Hysteresis and adhesion of a semicrystalline polymer

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Experiments on quenched and annealed samples of the semicrystalline polymer poly(1,4-dimethylene-*trans*-cyclohexyl suberate) (MCS) revealed high mechanical hysteresis over the temperature range 23–70°C. Thus it dissipates energy from regions of high stress. When this polymer was melted between strips of poly(ethylene terephthalate) (PET) support, and was quenched and annealed in the same manner as the hysteresis samples, strong adhesive bonds were produced over a considerably wider temperature range than those produced by an ethylene vinyl acetate (EVA) adhesive selected from among the best amorphous adhesives. Both adhesives produced bonds strong enough to exceed the rupture strength of the PET at 23°C, but the cohesive strength of the EVA weakened rapidly as the temperature was increased while the MCS retained much of its cohesive strength. Semicrystalline polymers such as MCS, because of their physical crosslinks (tie molecules) and related high hysteresis, will be better than amorphous adhesives for applications requiring strong bonds over wide temperature ranges.

(Keywords: hysteresis; adhesion; semicrystalline polymer)

INTRODUCTION

The failure of an adhesive has been extensively modelled as a crack propagation phenomenon, and therefore materials that prevent the formation of the high localized stresses necessary for crack initiation and growth have the potential of being good adhesives[1]. One property by which materials can be evaluated for their ability to do this is their mechanical hysteresis.

When an amorphous polymer is slowly elongated at a temperature far above its glass transition temperature (T_g), it fails cohesively at a low load[2]. However, as the test temperature is reduced, a point is reached where the load and ultimate elongation increase markedly, and on retraction little or no energy is recovered, i.e. the load drops nearly vertically to zero, as shown in *Figure 1*. Under these conditions the polymer is said to have high mechanical hysteresis[3]. The area under its load–elongation curve will be large.

A typical amorphous polymer, butadiene–styrene random copolymer, has load–elongation curves as shown in *Figure 2*[4]. This material will have high mechanical hysteresis at -5 and 3°C, because if retraction is run just before the material ruptures, the load will drop nearly vertically to the elongation axis, giving a large area under the load–elongation curve. This material also will be a good adhesive in the -5 to 3°C region under the strain rate conditions used to produce *Figure 2*[2,4]. However, at higher temperatures the material will fail cohesively at low force, and at lower temperatures the mechanical hysteresis will be low as shown in *Figure 3*, and the material will fail interfacially at low force[1].

Semicrystalline polymers show high mechanical hysteresis over a wider temperature region than amorphous polymers, making them potential adhesive candidates for a wider temperature region. The crystallites in a polycrystalline polymer link the linear polymer chains together, and retard the flow of the polymer as the temperature increases[2].

This paper (one of a series[5–7]) reports tests on adhesive peel samples and load–elongation samples of a semicrystalline polymer. By quenching and annealing at various temperatures, the combined effect of spherulite size and other changes caused by the thermal treatment could be evaluated and correlated with hysteresis and adhesive strength.

EXPERIMENTAL

Material

The semicrystalline polymer poly(1,4-dimethylene-*trans*-cyclohexyl suberate) (MCS) was prepared at Tennessee Eastman Company. The M_n and M_w values (polystyrene equivalent molecular weight), obtained by g.p.c., were 38 000 and 77 500, respectively. The T_m, T_g and per cent crystallinity of MCS are ~95°C, -20°C and 45, respectively.

Hysteresis tests

Test samples were cast in a 130°C oven, and on melting, were quenched in their moulds in water at 0, 27 or 55°C and then removed and annealed in an oven at the quench temperature for 72 h (the 0°C sample was annealed at ambient).

Rings were cut from the samples and tested on an Instron machine by a procedure described in ASTM Designation D412-75, with half-cylinders used as sketched in *Figure 4*. Energy, load and elongation-to-break (*BEN*, *BLD* and *BEL*, respectively) were read directly from a microcomputer (Microcon II). The load–elongation curves were also recorded on the strip chart of the computer.

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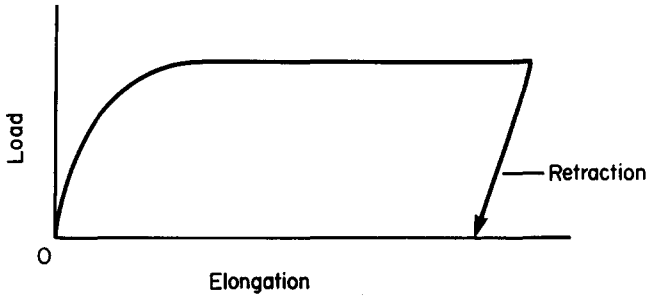

Figure 1 A characteristic shape of a load–elongation curve of an amorphous polymer at a temperature where mechanical hysteresis is high

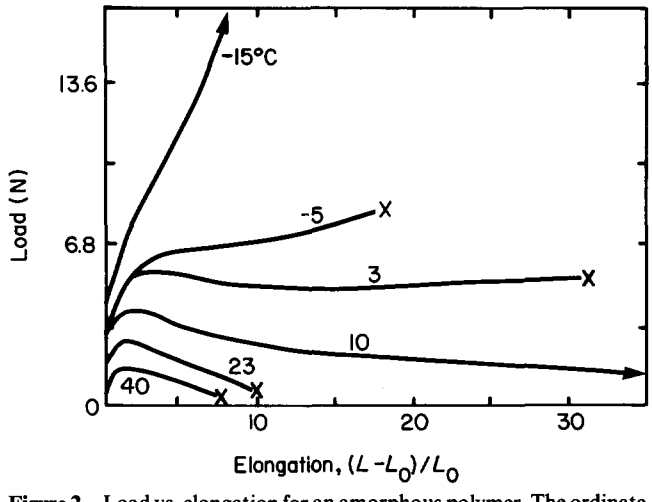

Figure 2 Load vs. elongation for an amorphous polymer. The ordinate in the paper by Gent and Petrich was scaled in kg cm^{-2}. For comparison purposes it has been converted to N for a sample with the same cross section as the samples used in this paper

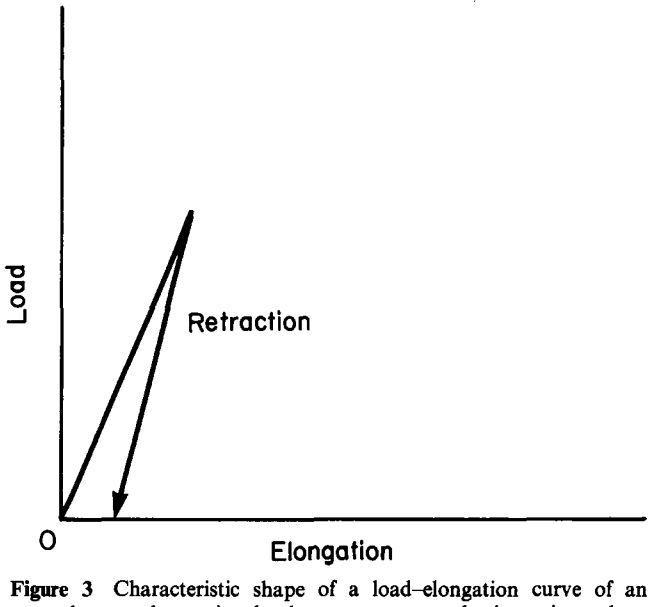

Figure 3 Characteristic shape of a load–elongation curve of an amorphous polymer in the low-temperature elastic region where mechanical hysteresis is low

Hysteresis data were obtained by running several samples to break, then running several samples to just short of break and retracting at the same speed as in the elongation. *Figure 5* is a typical curve, the details of which will be described later. In all this work the area under the retraction curve, i.e. the energy regained due to retraction, was negligible in comparison with the energy dissipated, as can be seen from *Figure 5*, and has been

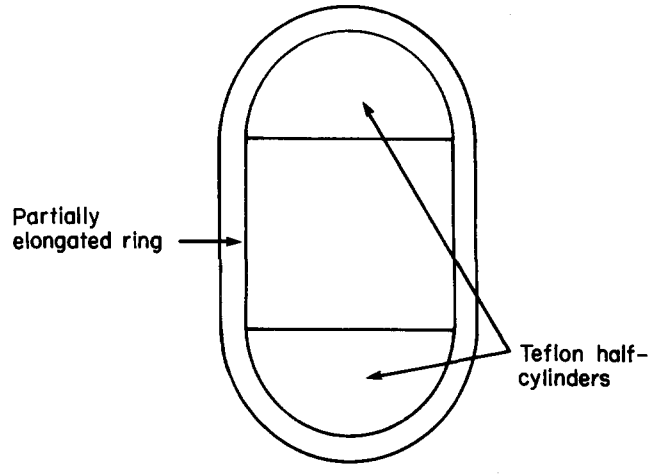

Figure 4 Diagram of the ring testing fixture

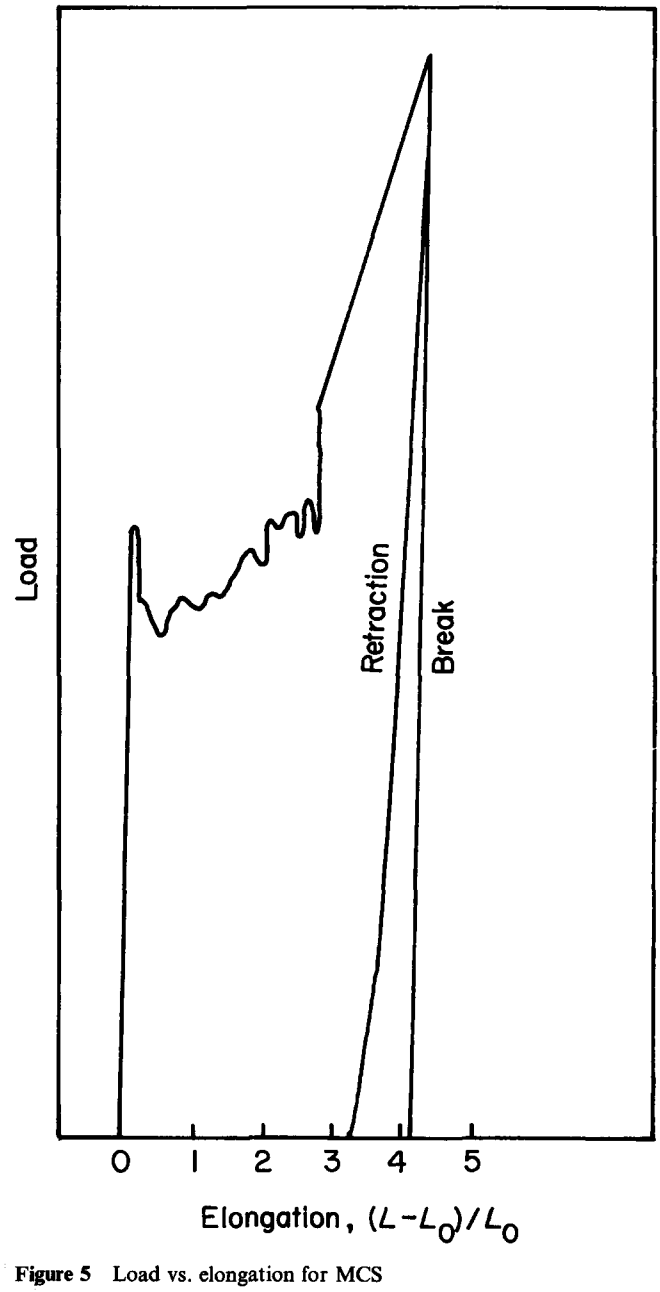

Figure 5 Load vs. elongation for MCS

neglected. Hysteresis was therefore taken as equal to the *BEN*.

Adhesion tests

For adhesion tests, MCS was dissolved in tetrahydrofuran (THF) and coated to a thickness of 25.4 μm on 102 μm poly(ethylene terephthalate) (PET) treated to promote adhesion. The coating was dried at ambient and vacuum baked at 120°C for 2 h. Strips of this material were bonded together at 130°C to give an MCS thickness of ~ 50 μm, then quenched from the 130°C oven into water at 0, 55 and 85°C, and annealed in ovens at the quench temperature, except as noted above for the 0°C sample. The annealed samples were cut into strips 1.5 cm wide, and adhesion was tested on an Instron machine at 23 and 70°C by the T-peel procedure[4].

RESULTS AND DISCUSSION

Hysteresis

When an MCS ring is elongated by an Instron machine, a curve like that in *Figure 5* is obtained. The load rises rapidly to a point where MCS extends without further increase in load, and then a neck begins to form, at which point the load actually decreases, mainly because of the reduction in cross section of the neck[8], and a 'plateau' forms as one or more necks propagate around the ring, with little change in the load. If retraction is carried out in the plateau area, little energy is recovered, showing high hysteresis in the plateau region. Beyond the plateau region, MCS starts to work (strain) harden, stressing tie molecules, and the load rises rapidly, the last phase of which is nearly linear[9,10].

Hysteresis as a function of temperature

In *Figure 2* the load–elongation curves of a typical amorphous adhesive are given. The material becomes very weak as the temperature rises by 15 or 20°C above the temperature where high hysteresis is obtained. This is typical of such polymers[2]. On the other hand, MCS produces load–elongation curves as shown in *Figure 6* for identical samples. Sample A was run at 70°C, and the load rises to 65 N. Samples B and C were run at 45 and 70°C, respectively, and should be evaluated by the right-hand scale. Owing to the tie molecules (physical crosslinks) and hysteresis, MCS resists cohesive failure to temperatures of 70°C.

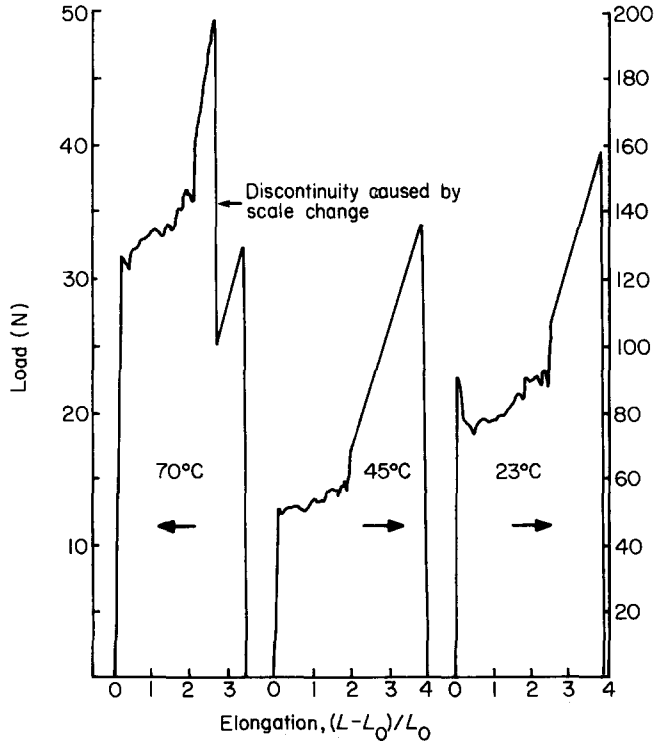

Figure 6 Load vs. elongation for MCS tested at 70, 45 and 23°C. The discontinuity in this curve is caused when the strip chart recorder was switched from full scale at 50 N to full scale at 100 N

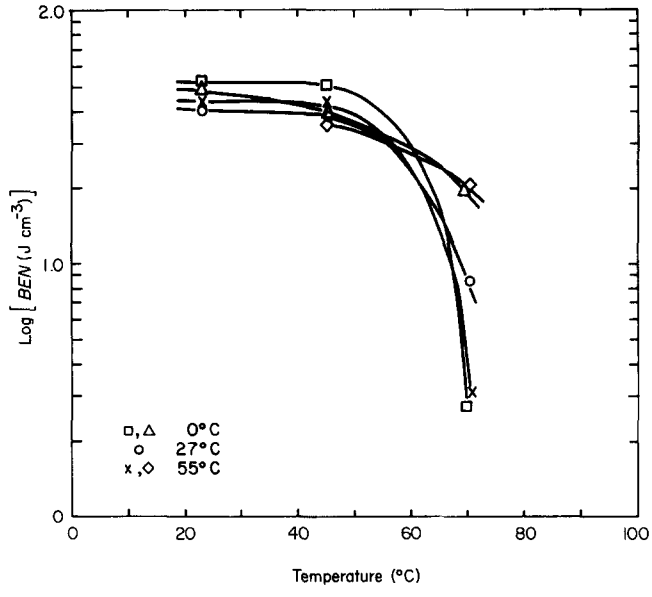

Figure 7 *BEN* vs. temperature for samples quenched at 0, 27 and 55°C

Further, the T_g values of MCS and the butadiene–styrene copolymer[4] of *Figure 2* were −20 and −40°C, respectively. Thus at 90°C above T_g, MCS shows substantial cohesive strength, whereas at 90°C or even 65°C above T_g, the butadiene polymer is relatively weak.

Figure 7 gives the results for a number of rings cut from samples quenched at 0, 27 or 55°C and tested at 23, 45 and 70°C. The data were selected from many runs and represent maximum values of *BEN* and *BEL*. Rings giving maximum values have the fewest microscopic and submicroscopic defects.

Since rings vary by a small amount in thickness, the *BEN*, which is being called hysteresis, is normalized by dividing it by the volume of the ring to give break-energy density. (*BEN* will be used for break-energy density in the rest of the paper.) The results plotted in *Figure 7* show that hysteresis decreases as temperature increases, but not drastically.

Hysteresis as a function of quench temperature

Spherulite size increases as the quench and anneal temperatures increase. As shown from recent and earlier work[5] on MCS, quenching at 0, 27 and 55°C produces spherulites of radii < 1 μm, somewhat over 1 μm and 10 μm, respectively. Also, this work showed that (1) the degree of crystallinity of MCS varied linearly from 40% for samples quenched and annealed at room temperature to 48% for samples quenched and annealed near the melting point (~95°C); and (2) the energy required to propagate a crack showed a trend towards higher energy as the quenching and annealing temperatures were lowered, i.e. as spherulite size and degree of crystallinity decreased. Other semicrystalline polymers show opposite

effects. For example Laghouat *et al.* as cited by Hertzberg and Mason[11] found that an 8% increase in the degree of crystallinity markedly reduced the fatigue crack propagation rate in low-density polyethylene.

The results shown in *Figure 8* were selected from many runs, and show the effect of crystalline characteristics on the *BEN*. In selecting the data, we chose runs with maximum and nearly the same per cent strain. This selection probably compares rings with a minimum of defects. *Figure 8* shows that *BEN* does not vary greatly with quench and anneal temperature (crystalline characteristics). Note that at 45°C even though the per cent strain of the more highly crystalline sample with larger spherulites is lower than that of the less crystalline sample with smaller spherulites, the *BEN* is greater, but at 23°C the opposite is true. There is no significant clear-cut variation of hysteresis with quench temperature.

Energy to form a neck

Because it may be pertinent to adhesion, the energy to form a neck was studied as a function of quench temperature. To get these data, we read the peak energy at necking. The values have been divided by the ring volume and will be referred to as *PEN*. *Figure 9* illustrates the difference in the load values of 0 and 55°C quenched samples. Specific results of *PEN* are plotted in *Figure 10*. More energy is required to form a neck in a sample quenched and annealed at 55°C than in samples quenched at 0 and 27°C. Although the differences in *PEN* are not large, these results were confirmed by numerous other runs. The reason for this interesting effect is not clear.

Peel studies of quenched and annealed MCS

Figure 11 presents the adhesive studies at 23°C in T-peel on MCS between PET supports. Samples quenched at 0, 55 and 85°C and annealed at their quench temperatures (except for the 0°C quenched sample, which was annealed at 23°C) were tested at various peel rates. (Hysteresis studies were not performed at 85°C because MCS quenched in 2 mm thicknesses and annealed showed wide variations in crystal structure with very

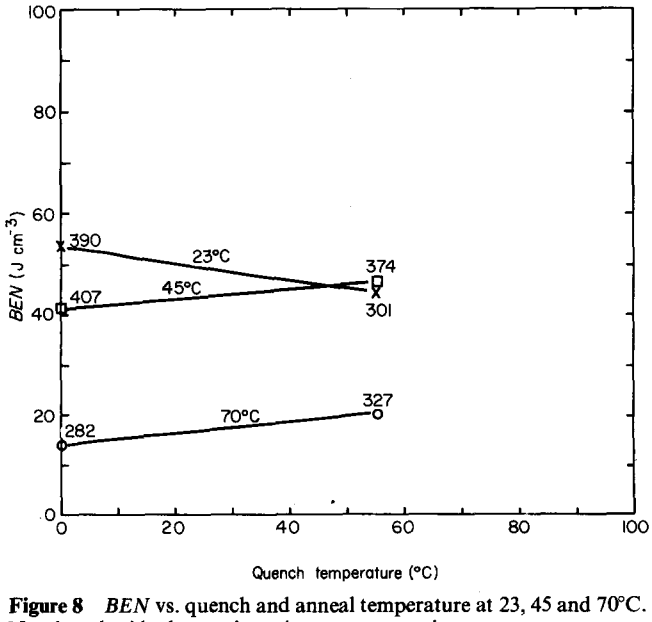

Figure 8 *BEN* vs. quench and anneal temperature at 23, 45 and 70°C. Numbers beside data points give per cent strain

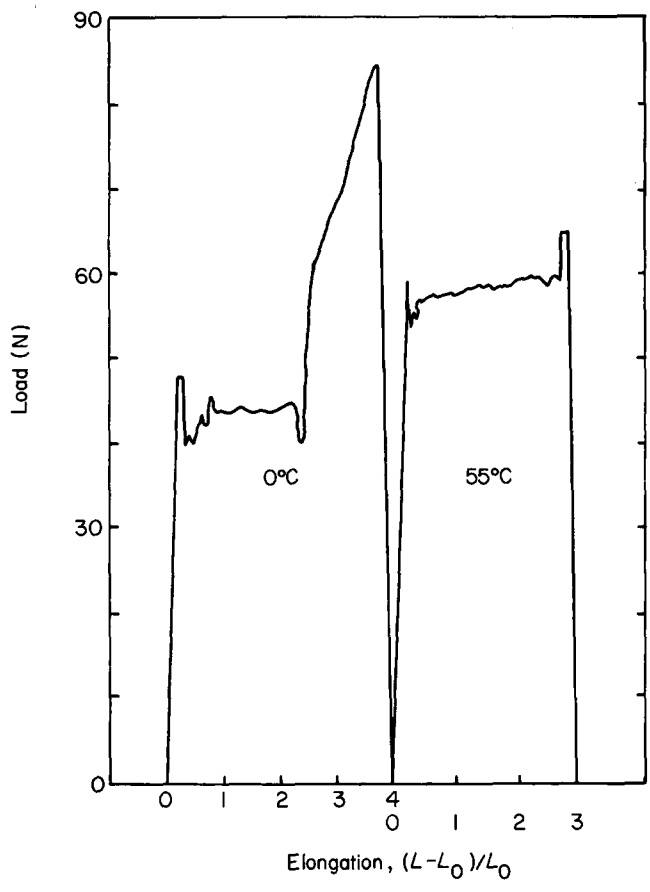

Figure 9 Load vs. elongation at 23°C for MCS quenched and annealed at 0 and 55°C

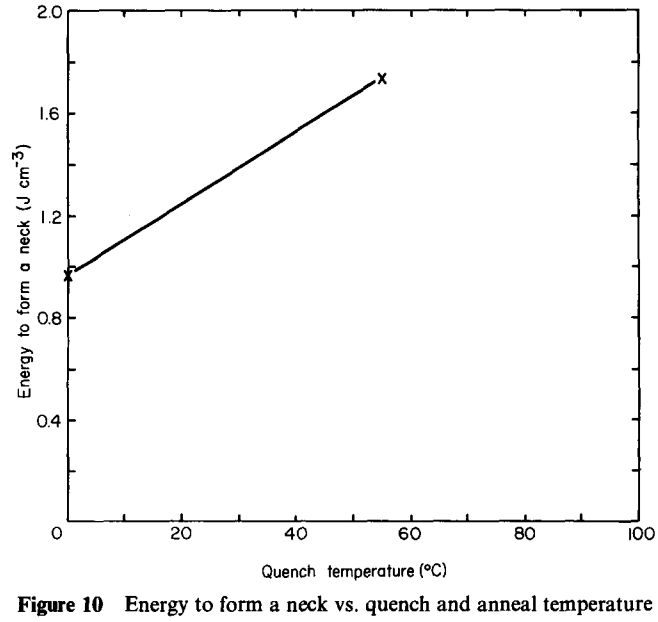

Figure 10 Energy to form a neck vs. quench and anneal temperature

weak areas.) MCS quenched at 0°C would have peeled at higher forces as peel rate was increased, but the PET failed at forces of ~30 N/1.5 cm. Thus the adhesive bond is stronger than the PET. All of these samples showed good adhesive strength. The reason the MCS quenched at 0°C outperforms the other samples is not clear but perhaps may be explained by its lower *PEN* value in *Figure 10*. The initial linear portion of the load–elongation curve shown in *Figure 9* dissipates no energy, so the lower the force (energy) at which MCS necks, the sooner energy will be dissipated from high-stress regions.

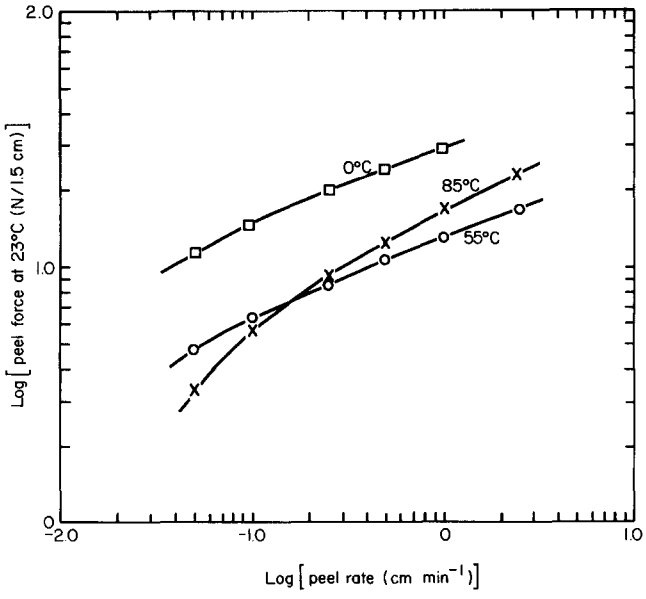

Figure 11 Peel force vs. peel rate at 23°C for samples quenched at 0°C and annealed at 23°C; quenched and annealed at 55°C; quenched and annealed at 85°C. Failure interfacial

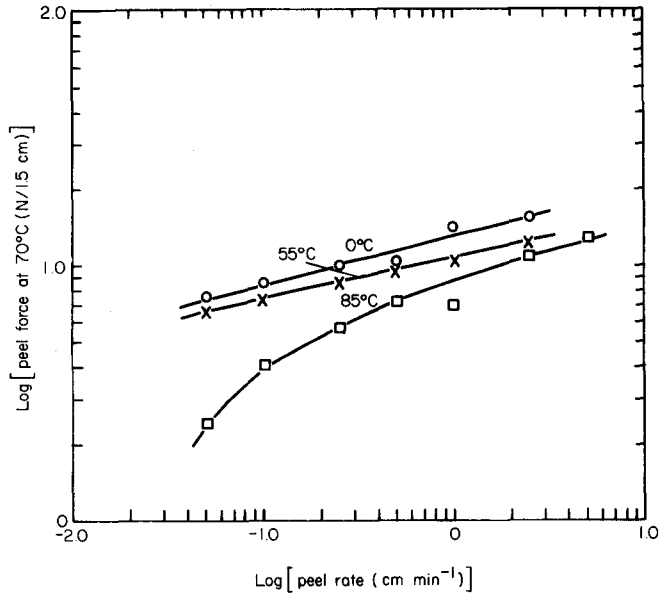

Figure 12 Peel force vs. peel rate at 70°C for samples quenched at 0°C and annealed at 23°C; quenched and annealed at 55°C; quenched and annealed at 85°C. Failure interfacial with spots of cohesive for the 85°C sample

Thus MCS quenched at 0°C will be less apt to form a crack or a precursor to a crack as peel force increases than the 55°C quenched MCS. Both samples will dissipate energy rapidly from *PEN* to failure.

Figure 12 presents the adhesive studies at 70°C, on MCS; it maintains high peel strength over a wide temperature range. There is little difference in peel force between MCS quenched at 0 and 55°C, and *Figure 8* shows little difference between the *BEN* values of the two at 70°C. Studies of *PEN* at 70°C do not show the differences in the 0 and 55°C quenched samples that were seen at 23°C. Thus energy to neck and hysteresis studies would predict similar peel forces for these two MCS samples.

Comparison of MCS and an EVA adhesive

To illustrate the difference in peel characteristics between MCS and an amorphous polymer, we present the peel results of the ethylene vinyl acetate (EVA) adhesive produced by Borden Chemical Division of Borden, Inc., designated as HC 6164. This adhesive with a T_g of -18°C is optimized for the 23°C region and has high peel forces at ambient, reaching 32 N/1.5 cm at a peel rate of 0.05 cm min^{-1} and probably would give higher forces at higher peel rates if the support did not fail. However, at 70°C at a peel rate of 2.5 cm min^{-1}, it reached a force of only 0.3 N/1.5 cm, whereas *Figure 13* shows that MCS peels at 15 N/1.5 cm. These results agree with other studies in this laboratory in which several of the best hot-melt adhesives were investigated over wide ranges of temperature, and all of them showed good adhesive strength under conditions for which they were optimized. However, as peel temperatures increased above optimum, adhesive strength deteriorated markedly in comparison with MCS.

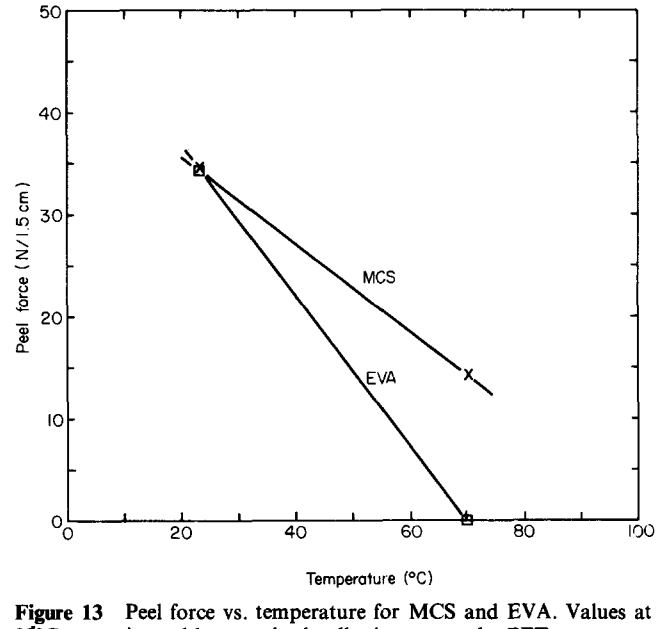

Figure 13 Peel force vs. temperature for MCS and EVA. Values at 23°C are estimated because both adhesives cause the PET to rupture

CONCLUSIONS

Molten MCS quenched and annealed over a range of temperatures to give various crystalline properties, e.g. degree of crystallinity and spherulite size, shows large mechanical hysteresis over the range 23–70°C. These results lead to the prediction that MCS will be a good adhesive in and beyond the two extremes of this temperature range because materials with high hysteresis dissipate energy from regions of high stress, preventing crack propagation, which is the mechanism by which adhesives fail.

Confirming the above prediction, MCS melted between strips of PET and quenched and annealed in the same manner as the hysteresis samples produced adhesive bonds that under optimum quench and anneal conditions exceeded, at a test temperature of 23°C, the rupture strength of PET (> 30 N/1.5 cm). At 70°C, peel forces as high as 15 N/1.5 cm were recorded. By contrast, one of the best amorphous adhesives (Borden's HC 6164 ethylene vinyl acetate polymer), which has good adhesive properties at 23°C, fails at low force at 70°C. This leads to

the conclusion that semicrystalline polymers such as MCS, because of their physical crosslinks (tie molecules) and related high hysteresis, will be better than amorphous adhesives for applications requiring a wide temperature range.

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