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A novel method to measure the elastic modulus of polymers as a function of tensile deformation

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A method to measure the elastic modulus of semicrystalline polyethylene during an instantaneous strain rate change is described. The elimination of machine transients during the strain rate change permits the observation of the stress reduction which must occur to maintain the abrupt change in non-elastic strain rate. This change can be implemented fast enough to precisely determine the incremental changes in stress and strain before relaxation processes take place. The results show that at 23.2° C the unrelaxed modulus decreases with strain whereas at 51° C it is constant. Furthermore, at room temperature the strain dependence of modulus change decreases with decrease in the degree of crystallinity. Such observations are in accordance with the thermal–mechanical data which indicate that both crystalline and viscous flow takes place near ambient but at elevated temperatures or slower strain rates, flow primarily occurs in the amorphous regions.

1. Introduction

The progress in the understanding of elastic and non-elastic deformation of polymers above the glass transition temperature has been greatly hindered because the elastic modulus cannot be measured precisely without including strain due to time dependent processes. Thus the conventional technique [1] accounts for this anelasticity by determining the relaxed modulus. However only by separating the unrelaxed modulus, E_u, from the anelastic processes can the physical basis of elastic properties of molecular aggregates be elucidated [2, 3]. From such a discrimination the theoretical predictions of entropy–elastic, kink isomer energy–elastic and extended chain elastic forces as reviewed by Kausch [4] can be critically examined. This study is an attempt to show that this separation of time independent and dependent processes in polyethylene is possible.

The present technique is to measure the changes in stress and strain while the specimen is being continuously deformed in tension. If an instantaneous drop or decrease in stress can be detected together with the change in displacement before relaxation can take place, the Young's modulus can be obtained. This measurement inherently assumes that the thermal activation of microscopic shear centres are stress induced. Hence the change in probability of activation (a change in non-elastic strain rate) results in a change in stress accompanied by an elastic displacement. This is the method to measure activation volume as discussed by Li *et al.* [5], which could not be precisely measured until the machine transient is eliminated as described below. In polyethylene at room temperature the nuclear magnetic resonance studies [6] show that the relaxation times after a perturbation are characterized by a short (~300 msec) and long (~30 min) times. Thus if the changes in stress can be monitored without transients in times shorter than 300 msec, the unrelaxed modulus may be determined.

The elimination of machine transients during strain rate change tests during tensile testing [7] to measure the strain rate sensitivity of metals has shown that stress and displacement changes can be recorded and stored digitally within 10 to 50 msec after an abrupt rate change. This modified tensile machine has a built-in compensating device such that the change in the elastic compliance of the machine and specimen is balanced out. If an extensometer is attached to the specimen, the appropriate compensation manually set by the operator can ideally result in a response schematically illustrated in Fig. 1. Should over-compensation or under-compensation take place the expected response follows the locus b and c, respectively. The transients illustrated in the displacement curves for conditions b and c result since the correction to ensure the desired non-elastic strain rate change, $\Delta \ln \dot{\varepsilon}_p$, occurs only at a given instance, not continuously. This becomes apparent when it is realized that displacement rate control imposes a total strain rate $\dot{\varepsilon}_t = \dot{\varepsilon}_p + \dot{\varepsilon}_e$ where $\dot{\varepsilon}_e$ is due to the machine and specimen compliance. Locus d in Fig. 1 shows the case whereupon ideal compensation for a strain rate change, relaxation processes take place after a time interval Δt. In the following section it will be shown that a facsimile of locus d is possible although the data is limited by the sensitivity of the extensometer and load cell.

2. Experimental procedure

The tensile tests were performed with screw driven tensometer similar to the one previously described [7] with an electromagnetically powered compensating

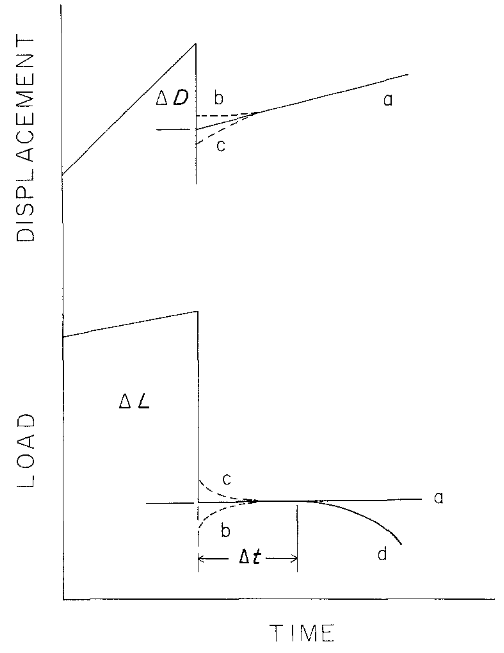

Figure 1 Schematic curves for load upon application of compensator at the time of strain rate change: (a) ideal; (b) overcompensated; (c) under compensated; and (d) ideal with stress relaxation after Δt time.

device to eliminate the machine and specimen compliance. The strain rate used was 3.9×10^{-5} and $1.95 \times 10^{-4}\,\text{sec}^{-1}$ and tests were performed at room temperature and 51.0° C using a constant temperature air bath. The true stress and true strain were calculated assuming constant volume during deformation [8].

The strain rate was altered by a factor of one quarter with a low inertial gear box equipped with magnetic clutches. Outputs of both the load cell and the clip-on strain gauge extensometer of 10 mm gauge length were interfaced to digitized data logging devices, the former through a d.c. amplifier to the A/D converter of the MINC (PDP 11/23) computer and the latter to a Hewlett-Packard 3456A digital voltmeter (DVM) also interfaced to the computer. Both signals were integrated at approximately 60 Hz to reduce noise and then stored on floppy disks. However, due to a slight difference in the data acquisition rate of the DVM a time lag takes place which results in an offset of the displacement curve with respect to that of load and a difference in the time calibration which is apparent when both data is plotted together (as in Fig. 3). With a metallic specimen the crosshead drive took less than 10 msec to change down in speed by a factor of four and about twice that for the up-changes.

Fig. 2 illustrates that without this compensation (non-compensated case) measurement of the unrelaxed modulus is not possible. The fact that overcompensation results in a positive reloading attests to the fact that the actual elastic response of the material is being examined. The ideally compensated case manifests a plot almost identical to the schematic one discussed and illustrated in Fig. 1.

The polyethylene specimens were made from experimental HDPE pipe samples supplied by DuPont Canada and clear PE resin plaque cooled at $15°\text{C}\,\text{min}^{-1}$. The physical properties are given in Table I. (1 1 0) and (0 2 0) pole figure determinations of these materials showed that detectable texture was not apparent although the contours were not ideally random. The variation of normalized intensities was within a factor of two. The 60 mm diameter pipe with 7 mm wall thickness were cut in a milling machine to produce square rods parallel to the tube axis. These rods were reduced on two sides to give a gauge section of about 4 mm × 6 mm × 30 mm by means of a modified holder adapted for the TensilKut shaper. The clear specimens were cut out on a special diamond wheel microslicer and its reduced gauge section was 3 mm × 3 mm × 27.5 mm. Both types of samples

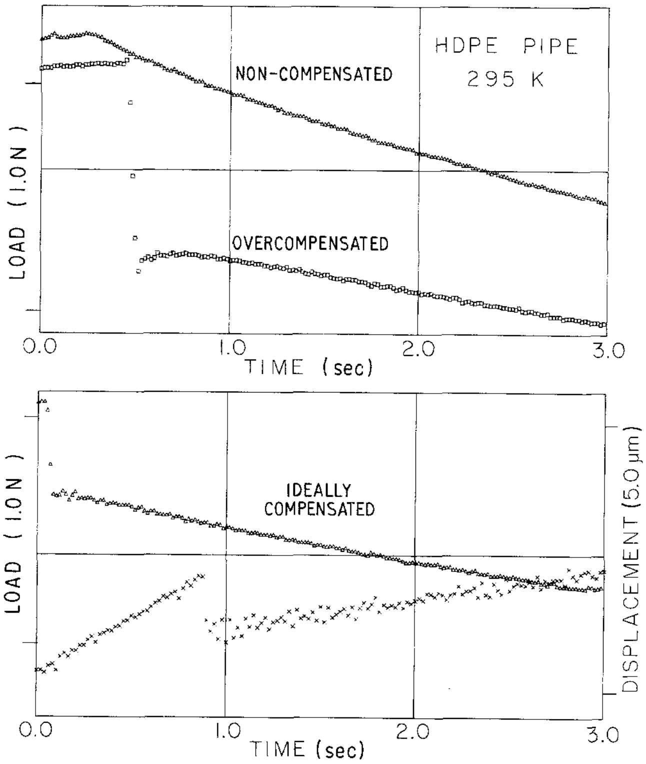

Figure 2 Transients due to 1/4 change in strain rate from $1.5 \times 10^{-4}\,\text{sec}^{-1}$ for HDPE pipe material at 295 K for non-compensated, over-compensated and ideally compensated cases. The lateral shift between the load and displacement curves is due to a small difference in the acquisition rate of the two instruments.

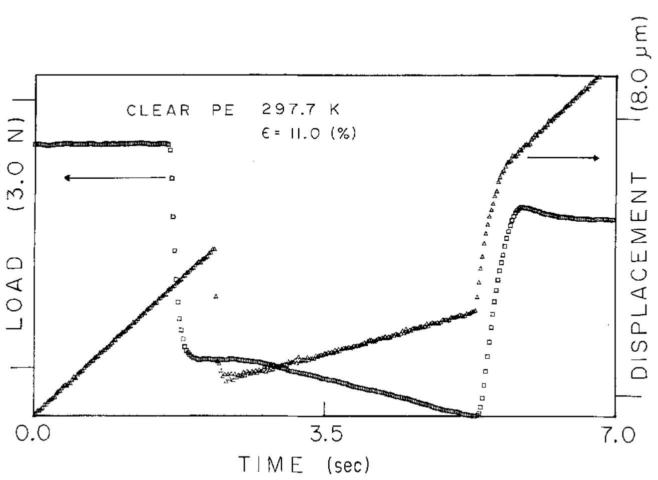

Figure 3 Load (upper) and displacement (lower) curves against time for resin #21 at 297.7 K at ≃11% strain illustrating the ΔL and ΔD values occurring during an up- and down-strain rate decrement. The data acquisition rates of the two curves are slightly different accounting for the lateral shift of the decrement position.

were polished with wet emery using 600 grit. Experience with many types of preparation method did not show detectable variation in mechanical and thermodynamic properties especially if the specimens were allowed to relax for at least one day after preparation.

3. Results and discussion

Fig. 3 shows a typical load and displacement change during a strain rate change at 24.4° C of 1/4 for a clear PE resin where Δt is about 0.5 sec. The unrelaxed Young's moduli are calculated using $\Delta\sigma/\Delta\varepsilon$ where E_{ud} refers to down-change and E_{up} to up-change. From a strain rate change viewpoint the down-change is more reliable than the up-change because it is faster and the transient is better defined; the microstructure just prior to rate change is in a state of near dynamic equilibrium whereas after the rate change a new equilibrium has not been established before the up-change. The measured E_u values at ambient temperature for the three semi-crystalline clear resins of varying amounts of crystallinity and molecular characteristics (Table I) are shown in Fig. 4. As expected the composite modulus increases with the degree of crystallinity. Although there are some detectable deviations at higher strains for the stiffest resin, the measured modulus seems to be insensitive to the magnitude of the imposed strain rate in accordance with the supposition that the unrelaxed modulus is the quantity being measured. Furthermore a decreasing trend with strain is observable wherein the slope seems to be largest for the most crystalline resin. In the case of HDPE gas pipe material, the E_u values were measured at two temperatures as depicted in Fig. 5. Note that at 23.2° C the modulus decreases with strain and the scatter between E_{ud} and E_{up} is large whereas at 51.0° C the modulus is strain independent and the scatter is small. The reason for this observation is attributed to the fact that for the imposed strain rate of $3.9 \times 10^{-5}\,\text{sec}^{-1}$ at 23.2° C the major deformation is in the crystalline portion whereas at 51.0° C only viscous flow in the amorphous portion takes place.

For low strain deformation of semi-crystalline polyethylene there seems to exist a demarcation between primarily viscous flow at low strain rates and viscous plus crystalline at higher strain rates. The strain rate at which this inception of crystalline deformation mode is observed increases with temperature. A detailed report describing this phenomenon will be published elsewhere [9, 10]. For the present purpose it will suffice to examine the parameter $\sigma S = (1/T)\,(\partial\sigma/\partial \ln \dot{\varepsilon}) = k/v$ where S is the strain rate sensitivity defined as $(1/T)(\partial \ln\sigma/\partial \ln\dot{\varepsilon})$; k, the Boltzmann constant and v, the activation volume. The σS–σ curves in Fig. 6 reveal that at 51.0° C it is almost constant and independent of σ whereas at 23.2° C there are portions of the curve which show a linear relationship indicating a constancy of S. In the case of Newtonian liquids $(\partial\sigma_v/\partial \ln\dot{\varepsilon})_T = \eta\dot{\varepsilon}$, thus its invariance at 51.0° C suggests that σ_v is insensitive to strain and/or to the total flow stress σ indicating $\sigma_v \ll \sigma$. For plastic flow in polycrystalline aggregates, on the other hand, S is more or less constant and this constancy of normalized flow stress change is called the Cottrell–Stokes relation [11, 12]. Thus even in crystalline flow of polymers one would expect deviations from constancy of $S\sigma$ towards that of constancy of S if crystalline flow took place. Despite this large variation in σS with strain (or stress) at 23.2° C the measured E_{ud} shows a systematic decrease with strain indicating the validity of this novel method in

TABLE I Physical properties of PE Resins*

Resin	Density (g cm^{-3})	Melt index ($\text{g}\,10\,\text{min}^{-1}$)	DSC		Spherulite radius by SALLS (μm)	Molecular wt distributions (g mol^{-1})				Degree of branching (per 1000 carbons)
			Crystalline (%)	Amorphous		M_N	M_W	M_Z	M_{Z+1}	
17–1	0.965	13.73	79.9	20.21	32	16 400	56 500	165 000	350 000	0.60
21–1	0.944	11.2	61.50	38.50	18	18 100	62 600	194 000	446 000	4.10
7–2	0.926	5.10	42.62	57.38	25	22 434	89 054	327 737	790 993	11.90
HDPE pipe	0.9415	0.3155	56.70	43.30	–	20 103	186 462	1 000 740	1 862 565	–

*Determined by the DuPont Canada Research Laboratory in Kingston, Ontario.

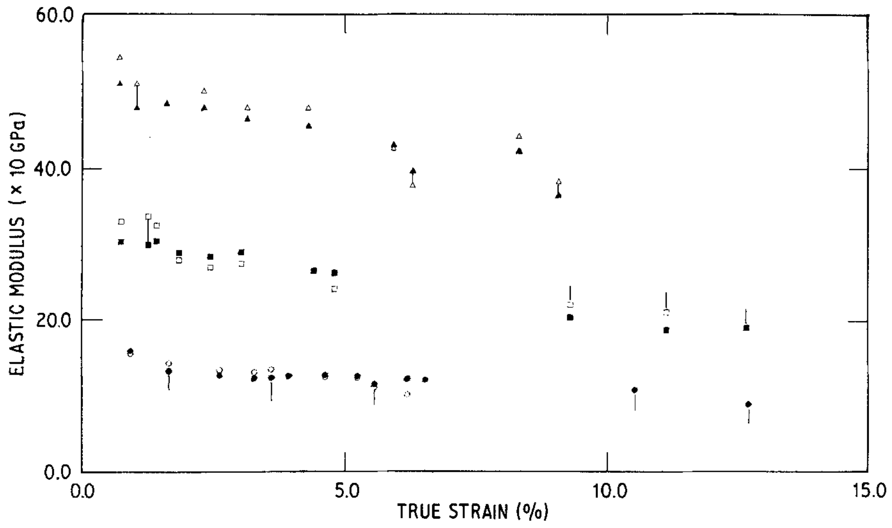

Figure 4 Composite modulus, E_u, against true strain at 298 K for three clear resins: #17 (triangle); #21 (square); #7 (circle). The down-changes, E_{ud}, are indicated by filled symbols and up-changes, E_{up}, by open ones as determined from strain rate change tests at 3.9×10^{-5} and $1.95 \times 10^{-4}\,\text{sec}^{-1}$: the latter is denoted by vertical markers.

determining E_u. Moreover the good correspondence between E_{ud} and E_{up} at 51.0° C but not at 23.2° C further supports the notion that more structural sensitive processes due to crystalline flow are occurring at the lower temperature. Hence with increasing temperature the strain dependence of E_u decreases. A corollary effect is seen in Fig. 4 where at constant temperature the strain dependence decreases with decrease in the degree of crystallinity.

Assuming that the present determination is that of the unrelaxed modulus, what inference can one draw from Figs 4 and 5? The observed values of about 2 to $5\,\text{GN}\,\text{m}^{-2}$ at 23.2° C is comparable to that for $E_{[020]}$ which is the lowest modulus for the orthorhombic structure of polyethylene [2]. However, according to Holliday [2] due to the large value of $E_{[001]}$, an estimate of E_{pc} for randomly oriented polyethylene crystallites is about $5\,\text{GN}\,\text{m}^{-2}$. Assuming a Reuss average, E_u, for a series composite of crystallites and amorphous regions, $1/E_u = V_a/E_a + (1 - V_a)/E_{pc}$ where V_a is the volume fraction of the latter. The calculated values corresponding to Fig. 4 are shown in Fig. 7. Although the arbitrary choice for the value of E_{pc} distorts the E_a value where $E_u > E_{pc}$, this figure strongly suggests that strain dependence of the modulus for the amorphous component, E_a, is highly dependent on the degree of crystallinity. Moreover the extrapolated values at zero strain are very near those calculated by Kausch [4] from the energy elastic contribution of kink isomers. This coincidence seems more than fortuitous because the activation energy measured from the temperature dependence of $\partial\sigma_v/\partial \ln \dot{\varepsilon}$ results in a value [9, 10] of about $37.8\,\text{kJ}\,\text{mol}^{-1}$ whereas Kausch predicts a sum of 46 to $63\,\text{kJ}\,\text{mol}^{-1}$ for a minimum process of simultaneously activating and annihilating two kinks to permit chain elongation.

The modulus decrease with strain has also been observed during creep at ambient temperatures [1]. Although such an effect can be attributed to accelerated anelastic process for the relaxed modulus, this rationale is not applicable to the unrelaxed one. From the Reuss averaging viewpoint, it means that V_a is increasing with strain. This infers that the specific volume of the amorphous regions is increasing with strain. Peterlin [13] has predicted that such an increase of specific volume would be linear with tensile strain. Recent volume change measurements by Zok [14] during low strain tensile and compressive deformation supports this prediction. His correlation of the volume change to craze formation on pre-etched surfaces of the test piece strongly corroborates the notion that crazing increases the specific volume in that localized region. Thus the observations in Figs 4 and 5 strongly suggest that the present technique is capable of detecting subtle microstructural changes such as microvoiding and/or microcrazing which accompany deformation of semicrystalline polymers. On the other hand, at the higher temperatures where flow is primarily viscous, one would not expect a decrease in E_a with strain but a small increase due either to

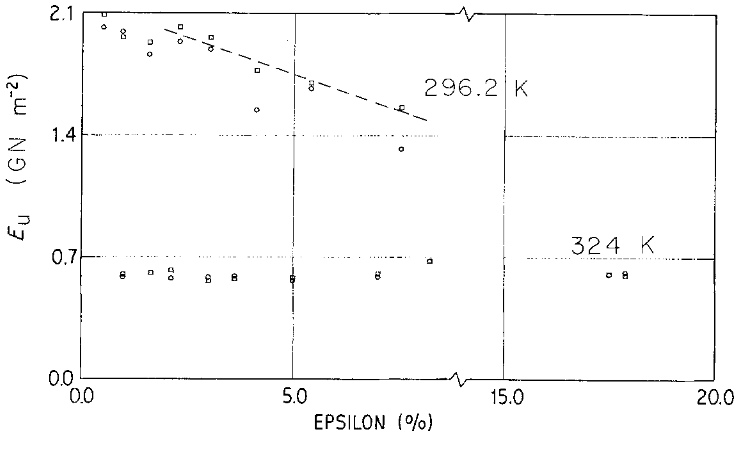

Figure 5 E_u against ε for HDPE pipe determined for 1/4 strain rate change from $3.9 \times 10^{-5}\,\text{sec}^{-1}$ at 296.2 and 324 K. (□) E_{ud}; (○) E_{up}.

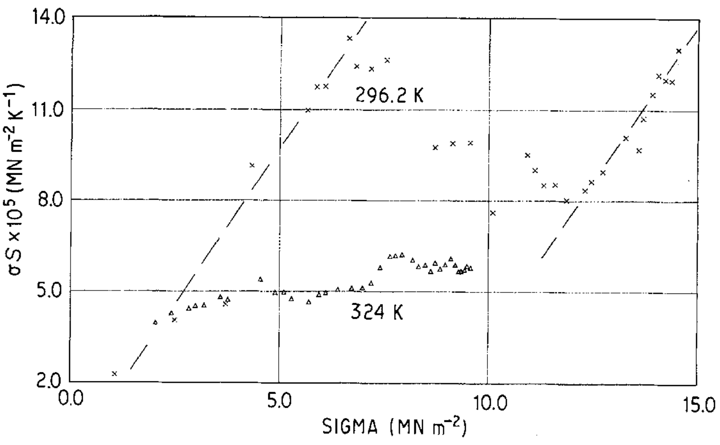

Figure 6 $S\sigma$ against σ plot of HDPE pipe material showing regions of crystalline flow (dashed line indicating constant S) interspersed with viscous flow. The data were determined simultaneously with data in Fig. 5.

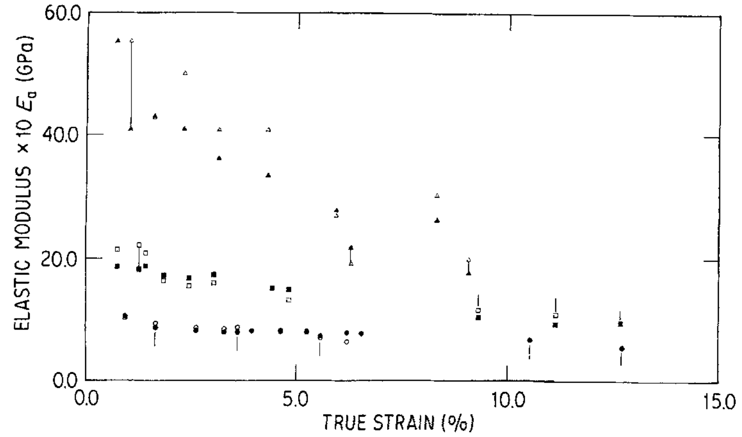

Figure 7 Elastic modulus attributed to amorphous component only against true strain. E_a values were calculated using the Reuss average from the E_u ones designated in Fig. 4.

elastomeric type stretching or to dekinking of molecular segments. Since E_{pc} could also vary due to strain induced textural changes [15], the present results do not negate these predictions. Hence the described method to measure the unrelaxed modulus could be a powerful tool in examining various mechanisms of low strain deformation as well as to measure the temperature dependence of E_u as indicated in these preliminary tests.

4. Conclusions

Measurement of Young's unrelaxed modulus of polyethylene in the highly temperature dependent regime is possible using the described strain rate change method. The measured values can be used to examine the theoretical predictions of kink isomer energy–elastic forces. Moreover the change of modulus with strain may be correlated to changes in specific volumes.

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