble fraction s equals 1 at the gel point D_g, *i.e.* the dose at which an insoluble network just begins to form. This leads to

$$D_g=\frac{B}{2-A} \, . \tag{2}$$

TABLE I
Swelling ratio Q and soluble fraction, s, of cross-linked PDMS

D [kGy]	Q	s
10	dissolved	1.0
20	dissolved	1.0
50	7.2	0.33
75	5.6	0.23
100	4.5	0.16
200	3.0	0.08
500	2.1	0.04
1000	1.65	0.02

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[1] 1 kGy = 1 kJ·kg^{-1}

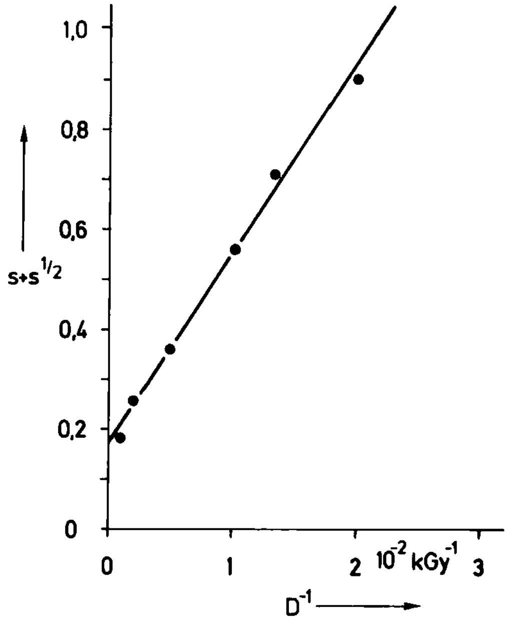

FIGURE 1 Correlation between the soluble fraction, s, and the radiation dose D according to Charlesby and Pinner,[3] for radiation cross-linked polydimethylsiloxane (PDMS)

The gel dose can thus be determined from a Charlesby-Pinner plot according to equation (1).

Figure 1 shows this plot for the PDMS samples which follow very well the predictions of the Charlesby-Pinner approach. The gel dose is found to be $D_g = 21$ kGy.

3 EXPERIMENTAL METHODS

The mechanical properties of the PDMS samples were characterized by measurements of the complex shear modulus $G^* = G' + G''$ as a function of frequency at 23°C with a dynamic mechanical analyser developed in our laboratory a number of years ago, using a parallel plate geometry with a plate diameter of 20 mm.

The tack was determined with an instrument also of our own development. As this instrument has been described with greater detail in a previous publication,[5] only a rather short description will be given here. By means of an electronically controlled motor, the surface of the polymer to be tested is brought into contact with a cylindrical probe of stainless steel which is connected to a piezoelectric force transducer. The motor is stopped when a certain preselected contact force between about 2×10^{-2} and 1×10^{2} N is reached. After an also preselected time intervall between about 1×10^{-2} s and arbitrarily long times, the contact period, the motor is driven in the opposite direction and separates the sample and probe surfaces with a definite velocity in the range between 1×10^{-1} and 2×10^{1} mm·s^{-1}. The piezoelectric load cell measures the force as a function of time during bond formation and bond separation. The energy necessary to separate the polymer from the probe surface is calculated from the force *versus* time curve during the debonding phase or the corresponding stress-strain curve. This energy, divided by the probe area, gives the fracture energy per unit of interface[6,7] and characterizes the strength of the adhesive joint. Under conditions of low contact force and short contact time, this fracture energy, w, is an appropriate measure of the tack of the sample.

The measurements described in this paper were carried out at 23°C with a contact time of 1 s and a contact pressure of 4×10^{-2} Nmm^{-2}. The rate of separation was 5 $\mathrm{mm\cdot s^{-1}}$, and the probe diameter 1.75 mm.

With the instrument briefly described here, not only the adhesive fracture energy can be determined as a function of the most important parameters such as contact pressure and time, rate of separation, and temperature, but also the form of the stress-strain curve during debonding which gives valuable insight into the deformation processes during bond separation.[5]

Peel measurements were performed with a commercial tensile tester. Strips of the PDMS samples with a width, b, of 15 mm were brought into contact with a steel plate by means of a roller with a mass of 1 kg, passing over the PDMS strip with a velocity of about 1 cm $\mathrm{s^{-1}}$, and peeled off under an angle of 180°. The peel rate was 1.67 $\mathrm{mm\cdot s^{-1}}$, the temperature 23°C as in the tack measurements. The time between contact formation and the start of the peel test was 1 min. The peeling force F divided by the width of the strip serves as a measure of the peel strength.

4 RESULTS AND DISCUSSION

4.1 Mechanical Properties

The PDMS samples irradiated with doses between 0 and 1000 kGy represent the complete transition from the state of a liquid to that of a cross-linked, rubberlike material. This can be concluded from Figure 2 where the storage modulus G′ and the loss modulus G″ are plotted *versus* the angular frequency ω. The curves are shown in two distinct plots in order to avoid too much overlap of the single curves. The unirradiated siloxane behaves like a viscoelastic liquid. G′ is much smaller than G″ and is proportional to ω^2 in the limit of low frequencies, whilst G″ increases proportional to ω with increasing frequency according to the well-known relation

$$G'' = \eta_o \cdot \omega ,$$

where η_o is the zero-shear viscosity [*e.g.*, Reference 8].

The same shape of the G′ and G″ curves is found for the sample irradiated with 10 kGy which is not shown in Figure 2. That means that this sample, too, behaves like a viscoelastic liquid, however with a higher viscosity than the unirradiated PDMS. A very interesting behaviour is shown by the sample irradiated with 20 kGy, *i.e.* slightly below the gel dose of 21 kGy. G′ and G″ have about the same values and increase proportional to $\omega^{1/2}$ over the whole frequency range of about 4 decades. This is in complete agreement with the investigations of Winter and Chambon[9,10] who were the first to find that G′ and G″ of polymers at the gel point are congruent

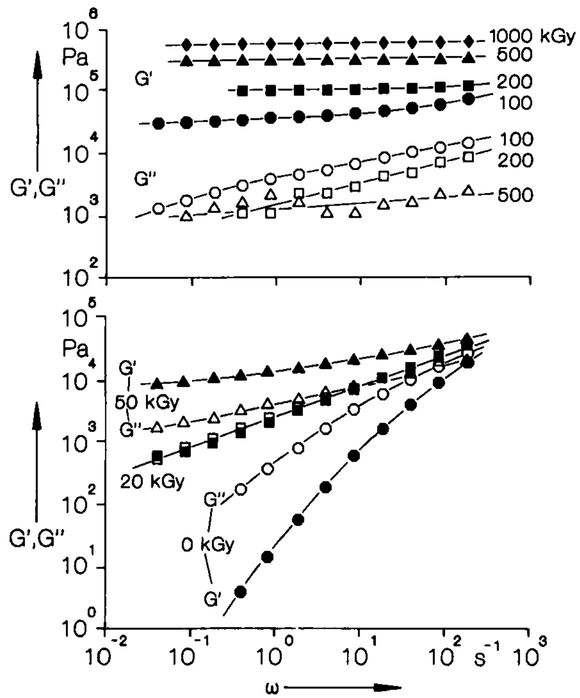

FIGURE 2 Storage modulus G′ and loss modulus G″ in dependence on angular frequency ω for PDMS, irradiated with various doses as indicated

and proportional to $\omega^{1/2}$. That, in our case, G″ is about 10% higher than G′ may be caused by the fact that the sample with 20 kGy is slightly below the gel point of 21 kGy, *i.e.* still in the liquid state. With increasing radiation dose (50 and 100 kGy) the storage modulus becomes higher than the loss modulus, *i.e.* the samples become predominantly elastic, however with a significant amount of internal losses. This behaviour is certainly influenced by the relatively large fraction of soluble material, and the imperfect and loose network structure, present in the samples in this dose range. At 200 kGy and higher radiation doses, G′ is independent of the angular frequency according to the theory of rubber elasticity.[11,12] G″ is more than two orders of magnitude smaller than G′ and can only be determined with a fairly large scatter.

4.2 Fracture Energy (Tack) and Peel Strength

Figure 3 shows a double logarithmic plot of the fracture energy, w, *versus* the radiation dose for the PDMS samples at 23°C. The fracture energy of the unirradiated polysiloxane is shown at the left side of the figure, however, outside the logarithmic dose axis. Figure 3 additionally exhibits the storage and the loss moduli G′ and G″ at an angular frequency of 1 s^{-1} which corresponds to the reciprocal of the contact time (1 s) chosen in the tack experiments. The gel dose (21 kGy) is indicated as a broken line.

The fracture energy, w, as a measure for the tack increases with increasing radiation dose until it reaches a maximum at about 45 kGy, *i.e.* above the gel dose D_g. At higher doses w drops very rapidly by more than two orders of magnitude. The storage modulus G′ increases in the studied dose range by more than 4 powers of ten. The loss modulus G″ exactly equals G′ at the gel dose and shows a maximum at about 70 kGy for the angular frequency chosen in Figure 3. That means that the adhesive fracture energy obtains appreciable values predominantly in the dose range between the gel point and the G″-maximum where the PDMS samples are only very slightly cross-linked and have large soluble fractions between about 0.2 and 0.7. It was observed that the debonding occurred by cohesive fracture in the PDMS at doses below the gel point, whilst adhesive separation was found above the gel dose.

The peel strength F/b is plotted *versus* the radiation dose D in Figure 4, in a quite analogous manner as the fracture energy or tack in Figure 3. The polydimethylsiloxane shows liquid-like behaviour with low strength and cohesive fracture at doses below the gel point, similar to the tack. A very pronounced maximum is found for the peel strength, also, at doses above the gel dose. Contrary to the tack measurements, we found cohesive fracture also in this dose range. A sharp transition from cohesive to adhesive failure is observed at a dose of about 80 kGy which is connected with a decrease of the peel strength by nearly two orders of magnitude.

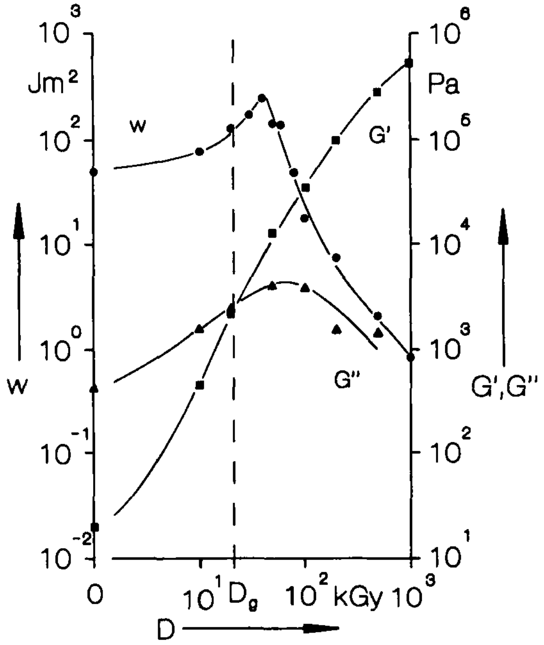

FIGURE 3 Adhesive fracture energy, w, and storage and loss moduli, G′ and G″, plotted *versus* the radiation dose for PDMS

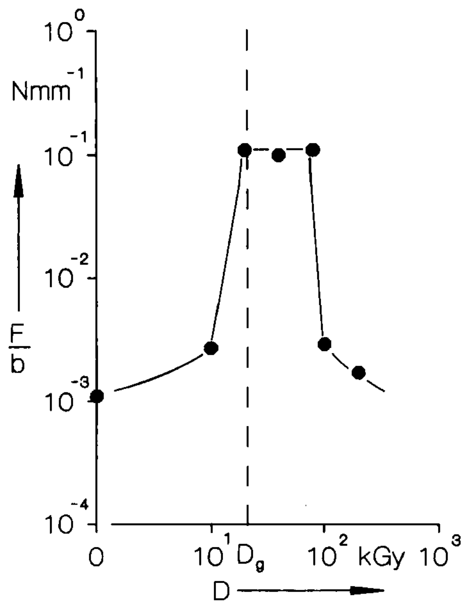

FIGURE 4 Peel strength F/b as a function of the radiation dose D

4.3 Stress-strain Behaviour During Debonding

The fracture energy, w, characterizes the strength of the adhesive bond. Additional information about adhesive performance and deformation behaviour during debonding can be obtained from the stress-strain curve of the debonding process, *i.e.* the tensile stress as a function of the tensile strain during bond separation. There have generally been found three types of stress-strain curves from investigations of a large number of polymers, *e.g.* rubber/resin blends, polyacrylates.[5] The first type is observed for polymers of comparatively low viscosity. The adhesive joint breaks by cohesive fracture within the polymer, and the debonding process is governed by viscous flow. In many cases high molecular mass polymers exhibit another type of stress-strain behaviour which we have called "brittle" fracture. A sharp stress maximum is reached at rather low strains, and debonding occurs by purely adhesive fracture. The third type of deformation behaviour is connected with high tack values and is characterized by a stress-strain curve with a large "shoulder" following the stress maximum and a high strain at break. It is revealed by polymers with a high molecular mass, too, but additionally with a large mean molecular mass M_e between entanglements. Examples are polyethylhexylacrylate and blends of natural rubber and tackifying resins. It could be shown by high-speed photography that this characteristic is connected with the formation of fibrillar structures within the adhesive. These fibrils are increasingly stretched causing the storage and dissipation of energy. At least, the fibrils separate from the probe surface by a purely interfacial failure, and the deformed polymer recovers and finally restores the original film surface.

The occurrence of these three types of deformation behaviour, liquid-like, "brittle" and fibrillar behaviour, and its correlation with molecular parameters, especially the mean molecular mass between entanglements, has been discussed with greater detail in a preceding publication.[5]

Some examples of stress-strain curves are given in Figure 5 for samples, irradiated with different radiation doses, whereby different scales have been chosen for the various plots. Liquid-like behaviour with cohesive fracture is found for the original polysiloxane and also the sample irradiated with 10 kGy, *i.e.* well below the gel point and the tack maximum. The stress has a maximum and then falls off gradually, giving rise to very large strains of about 10. At 40 kGy, *i.e.* near the tack maximum, the deformation behaviour changes, and the type of the stress-strain curve is observed which represents fibrillar behaviour. The shoulder in the stress-strain plot leads to a large area under the curve *i.e* a high fracture energy. The deformation behaviour gradually changes to "brittle" fracture at higher radiation doses, in Figure 5 represented by 100 and 1000 kGy, and the area under the curve, which is proportional to w, decreases drastically. Figure 5, thus, very nicely illustrates that the PDMS studied in this work shows all three types of deformation behaviour during debonding, depending on the viscoelastic state of the material which has simply been obtained by different radiation doses.

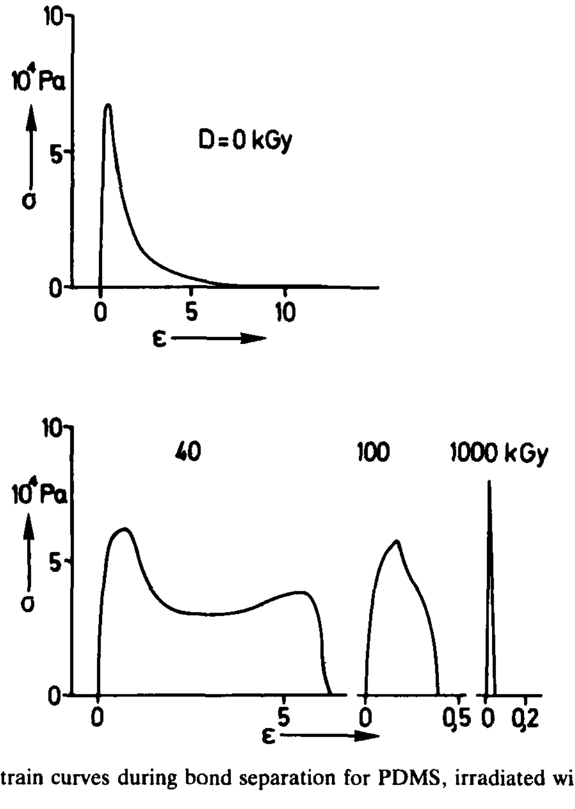

FIGURE 5 Stress-strain curves during bond separation for PDMS, irradiated with various doses.

5 CONCLUSION

The investigations presented in this paper show that the gel point where a polymer passes from the state of a viscoelastic liquid to that of an elastic rubber has a great significance with respect to adhesion and tack. Just above the gel point, a polymer consists of a very loose and imperfect network, which forms a coherent molecular structure throughout the entire sample, and a large fraction of uncross-linked material with a presumably broad distribution of molecular masses and a high degree of branching. This morphology results in high internal losses which make their appearance in a maximum of the loss modulus, determined in a dynamic experiment. In the range between the gel point and this maximum, the adhesive fracture energy as a measure of the tack and the peel strength which equals the peel energy per unit of interface show very pronounced maxima which are connected with a transition from cohesive to adhesive separation. Additionally, the formation of fibrillar structures during bond separation was observed in the tack measurements.

References

1. J. D. Ferry, *Viscoelastic Properties of Polymers, 3rd ed.*, (New York 1980), p. 406 and 409.
2. A. M. Bueche, *J. Polym. Sci.* **19,** 297 (1956).
3. A. Charlesby and S. H. Pinner, *Proc. Roy. Soc.* **A249,** 367 (1959).
4. O. Saito in M. Dole (Ed.), *The Radiation Chemistry of Macromolecules,* vol. 1 (Academic Press, New York, 1972), p. 223.
5. A. Zosel, *J. Adhesion* **30,** 135 (1990).
6. A. N. Gent and J. Schultz, *J. Adhesion* **3,** 281 (1972).
7. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc.* **A332,** 385 (1973).
8. Ref. 1, p. 71.
9. H. H. Winter and F. Chambon, *J. Rheology* **30,** 367 (1986).
10. F. Chambon, Z. S. Petrovic, W. J. MacKnight and H. H. Winter, *Macromolecules* **19,** 2146 (1986).
11. L. R. G. Treloar, *The Physics of Rubber Elasticity, 2nd ed.* (Clarendon Press, Oxford, 1967).
12. K. Dusek and W. Prins, *Adv. Polymer Sci.* **6,** 1 (1969).