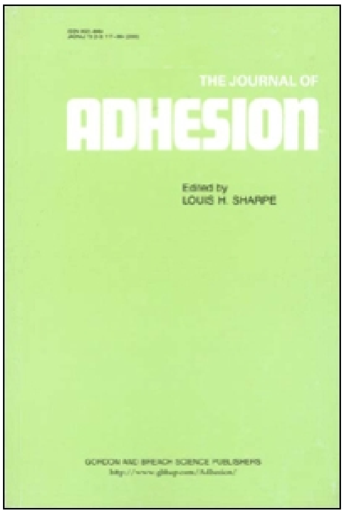

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The Effect of Temperature of Test on the Adhesion of Polyethylene Coatings Applied to Metals as a Hot Melt

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The adhesion of polyethylene coatings applied as a hot melt to steel, zinc and copper with various surface pretreatments has been studied over a temperature range from ambient to 70 or 80°C. Tensile properties and tear strength of the polymer itself were measured over the same temperature range. Substrates which give high adhesion at room temperature give a fall in adhesion with temperature. This can be understood in terms of a fall in fracture energy of the polymer as indicated by tensile and tear tests. Substrates which give low adhesion at room temperature show first a significant rise and then a fall in adhesion as temperature is raised. Examination of the fracture surfaces by electron microscopy shows a progressive increase in plastic deformation of the polymer as the adhesion rises. The rise in adhesion and change in failure mode are interpreted in the light of the change in mechanical properties of the polymer. The adhesion maxima are not viscoelastic in origin as time-rate equivalence was not observed.

INTRODUCTION

The strength of an adhesive joint judged from its failure either in service or under laboratory test conditions reflects its toughness—the energy required for fracture to occur. In general this fracture energy will be determined by an interaction between the various parts of the joint, substrate, interfacial regions

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and adhesive. Some tests of adhesion, such as the peel test, directly measure a fracture energy per unit area, but it has been argued that even those tests which measure a force per unit area depend upon the toughness of the joint.[1]

Earlier work in these laboratories on the heat treatment of polyethylene melt coatings on metals attributed improved adhesion obtained at room temperature on quenching the coating from the melt to increased toughness of the polymer itself.[2] When adhesion was measured at elevated temperatures preliminary results presented a confusing picture: some substrates gave higher adhesion, others lower.

Although there is much literature on the influence of temperature on adhesion (e.g., Refs. 3–10), qualitatively different effects for the same polymer on various metallic substrates have not generally been found. Only a few papers refer to polyethylene itself. Reports of Kraus and Manson[4] and of Huntsberger,[6] although using different types of test and ranges of temperature, concur in finding a fall in the adhesion to steel with rise of temperature. It was therefore decided to study the effect for melt coatings of polyethylene on various metals.

Present work

The substrates chosen for the present work were those of which the room temperature adhesion had previously been studied in some detail. Good adhesion is often associated with conditions under which the polymer can oxidise during melt coating.[11] Iron catalyses this oxidation so adhesion to steel is high, but zinc is relatively inert and copper inhibits the oxidation so adhesion to polished zinc and copper is low.[12,13] If antioxidant is included in the polymer, adhesion, even to steel, is low. Where high adhesion is found the substrate has tufts of drawn polymer still adhering after peeling, and these may be observed in the scanning electron microscope. Substrates giving low adhesion show little sign of residual polymer.[2,14]

Good adhesion, which is independent of oxidation of the polymer, can be obtained if a suitable microfibrous surface is prepared on the substrate.[14] The fibres provide discontinuities at the interface which lead to localised stress concentrations during peeling and to extensive plastic deformation of the polymer which may be seen on the substrate after peeling.[14] The work expended in plastic deformation contributes to the high peel strength. Suitable surfaces may be prepared on copper by oxidation in an alkaline chlorite solution or by anodising in aqueous sodium hydroxide.[14]

In parallel with a study of the effect of temperature on adhesion to these substrates discussed above investigation was made into the variation of mechanical properties of the polymer itself over the same temperature range.

EXPERIMENTAL DETAILS

Polyethylene

Low density polyethylene, Alkathene 190400 from I.C.I. Ltd. was used. The manufacturer stated it to be additive-free and to have a density of 0.916 g/cm^3 and a melt flow index of 20. For some experiments antioxidant (2,6-di-tert-butyl-p-cresol) was incorporated into the polymer from solution in methylene chloride. The polymer was soaked in the solution and the solvent was allowed to evaporate.

Steel

10 × 15 cm panels of general purpose bright mild steel 1–2 mm thick (B.S. 1149) were prepared for bonding by degreasing in trichloroethane followed by etching for 30 seconds at room temperature in 6 M hydrochloric acid and rinsing in water and acetone.

Copper

Deoxidised sheet 1.2 mm thick (B.S. 1172) was cut into panels 10 × 15 cm and rinsed in dilute hydrochloric acid, followed by water and acetone. They were then degreased in trichloroethane.

Chemical polishing Degreased panels were immersed for 10 minutes at room temperature in a solution of ortho-phosphoric acid (60 ml, S.G. 1.75), nitric acid (10 ml, S.G. 1.42), acetic anhydride (30 ml) and water (8 ml). They were then rinsed with distilled water and acetone.

Chlorite-formed films Some chemically polished panels were oxidised by immersion for 30 minutes in an aqueous solution at 90°C containing 18 g/*l* of a mixture of sodium chlorite, trisodium phosphate and sodium hydroxide (3 : 10 : 5 pbw).

Other chemically polished panels were similarly oxidised except that the concentration of the chlorite, phosphate, hydroxide mixture was 180 g/*l*.

Anodising Chemically polished panels were anodised at 90°C in 4 M sodium hydroxide solution using a copper cathode. A current density of 143 amp/m^2 was used until, after 5 minutes passivation occurred.

Zinc

10 × 15 cm panels of zinc sheet (B.S. 849) 0.8 mm thick were degreased in trichloroethane and etched for 30 seconds in 10% sulphuric acid. They were

transferred wet to a chemical polishing bath consisting of chromium trioxide (200 g), sodium sulphate (10 g) and nitric acid (S.G. 1.42, 85 ml) diluted with water to 1 litre and were agitated for 2 minutes. After thorough rinsing in distilled water baths, the panels were rinsed with acetone and allowed to dry.

Polymer coating and peel testing

The metal panels were put in an oven at 200°C which was immediately filled with nitrogen. After 10 minutes they were removed and one side was covered with polyethylene powder. After two minutes excess powder was tipped off and the panels were returned to the oven, now containing air, for 20 minutes coating time. They were then allowed to cool in air to room temperature.

The polymer coating was scored with a sharp blade to enable 2 cm strips to be peeled on an Instron testing machine at a peel angle of 180°. The standard peel rate was 250 mm/min, but other values were used in the experiments where indicated. For tests above room temperature, the specimens on the Instron were enclosed in a temperature-controlled cabinet.

Polymer sheet preparation

Polyethylene sheets about 1 mm thick were moulded from powder for 5 minutes between sheets in a press at 200°C. Samples were removed from the press and were allowed to cool in air.

Tensile tests

Dumb-bell shaped test specimens (33 mm gauge length, 6 mm wide) were cut from the polymer sheet and tested at various temperatures and various rates on an Instron tensile testing machine. Gradients of the initial portion of the load-extension curve were used to calculate the initial modulus. The maximum load before the yield drop was used to calculate yield strength.

Tear tests

"Trouser leg" test specimens were made by cutting polymer sheet into strips 4 cm × 15 cm and making a 2 to 3 cm cut in the centre of one short side parallel to the long edge. The tear was propagated down the specimen by pulling the two free ends in an Instron machine at a cross-head speed of 500 mm/min. Various test temperatures were used. The tear strength was calculated from the average load recorded divided by the specimen thickness. Care was taken to minimise thickness variations between specimens.[15]

RESULTS AND DISCUSSION

For some substrates the peel strength fell monotonically with rise in temperature (Figure 1). Copper with a black oxide film formed either by anodising or in the more concentrated chlorite solution came into this category. Other substrates showed an initial rise in peel strength to a broad maximum, generally around 50 to 60°C, followed by a fall at higher temperatures. Substrates such as polished copper or zinc which have a low peel strength at room temperature give this type of behaviour most clearly. Other systems such as steel with antioxidant-free polyethylene show intermediate behaviour giving a maximum at a lower temperature and then a fall in peel strength.

Mechanical properties

To aid understanding of the variation in adhesion, the tensile properties and tear strength of the polymer were measured over the temperature range

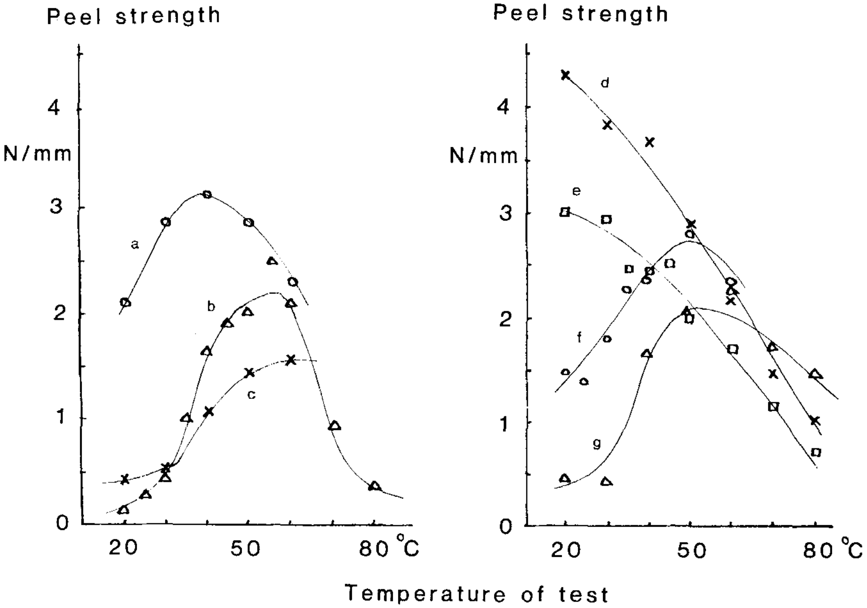

FIGURE 1 Effect of test temperature on the peel strength of polyethylene peeled from the following substrates at a peel rate of 250 mm/min : (a) steel (etched in hydrochloric acid), (b) copper (chemically polished), (c) as (a) but with polymer containing antioxidant, (d) copper (treated in 180 g/l alkaline chlorite), (e) copper (anodised in sodium hydroxide), (f) copper (treated in 18 g/l alkaline chlorite), (g) zinc (chemically polished).

involved. As would be anticipated the modulus and yield stress both fell with temperature (Figure 2). The elongation to break however remained constant at about 130%. Thus the energy to fracture the polymer under the conditions of the tensile test fell with temperature. The tear strength which gives a measure of fracture energy under different experimental conditions,[15] also fell with temperature (Figure 2).

The substrates in Figure 1 which show a consistent fall in adhesion with temperature exhibit cohesive failure in the polymer when tested at room temperature. Their high room temperature peel strength is associated with considerable plastic deformation of the polymer in the interfacial region during peeling. The fall in adhesion with temperature then would seem to be a consequence of the fall in fracture energy of the polymer in this temperature range.

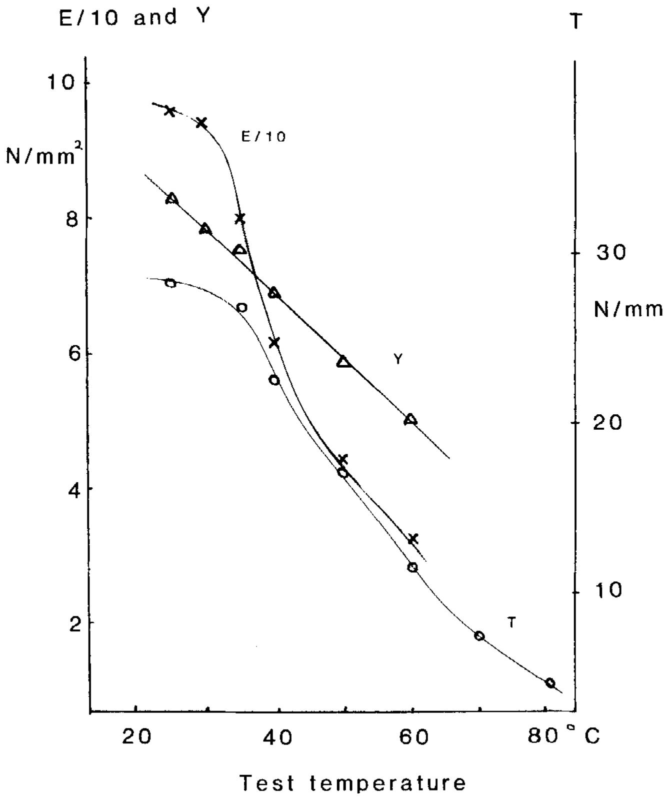

FIGURE 2 Mechanical properties of the polyethylene. The effect of temperature on tensile modulus (E), yield stress (Y) (both measured at a test rate of 50 mm/min) and tear strength (T) measured at a test rate of 500 mm/min.

Substrates giving an adhesion maximum

For a number of other polymer-substrate combinations maxima in adhesion at various temperatures have previously been reported.[3,5–10] These often show a typical rate-temperature dependence indicating a viscoelastic origin.

If the maxima in Figure 1 are viscoelastic in origin, they would be expected to shift to lower temperatures at lower test rates. Chemically polished copper was chosen as a substrate giving behaviour typical of this category, and the peel strength was measured over the temperature range at peel rates varying from 0.25 mm/min to 500 mm/min. Time-temperature equivalence was not observed: at lower test rates the peel strengths were low over the whole temperature range (Figure 3).

To obtain further information on the effect of temperature careful examination both with the naked eye and scanning electron microscope was made of the peeled surfaces for the series of polished copper specimens peeled at 250 mm/min over the temperature range.

At room temperature (peel strength 0.2 N/mm) failure left fine ridges of drawn polymer on the peeled strip, corresponding to peaks on the Instron chart. Between the ridges the polyethylene surface was mostly featureless. The copper surface showed similar, but less pronounced polymer ridges, but no other features of significance. As the temperature increased the amount of

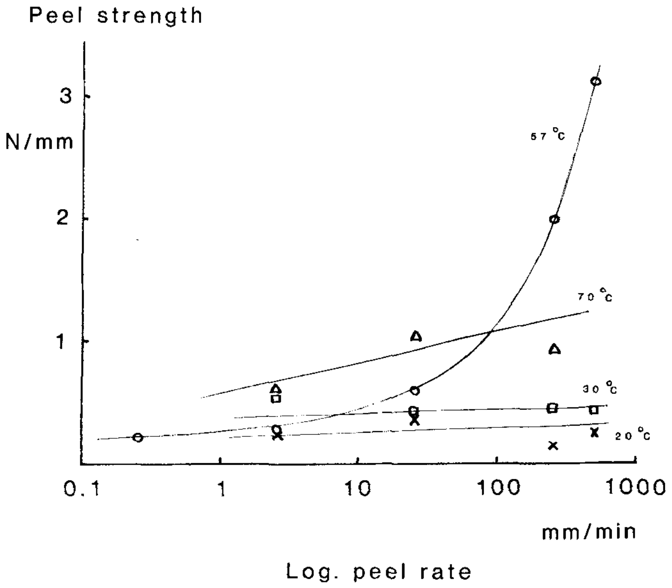

FIGURE 3 Adhesion of polyethylene to chemically polished copper. Effect of peel rate on peel strength at different temperatures: 20°C (×), 30°C (□), 57°C (○), 70°C (△).

drawn polyethylene increased and the failure pattern became steadier. Thus by 57°C (peel strength 2.0 N/mm) a surface gloss was visible to the naked eye on the copper. In the electron microscope tufts of drawn polymer could be seen over much of the area (Figure 4(a)). The polymer strip appeared frosty and in the electron microscope cavitation and drawing of the polymer was apparent over most of the surface (Figure 4(b)). Thus as the temperature increased from 20 to 57°C and the peel strength from 0.2 to 2.0 N/mm, the failure mode changed from one involving a little drawing of the polymer but mainly fracture very close to the interface to failure substantially in the polymer involving significant plastic deformation.

For other polymers a transition from adhesive to mixed to cohesive failure associated with a maximum in adhesion has been reported.[5–8,10] Gent and Petrich[8] interpreted this in terms of the tensile properties of the elastomer they studied. With suitable adaptation similar ideas may be applied to these results. Tensile stress-strain curves for the polyethylene tested at a rate of 50 mm/min are shown schematically in Figure 5(a). Gent and Petrich suggested that it is valid to consider a maximum stress, represented by f_a, which just causes interfacial polymer-substrate bonds to break. f_a would vary little with temperature. Thus at room temperature, the stress f_a is transmitted to the interface and the bond fails before the yield point of the polymer is reached. Failure is predominantly adhesive and, as the area under the stress strain curve up to a stress of f_a is small, the peel strength is low. At higher temperature (*e.g.* 57°C) the polymer is strained to failure without reaching a stress of f_a so failure is cohesive, with a high peel strength corresponding to the entire area under the stress-strain curve. At higher temperatures the area under the curve is smaller and the peel strength falls (Figure 1).

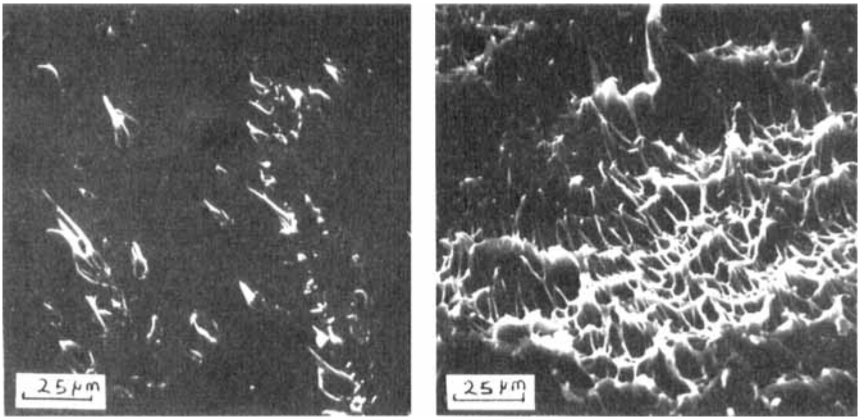

FIGURE 4 Scanning electron micrographs of the surfaces of (a) copper and (b) polyethylene after peeling at 57°C at a peel rate of 250 mm/min.

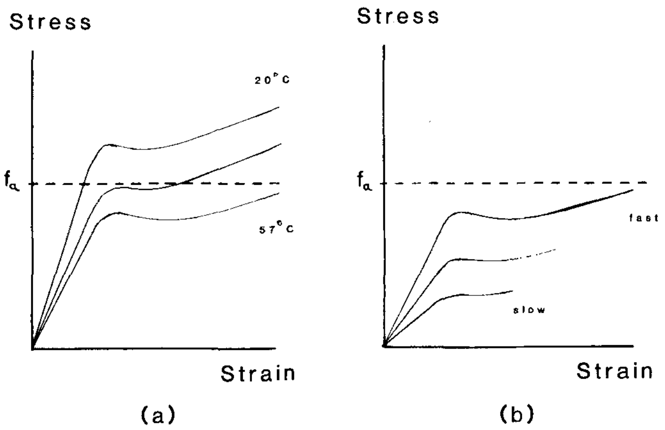

FIGURE 5 Schematic representation of stress-strain curves for polyethylene tested (a) at 50 mm/min at various temperatures (b) at different rates at 57°C. f_a represents the level of stress which if transmitted to the interface will cause the interfacial bonds to fail.

Effect of peel rate

It remains to be shown how the results for the effect of peel rate on peel strength at 57°C (Figure 3) fit into this pattern.

The failure mode was again investigated. At the highest peel rate (500 mm/min) the surfaces (Figure 6) were similar to those discussed for a peel rate of 250 mm/min (Figure 4). Many tufts of drawn polymer remained on the substrate; the polymer surface showed extensive deformation. However at low peel rates (giving lower peel strengths) failure remained cohesive and indeed the deformed polymer on both surfaces was more apparent, even to the naked eye (Figure 7).

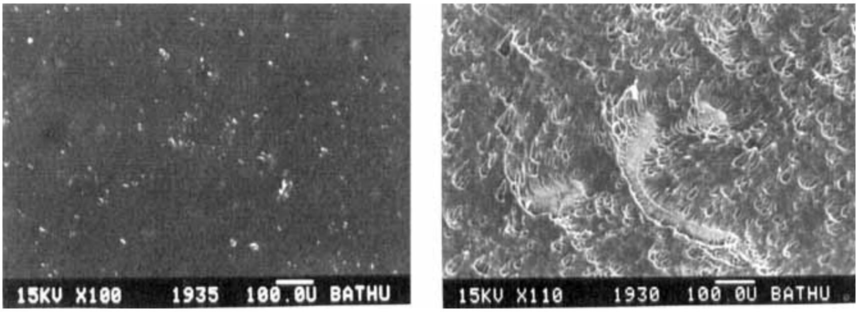

FIGURE 6 Scanning electron micrographs of the surfaces of (a) copper and (b) polyethylene after peeling at 57°C at a peel rate of 500 mm/min. (N.B. Scale bars represent 100 μm.)

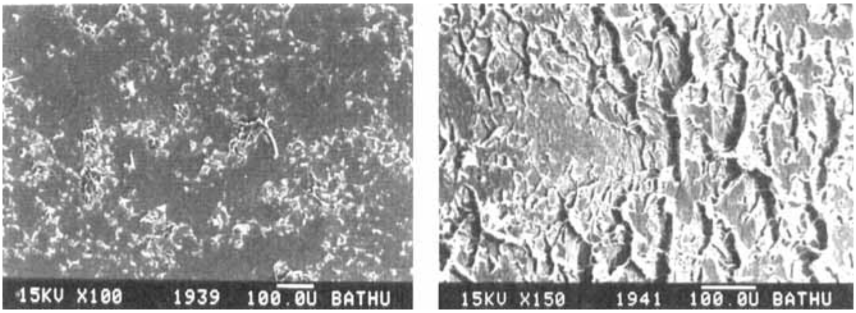

FIGURE 7 Scanning electron micrographs of the surfaces of (a) copper and (b) polyethylene after peeling at 57°C at a peel rate of 0.25 mm/min. (N.B. Scale bars represent 100 μm.)

The tensile properties of the polyethylene at 57°C were studied at a range of rates of test. With reduction in rate, the modulus and strength fell, as did the elongation to break (Table I). The reduced ductility was unexpected,[16] although it has been previously noted[17,18] and ascribed to adiabatic conditions at higher test rates.

The rate of strain of the polymer in an 180° peel test is considerably greater than the peel rate, so rates of strain in Table I are not directly comparable with the peel rates in Figure 3. Nevertheless the trends would be expected to be applicable.

The tensile curves at 57°C, shown schematically in Figure 5(b), provide an explanation of the effect of rate on peel strength again using the concept of the stress f_a which when transmitted to the interface causes polymer-substrate bonds to fail.[8] At 57°C f_a is not reached at any rate of test so failure is cohesive. The energy to failure falls as the rate decreases, so the peel strength falls accordingly.

TABLE I

Effect of test rate on the tensile properties of the polyethylene at 57°C

Test rate cm/min	Initial modulus N/mm^2	Yield strength N/mm^2	Elongation to break %
0.05	30.6 ± 4.0	4.55 ± 0.10	131 ± 18
0.5	40.5 ± 7.0	4.87 ± 0.07	209 ± 40
5	35.1 ± 2.0	4.91 ± 0.00	329 ± 76
50	60.7 ± 16.9	5.36 ± 0.05	504 ± 40
100	44.2 ± 10.9	5.46 ± 0.15	525 ± 43

(95% confidence limits indicated)

SUMMARY

The effect of temperature and rate on the adhesion of polyethylene under the conditions studied is complex, but may be understood with reference to the bulk and interfacial properties of the system.

1. Where chemical or physical effects (such as surface topography) produce high adhesion at room temperature with failure well into the bulk polymer, the peel strength is dominated by the mechanical properties of the polymer. Increase of temperature lowers the fracture energy of the polymer, and so the peel strength falls.

2. Where such chemical and physical effects are absent, the modulus of the polymer at room temperature is high enough for sufficient stress to be transmitted to the interface to cause failure there with little plastic deformation of the polymer and so a low peel strength. As temperature is raised, the yield strength of the polymer falls and progressively more plastic deformation takes place leading to an increase in peel strength and to cohesive failure. When there is substantial plastic deformation at the interface and cohesive failure the peel strength falls with further temperature increase, following the reduction of fracture energy of the polymer.

3. At the temperature of the adhesion maximum a reduction of the peel rate produces a reduction in peel strength. This is associated with a reduction with strain rate of the fracture energy of the polymer itself.

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References

1. R. G. Good in *Adhesion Measurement of Thin Films, Thick Films and Bulk Coatings*, ed. K. L. Mittal (A.S.T.M. Special Tech. Publication No. 640, 1978), p. 18.
2. D. E. Packham and J. R. G. Evans, *Internat. J. Adhesion Adhesives* **1**, 149 (1981).
3. H. P. Meissner and E. W. Merrill, *A.S.T.M. Bull.* No. 151, 80 (1948).
4. G. Kraus and J. E. Manson, *J. Polym. Sci.* **6**, 625 (1951).
5. W. M. Bright in *Adhesion and Adhesives*, ed. J. Clark, J. E. Rutzler and R. L. Savage (Wiley, New York 1954), p. 130.
6. J. R. Huntsberger, *J. Polym. Sci.* **A1**, 2241 (1963).
7. D. H. Kaelble, *J. Colloid Sci.*, **19**, 413 (1964).
8. A. N. Gent and R. P. Petrich, *Proc. Roy. Soc.* **A310**, 433 (1969).
9. N. I. Egorenkov and V. A. Belyi, op. cit. (1), p. 362.
10. W. F. Parson, M. A. Faust and L. E. Brady, *J. Polym. Sci.* (*Polym. Phys.*) **16**, 755 (1978).

11. D. E. Packham in *Developments in Adhesives—2*, edit. A. J. Kinloch (Applied Science, London 1981).
12. K. Bright and B. W. Malpass, *Europ. Polym. J.* **4,** 431 (1968).
13. N. I. Egorenkov, D. G. Lin and V. A. Belyi, *Dokl. Akad. Nauk. S.S.S.R.* **5,** 1148 (1973).
14. J. R. G. Evans and D. E. Packham, *J. Adhesion* **10,** 177 (1979).
15. D. S. Chiu and A. N. Gent, *Bull. Amer. Phys. Soc.* **21,** 372 (1976).
16. J. A. Faucher and F. P. Reding in *Crystalline Olefin Polymers*, eds. R. A. Raff and D. W. Doak (Wiley, New York 1965), part I, p. 712.
17. M. Nakamura and S. M. Skinner, *J. Polym. Sci.* **18,** 423 (1955).
18. J. M. Andrews and I. M. Ward, *J. Mat. Sci.* **5,** 411 (1970).