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Extensional and adhesion characteristics of a pressure sensitive adhesive

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The extensional viscosity characteristics of a terpolymer synthesized from acrylic acid, n-butyl acrylate and 2-ethyl-hexyl acrylate and used as a pressure sensitive adhesive, have been examined. By using a tensile test instrument it has been shown to be possible to generate three-dimensional plots of instantaneous extensional viscosity, Hencky strain and time of extension. The terpolymer was found to be strain hardening. During extension it also formed fibrils due to partial failure of the adhesive bond with an aluminium surface. The generation of the fibrils could be related to rate of extension and hence to the strain hardening behaviour. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Since pressure sensitive adhesives are normally low molecular weight polymers their deformation characteristics are such that they fall within the category of materials whose rheology is midway between that of solids and liquids. As a result they are amenable to study using rheological techniques generally applied to polymer solutions, melts and to gel-like fluids. This applies both to the bulk deformation and to the problem of tack (adhesion) between the adhesive and substrate. A number of papers have recently used such a rheological approach[1,2]. In this paper extensional viscosity measurements have been employed to study the deformation characteristics of a typical adhesive using a novel experimental technique.

Measurement of extensional viscosity has been the subject of much study recently[3,4]. For high viscosity fluids measurement of equilibrium data is comparatively easily carried out, sample preparation being, perhaps, the area where experimental difficulty is most often experienced[5]. Assuming that the polymer melt has been adequately relaxed it can be extended at a controlled strain rate, stress being measured as a function of time. When stress reaches an equilibrium the steady state value allows the calculation of true extensional viscosity. The same end can be achieved by applying a controlled stress, the strain rate at equilibrium being used to calculate extensional viscosity. In both cases extensional viscosity (η_E) is given by

$$\eta_E = \sigma_E / \dot{\epsilon}$$

where σ_E is extensional stress and $\dot{\epsilon}$ is strain rate.

Munstedt and Laun[6] using such a technique have been able to show that the shape of the extensional flow curve can be related to molecular weight distribution (MWD), *Figure 1*, for low density polyethylenes with a constant degree of branching. As MWD widens the peak in extensional viscosity occurs at progressively lower stress values and increases in magnitude. Increasing the degree of long chain branching has a similar effect. Meissner[7] has recently reported the development of a new melt extensional rheometer which will be capable of extending the range of data obtainable.

Low viscosity polymeric fluids present other problems since with one possible exception[8] the extensional viscosity data are non-equilibrium and the values obtained depend on the method of measurement used[9]. This results from the fact that the sample cannot be held at each end and extended slowly for long enough to reach a steady value of strain rate or stress under conditions of controlled stress or strain rate, respectively. Thus the condition for steady deformation in a Lagrangian sense cannot be attained. Nevertheless, it is possible to attain a steady state in the Eulerian sense in that the values of the rheological parameters remain constant at any point in the fluid under extension, although they change with position. The extensional viscosity values that result are transient.

It is worthwhile to summarize these techniques as they have considerable similarity to the Instron method adopted in the current paper.

Using the spinline method[10] a filament of a low viscosity fluid is extruded from a spinneret and extended by a rotating drum or vacuum tube. The filament profile is measured using a video camera, allowing the calculation of rate of extension along the filament length. The load generated is measured by deflection of the thin walled stainless steel tube along which the fluid flows to the spinneret. Allowing for inertia, gravity, relaxation from shear and surface tension, the extensional stress at any point in the filament can be calculated. An averaging technique can also be employed[11].

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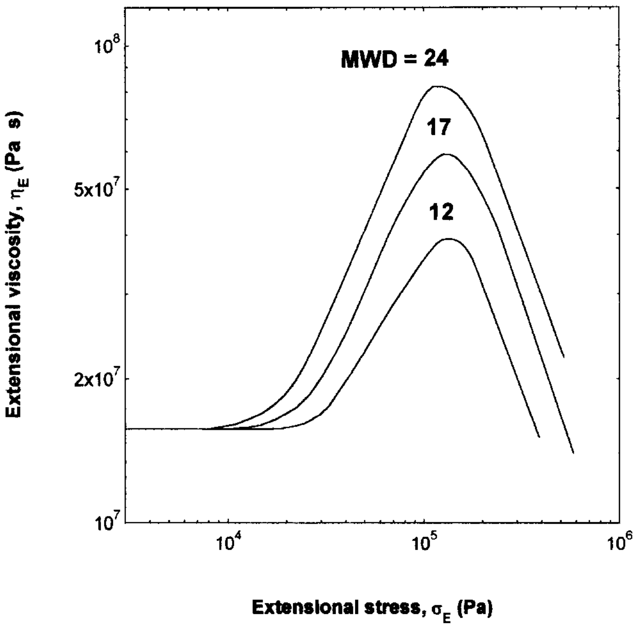

Figure 1 Variation of extensional viscosity with strain rate for three low density polyethylenes with the same degree of branching but different molecular weight distributions

In the opposed jets method[12] the fluid under investigation is sucked under vacuum into two orifices set a small distance apart in a bath of the fluid. The extensional stress in the stagnation region thus created is measured by deflection of the flexible pipes holding the orifices. Strain rate is obtained from the fluid flow rate and the geometry of the system.

In the falling drop method[13] a drop of the fluid is allowed to form at, for example, the tip of a burette. As the drop releases itself from the burette a filament is formed, provided the fluid is spinnable, between the drop and the burette. This filament is normally cylindrical for most of its length and is elongated by the falling drop. From the rate of descent of the drop, extension rate is found. Extensional stress is calculated from the difference between the body force and the surface tension acting on the drop divided by filament cross sectional area. The method can be adapted to produce high strain rates by replacing the drop with a falling weight[14].

Using these techniques and a variety of other methods such as the inverted siphon and converging flows[15] the flow properties in extension of two test fluids, M1 (a solution of 0.244% w/w polyisobutylene with a molecular weight of approximately 5.0×10^6, 6.98% w/w kerosene and 93% w/w polybutene oil) and A1 (a 2.0% w/w solution of polyisobutylene, molecular weight 4.3×10^6, in decalin) have been the subjects of a round robin exercise. Excellent agreement was found for results in steady and oscillatory shear from all laboratories. However, extensional flow results gave widely differing results depending on the technique employed. Recently[16], however, it has been shown that such non-equilibrium extensional viscosities can be reconciled by taking into account the time scale of the deformation process (*Figure 2*). This shows a 3D plot of transient extensional viscosity, time of deformation and Hencky strain for a solution consisting of 2.5% polyisobutylene, 47.5% decalin and 50% polybutene oil. The fluid named S1 has been the subject of much rheological analysis[17].

The surface was created using extensional flow data from a number of different experimental techniques, see above. A similar surface has been formed using the polyisobutylene incorporated into S1[18]. In the latter, extensional experiments were carried out using an Instron Tensile Tester. The results of the success of this approach make it possible to use such a tensile test instrument to obtain transient extensional viscosities of both high and low molecular weight polymers such as adhesives.

EXPERIMENTAL

Adhesive

The pressure sensitive adhesive is used on surgical dressings and comprises a terpolymer of acrylic acid, n-butyl acrylate and 2-ethyl-hexyl acrylate. The adhesive is formed by polymerization of the monomers in acetone followed by dilution to 10% solids content to give a solution of suitably low viscosity. This was poured onto a non-stick tray. The solution, initially about a

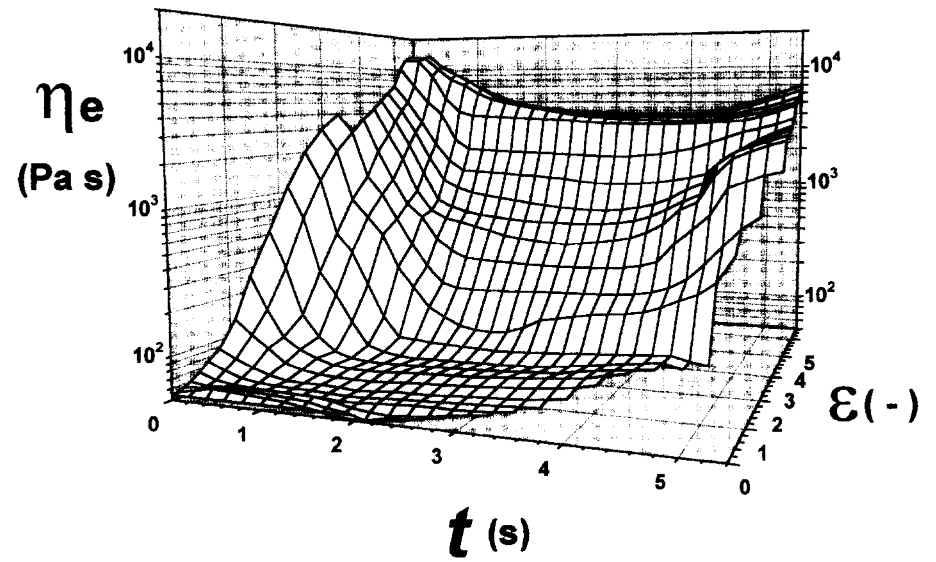

Figure 2 3-D plot of the variation of instantaneous extensional viscosity with time of extension and Hencky strain for fluid S1

millimetre deep, was allowed to dry at room temperature over a period of a few days. A second layer of solution was then poured on top of the first and again allowed to dry. This process was repeated about 20 times until an adhesive slab about two millimetres thick had been prepared. This was then dried to constant weight in a vacuum oven. The lengthy preparation of the adhesive slabs was necessary if the slabs were not to contain bubbles.

Sample preparation

The adhesive slab was cut into slices and rolled to form cylindrical test specimens with diameters in the range 4–6 mm. The ends of the specimens were then carefully cut to give smooth ends and the samples allowed to relax for 3 h before measurements were carried out.

Measurement technique

Tensile measurements were carried out using an Instron tensile tester (type 1122) incorporating computer controlled data acquisition and processing. All measurements were carried out at 20°C and 65°C relative humidity.

To avoid distortion of the gel-like sample in the jaws of the Instron tensile tester, the test specimens were attached directly to aluminium electron microscope stubs which previously had been cleaned using fine emery paper and acetone solvent. The stubs could then be clamped conveniently in the Instron jaws so that the test specimen was under slight pre-tension. When this had fully relaxed extension was commenced.

In order to obtain as wide a range of strain rates as possible cross-head speeds of 20, 50, 100, 200, 500 and 1000 mm min^{-1} were used. Test specimen lengths were 5, 10 and 20 mm with diameters of 4 or 6 mm. In a number of experiments the terpolymer was spread over the entire surface of the stubs giving a sample 2 mm thick and 12.5 mm diameter. This allowed us to increase the range of strain rate and study in more detail the effect of fibril formation. Between six and 10 repeat experiments were carried out on each sample, uniformity of diameter in the specimen being checked throughout the test using a vertically travelling microscope.

RESULTS AND DISCUSSION

In the typical tensile experiment as carried out on solids the sample is held between two grips, one fixed and the other attached to a cross-head which moves at a pre-set speed. Since Hencky strain is defined as

$$\epsilon = \ln(L/L_0)$$

where L is the length at some time t and L_0 is the original length and rate of strain, $\dot{\epsilon}$ is $d\epsilon/dt$, the sample experiences a strain that increases with time, *Figure 3*, and a strain rate that decreases with time, *Figure 4*. The variation of these two parameters will, of course, depend both on sample length and cross-head speed.

Typical load extension curves for a 20 mm sample are shown in *Figure 5*. An initial rapid rise in load was observed at all cross-head speeds corresponding to the region where strain rate was a maximum. The fact that at all cross-head speeds the load extension curves were indistinguishable would suggest that the deformation was purely elastic. In a pure Hookean solid, of course, the ratio of stress to strain would be Young's modulus and independent of strain rate. The curves in *Figure 5* are of load against extension. However, as the reduction in cross sectional area was always the same at a given extension the load values are equally proportional to stress in all samples.

At greater extensions the load/extension curve was strongly influenced by cross-head speed, continuing to rise rapidly at high speed and tending to form a plateau at low speeds. In contrast, extensional stress, defined as the ratio of load to cross sectional area of the sample at

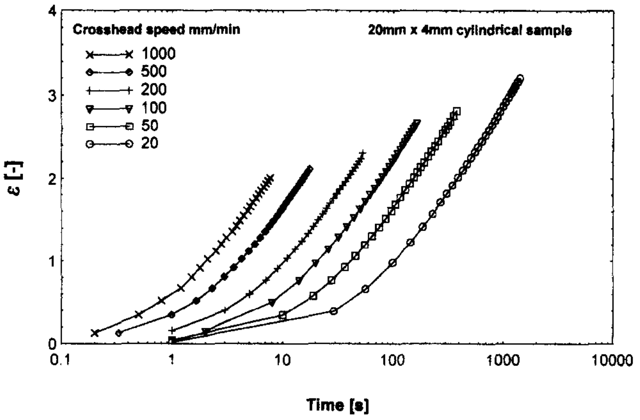

Figure 3 Variation of strain with time for a 20 mm sample extended at a range of constant cross-head speeds

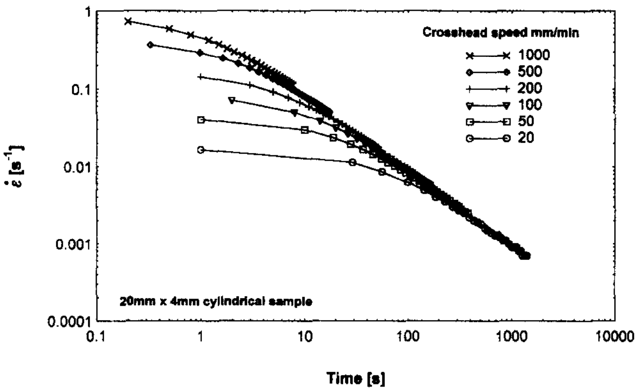

Figure 4 Variation of strain rate with time for a 20 mm sample extended at a range of constant cross-head speeds

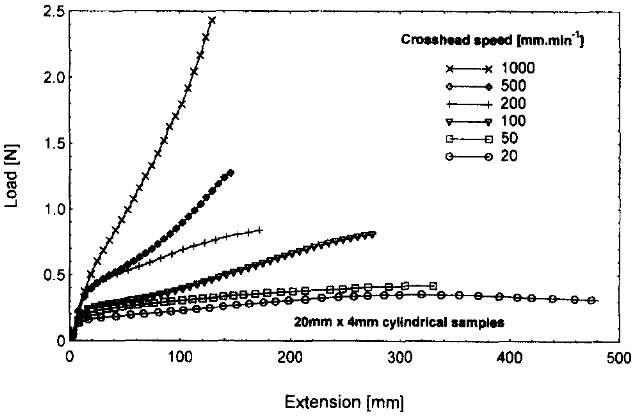

Figure 5 Typical load extension curves for a 20 mm long, 4 mm diameter sample of terpolymer extended at various cross-head speeds

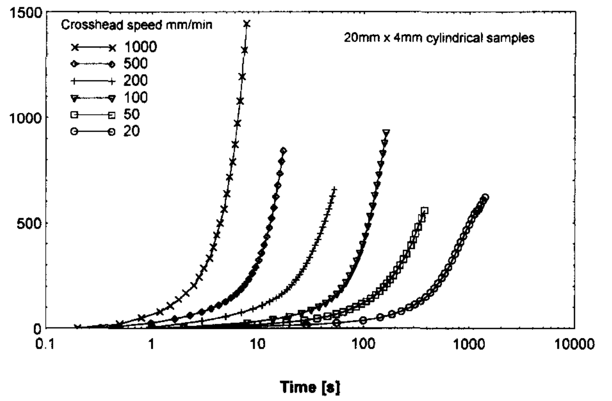

Figure 6 Stress–time plots for a 20 mm long, 4 mm diameter sample of terpolymer extended at various cross-head speeds

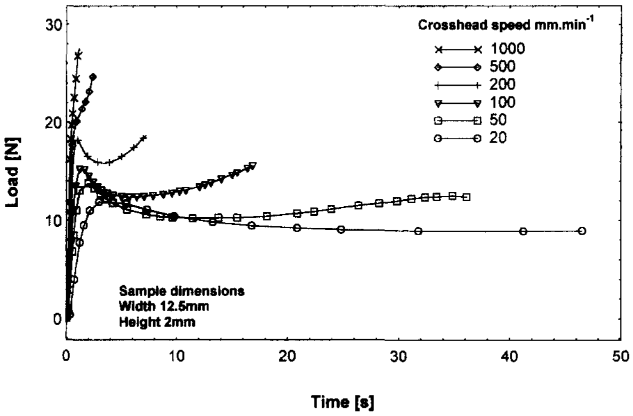

Figure 8 Load vs time of extension curves for samples of terpolymer, of dimensions 2 mm × 12.5 mm at various cross-head speeds

Figure 7 Fibrils of terpolymer

any time of extension, *Figure 6*, increased slowly, initially, with time of deformation then with increasing speed as extension continued at all cross-head speeds. The difference in the load and stress curves must be due to the decrease in sample diameter since extension was at a constant speed. It is worth noting that in all experiments the sample diameter remained extremely uniform along its length with the exception of those areas showing 'fibril' formation close to the stubs. 'Fibrils' can be defined as the individual strands of adhesive formed between the surface of the stub and the body of the extending sample. They are generally somewhat irregular in shape with a total cross-sectional area considerably smaller than the cross-section of the bulk filament.

The maximum values on each of the curves corresponded to failure of the adhesive bond between the stub and the filament. The failure mechanism was not simple with the intact filament adopting a state of partial failure at the interface between stub and filament (possibly lasting many seconds) before continuing towards complete detachment. In each case the area of adhesive failure left islands of attachment which gave the appearance of adhesive fibrils (*Figure 7*). Clearly, the result of fibril formation was an increase in stress in the material forming the fibrils since they were subjected to the same load as the bulk of the sample over the much reduced cross-sectional area. They might under these circumstances have been expected to fail or to continue to propagate along the entire length of the sample but this did not happen.

The load extension time curves (*Figure 8*) for the samples with dimensions 2 mm × 12.5 mm were apparently very different in type from those obtained from the rod shaped specimens. Part at least of this effect must arise from the fact that with a very short but broad sample under extension the loading in the initial stages of deformation is triaxial rather than the uniaxial loading experienced by a long thin filament. Under these circumstances a pure uniaxial flow regime could not be developed until the stub surfaces had moved far enough apart to create a parallel sided filament. This problem has been recognized for the measurement of extensional viscosity of fluids held between parallel sided plates. Adhesion of the sample to the plates causes the sample to take up a wine-glass shape[19] at each end. Shipman *et al.*[20] have investigated these effects using numerical simulation. They showed that flow close to the plates is complex and not necessarily in the direction of extension. This means that interpretation of the load extension curves of thin samples at low extensions is not simple. As a result efforts have been made to ensure that for extensional viscosity measurements a cylindrical shape of sample is maintained at all times[21,22].

At low crosshead speeds, up to 200 mm min^{-1}, a peak in load was observed which corresponded to the onset of fibril formation. Note that once the sample had reached 250% strain it was longer than it was wide and loading could be considered uniaxial. Once the fibril length had

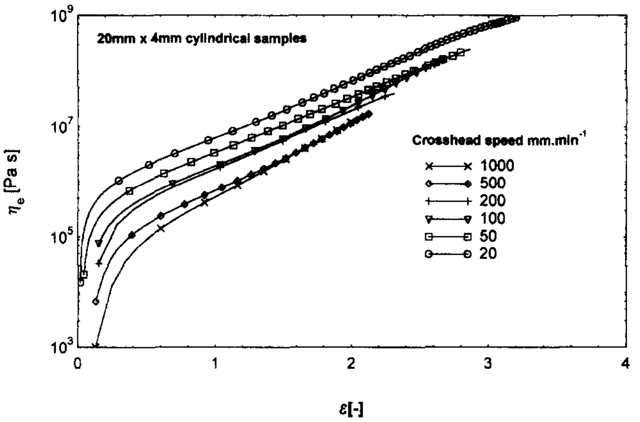

Figure 9 Transient extensional viscosity variation with Hencky strain at a range of cross-head speeds

stabilized, the load began to rise again until failure of the adhesive bond finally took place. Significantly, at the highest crosshead speeds of 500 and 1000 mm min^{-1} no peak in the load and no fibril formation were observed. The load in both cases continued to rise rapidly until adhesive failure occurred.

No peaks were found in the load extension curves for 4 and 6 mm samples even at the lowest rates of extension although fibril formation was observed. The explanation would seem to be that the smaller surface area of the adhesive bond with these samples resulted in a fall in load on fibril formation that was insignificant.

When the above data were converted into extensional viscosity vs strain plots, *Figure 9* was obtained. An apparently rapid rise in extensional viscosity, on a log–log scale, followed by a power law region was obtained in all cases. On a linear plot, extensional viscosity is revealed as being strongly strain hardening at large strains. Similar results were obtained with 5 and 10 mm samples.

Mechanism of fibril formation

In all the experiments described above sample failure took place by failure of the adhesive bond between the terpolymer adhesive and the stub. At no time did breakage of the bulk of the sample or of the fibrils take place. The question now arises as to the cause of fibril formation. Fibril formation has been described by Speigelberg and McKinlay[23] and is a common phenomenon when the adhesive bond formed from pressure sensitive adhesives is broken by a peel test. Kaelble[24] has discussed it in detail and Good and Gupta[1] have discussed the possibility that fibrils might be caused by a 'meniscus instability' or the presence of flaws at interfacial unwetted areas. Clearly, failure of the adhesive bond at a number of points on the stub surface took place as extension proceeded. The additional stress experienced by those areas of the adhesive still attached to the stub could only result in a rapid extension, elongating the adhesive still attached to the stub and creating the fibril. Presumably the point at which propagation of the split in the bulk filament stopped would be governed by the same laws of crack propagation that control failure of any solid. At the leading edge of the split viscous flow takes place increasing the radius of the crack tip and reducing the energy of crack propagation. When the energy is dissipated sufficiently the crack, or in this case the fibril, stabilizes.

The extension of the fibril would, however, become self limiting if the polymer was strain hardening as, indeed, it

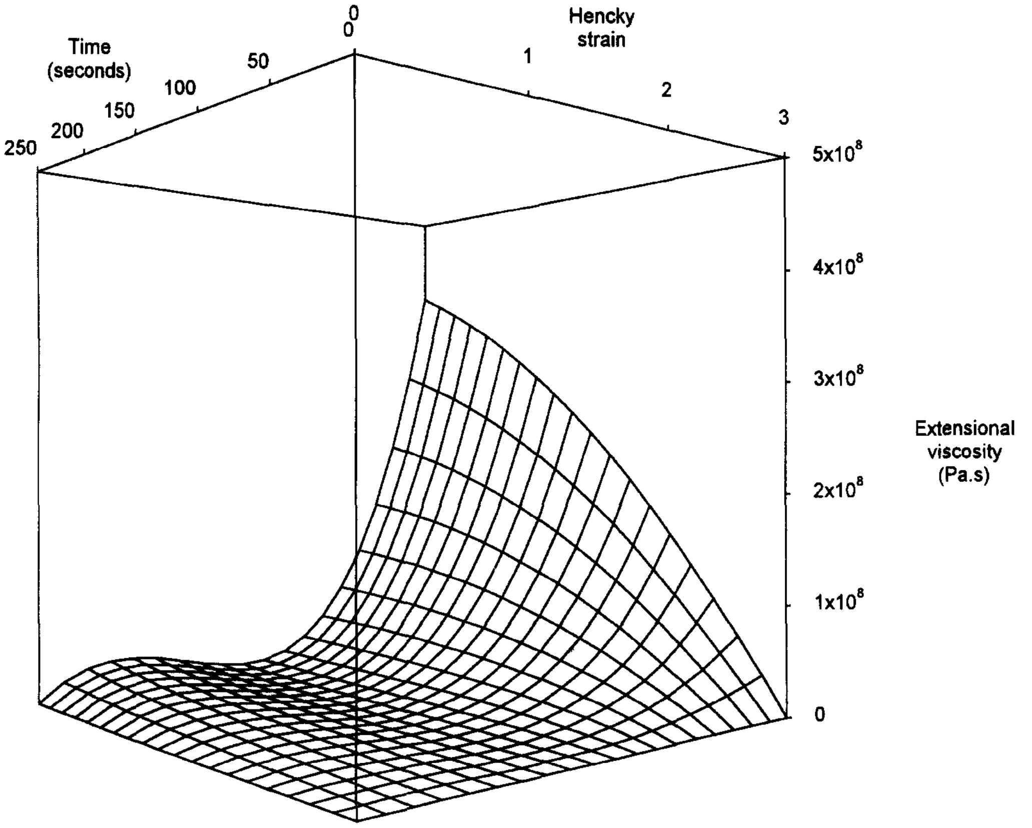

Figure 10 3-D transient extensional viscosity surface for the terpolymer

has been found to be in this case (see below). Once the extensional viscosity reaches a value at which the fibrils can resist the applied load, further deformation will cease with the fibrils stabilizing at the strain value attained. Further deformation would then occur in the bulk of the sample which had not deformed enough to strain harden sufficiently. Once it did, the remaining adhesive bond would break. This mechanism was supported by the fact that when the series of samples 2 mm in length, *Figure 8*, were extended at the highest speeds attainable no fibril formation was observed. The highest rates of extension were such that all of the adhesive was deformed at a rate well into the strain hardening region with the stresses generated eventually exceeding the strength of the adhesive bond.

Extensional viscosity

Figure 10 shows the three-dimensional plot of transient (non-equilibrium) extensional viscosity, time and strain obtained when all data were combined. The various extensional viscosity experiments produced values that formed a smooth surface fitting the equation

$$\begin{aligned} z = {} & 0.163x^3y^3 - 0.857x^3y^2 - 1.996x^3y - 104.4x^2y^3 \\ & - 308.7x^2y^2 + 263.5x^2y + 245100xy^3 \\ & - 554900xy^2 + 355700xy \end{aligned}$$

where z = transient extensional viscosity, x = time of extension and y = Hencky strain. The strain hardening found in the individual curves is clearly visible. While this surface represents the transient extensional behaviour of the adhesive, at very long times the transient values of extensional viscosity would tend to the equilibrium values of extensional viscosity obtainable under very slow deformation conditions.

It could be considered that strain history might influence transient viscosity results. As mentioned previously, experiments using polyisobutylene[18] showed that extensional viscosity results, obtained with a strain rate varying from very high values initially to low values as the sample extended, fell on the same surface as curves obtained at a constant strain rate. This suggests strongly that the surface is truly representative of non equilibrium extensional viscosity behaviour.

The molecular origins of the rheological characteristics must lie both in the entanglement behaviour of the macromolecules as they are stretched and possibly the formation of structure between the elongated chains. Treloar[25] as long ago as 1958 discussed the formation of temporary crystallites produced in rubbers when stretched. These disappeared when the rubber was allowed to relax. The effect has been attributed by Hull[26] to the increase in entropy from stretching causing the rubber to seek a lower free energy state, the crystalline state having a lower free energy than the amorphous stretched state but a higher free energy than the amorphous relaxed state. Piau has recently reported[27] such a phenomenon when X-ray diffraction studies on polyisobutylene during extension showed that a temporary form of crystallinity was induced at those regions of deformation at which strain hardening was observed. The possibility of structure formation in the terpolymer adhesive is currently under investigation by us. Preliminary results indicate strongly that some form of ordered structure does indeed form on extension.

Finally, the use of a tensile test instrument can be shown to be capable of producing instantaneous extensional viscosity data that is of considerable value in describing the behaviour of materials under non-equilibrium conditions.

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