Materials Science and Engineering, 18 (1975) 213–220

Heat Treatment of Cold Extruded Polycarbonate: Some Implications for Design Engineers

C.S. LEE, R.M. CADDELL and A.G. ATKINS

Department of Mechanical Engineering, The University of Michigan, Ann Arbor, Mich. (U.S.A.)

(Received in revised form August 6, 1974)

SUMMARY

Polycarbonate was subjected to various combinations of mechanical - thermal histories to investigate such effects on subsequent tensile mechanical properties. This was accomplished by "cold extruding" the material initially; nominal "reductions in area" of 18, 40 and 64% were used. Cold extruded bars were then heat treated at three temperature levels, all being less than T_g (150°C) of polycarbonate. As compared with the material that was only cold extruded, it was found that in general, heat treating tends to raise the yield stress while lowering the tensile strength, elastic modulus and stress at fracture. The results suggest that a desired combination of properties may be obtainable by the use of a cold work - heat treating sequence.

INTRODUCTION

The influence of cold forming upon the subsequent mechanical behavior of various polymers has received the attention of several investigators. Cold rolling of sheet material was used in some studies [1 - 4] as was cold extrusion [5,6]. Cold drawing, in its historical context in metal forming, has also been reported [6]. Increases in tensile strength of cold rolled polymers have been reported [7] and biaxial cold rolling improved the deep drawability of polymers [8]. Perhaps because of its attractive combination of properties (strength and ductility), polycarbonate (PC) has been used in many of these studies.

When the nominal amount of "cold working" exceeds 15 to 20%, PC displays an increase in *tensile strength* as compared with the virgin material; the same cannot be said about *yield stress*. A detailed discussion regarding these two properties is given in the Appendix since there appears to be confusion in the published literature regarding the meaning of these terms.

From a design viewpoint, the yield stress of a solid is usually of greater concern than is the tensile strength which merely defines the maximum load carrying capacity. Thus, studies which concentrate on tensile strength measurements alone may not be of paramount interest to the design engineer.

The results reported in this paper suggest that the mechanical behavior of cold formed PC, subjected to subsequent heat treatment, may be altered to produce a combination of properties most useful to the design engineer. It appears that the yield stress of the cold extruded material (extrudate) may be increased without a noticeable decrease in tensile strength. This suggests a relatively unexplored method for altering the mechanical properties of polymers.

EXPERIMENTAL PROCEDURE

All test specimens were produced from a single bar of PC; it was 19.1 mm (0.750 inch) in diameter and obtained from a commercial source.

A tensile specimen of 6.35 mm (0.250 inch) diameter and having a 50.8 mm (2 inch) gage length was machined from the bar so as to determine the properties of interest of the "as-received" material. Solid cylinders of 17.1 mm (0.675 inch) diameter and 76.2 mm (3 inches) long were machined from the supply bar pre-

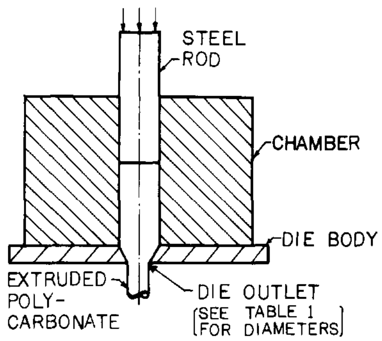

Fig. 1. Schematic illustration of extruding operation.

paratory to being cold extruded. By using three dies of varying outlet diameters, three "nominal" reductions were available; these were about 18, 40 and 64% respectively in terms of percent reduction in area. Figure 1 is a schematic version of the extrusion operation. Four extruded specimens were produced for each reduction, with one specimen per reduction used to provide a tensile specimen as described earlier. The remaining three specimens per reduction were heated for two hours at temperatures of 100°, 117° and 140°C respectively; they were then air cooled. Since the glass transition temperature (T_g) of PC is about 150°C, the highest temperature used had to be less than T_g to prevent all effects of the prior cold extrusion from being erased. This led to an arbitrary choice of 140°C; the other two temperatures were chosen so as to give a spread of possible heat treatment effects.

Following the heat treatment, each of these nine specimens was machined to produce a tensile specimen similar to that described above. Using an Instron machine, the tensile specimens of different mechanical - thermal histories were loaded at a crosshead speed of 8.33 μm/sec (0.05 cm/min) to produce thirteen sets of load - extension data. During the early portion of each test, an Instron extensometer was employed to sense length changes and to drive the recording device. In those tests where a localized neck formed and eventually stabilized, concurrent measurements of load and neck diameter were monitored to provide continuing information. All diameter measurements were obtained with a pair of point micrometers.

Each set of load - extension (or diameter) data was converted to true stress - true strain information using the standard definitions that

$$\sigma \equiv \frac{L}{A} \text{ and } \epsilon = \ln\left(\frac{A_o}{A}\right) = 2\ln\left(\frac{D_o}{D}\right), \qquad (1)$$

where L and A (or D) correspond to instantaneous values of load and area (diameter) and A_o is the original area prior to loading. Every test was carried to fracture. With specimens that displayed a stable neck, fracture always occurred when the neck had fully propagated to the shoulders. Those that showed no tendency towards localized necking usually fractured away from the shoulders.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Dimensional changes

Table 1A contains information about the dimensions of specimens at various stages prior to being machined for tensile tests. The changes are expressed both in terms of diameter and percent reduction in area from the

*TABLE 1B

Percent recovery of deformation for different mechanical - thermal treatments

Diam. of extrudate (inches)	% Recovery at room temp.		% Recovery after heat treatment		
	3 min	48 hours	100°C	117°C	140°C
0.610	23.8	26.8	+38.9	41.9	57.3
0.524	12.9	15.4	22.7	25.9	41.9
0.407	20.4	21.2	25.0	27.0	40.9

* A starting of 0.675 inch (area of 0.3578 in^2) was used in all calculations.
\+ Sample calculation (subscripts o,e,r refer to original, extruded and recovered sizes)
D_o = 0.675 inch, A_o = 0.3578 in^2 Area reduced = 0.3578 — 0.2922 = 0.0656 in^2
D_e = 0.610 inch, A_e = 0.2922 in^2 Area of recovery = 0.3177 — 0.2922 = 0.0255 in.^{2}
D_r = 0.636 inch, A_r = 0.3177 in^2 % Recovery = 0.0255/0.0656 (100) = 38.9.

*TABLE 1A

Dimensional variations for different mechanical - thermal treatments

Nominal conditions of extrudate			Measurements after room temperature relaxation						Measurements after relaxation caused by heat treatments								
Diam.		% Red.	180 sec (3 min)			173 Gs (48 hours)			100°C			117°C			140°C		
mm	in.		Diam.		% Red.	Diam.		% Red.	Diam.		% Red.	Diam.		% Red.	Diam.		% Red.
			mm	in.		mm	in.		mm	in.	m	mm	in.		mm	in.	
15.5	0.610	18.3	15.9	0.626	14.0	15.96	0.628	13.4	16.15	0.636	11.2	16.21	0.638	10.7	16.46	0.648	7.8
13.31	0.524	39.7	13.9	0.546	34.6	13.97	0.550	33.6	14.28	0.562	30.7	14.41	0.567	29.4	15.04	0.592	23.1
10.34	0.407	63.6	12.04	0.474	50.7	12.09	0.476	50.3	12.40	0.488	47.7	12.55	0.494	46.4	13.58	0.533	37.6

* % Reduction values based upon a starting diameter of 0.675 inch; all values rounded off to first significant decimal place.

TABLE 2

Mechanical properties of PC after various mechanical - thermal treatments

Nominal % red. in area	*Heat treatment	Elastic modulus		1% Offset yield stress		++Tensile strength		Fracture conditions True stress		True strain
		k.s.i.	GN/m^2	k.s.i.	MN/m^2	k.s.i.	MN/m^2	k.s.i.	MN/m^2	
	None	347	2.39	9.2	63.4	9.6	66.2	18.0	124.2	0.75
18	None	390	2.69	6.75	46.5	11.76	81.1	23.7	163.2	0.70
	100°C	366	2.52	8.5	58.6	10.97	75.6	23.0	158.6	0.64
	117°C	338	2.33	8.65	59.6	9.25	63.8	16.7	115.4	0.60
	140°C	327	2.25	8.65	59.6	9.30	62.8	17.7	122.0	0.66
40	None	467	3.22	8.2	56.5	17.2	118.6	28.7	198.2	0.51
	100°C	435	2.99	9.3	63.8	13.8	94.8	22.7	156.2	0.48
	117°C	374	2.58	9.9	68.3	13.9	95.7	21.8	150.3	0.46
	140°C	334	2.30	9.4	64.6	11.7	80.3	20.5	141.3	0.56
64	None	520	3.58	9.0	62.1	17.6	121.1	20.6	142.0	0.16
	100°C	515	3.55	11.0	75.9	16.4	112.9	20.2	139.4	0.19
	117°C	474	3.27	11.0	75.9	16.6	114.7	21.1	145.8	0.22
	+140°C	—	—	—	—	—	—	—	—	—

*Heat treatments were at indicated temperature for 2 hours followed by air cooling.
+Specimen damaged during machining so no tensile test was conducted.
++Calculated from largest observed load divided by original cross sectional area.

pre-extruded diameter. As may be noted, the specimens show significant relaxation immediately after being extruded. Although a greater recovery in the absolute diameter accompanied the higher degree of initial cold work no consistent trend pertained in regard to the percent recovery of deformation. Additional recovery may be seen for the heat treated specimens, with the degree of recovery correlating directly with temperature of heat treatment. Table 1B contains the information in terms of percent recovery of deformation.

2. Tensile true stress - true strain behavior of non-heat treated specimens

Figure 2 shows the influence of the degree of cold extrusion on the tensile behavior of PC for the reductions used in this study. It may be noted that the observed behavior is quite similar to that for cold rolled PC where similar levels of "cold working" are used. Values of tensile strength, yield stress based upon a 1% offset, elastic modulus and the true stress and strain at fracture are listed in Table 2. Both English and SI units are included where applicable. It may be seen that small amounts of cold working (here 18%) lead to a substantial *decrease* in the 1% offset yield stress as compared with the material in the "as-received" condition (*i.e.* no cold work). With increasing levels of induced cold working, however, the yield stress increases but never exceeds that of the initial condition even when the percent cold work was as high as the 64% used in this study. Cold working increases the elastic modulus and decreases the fracture strain in a consistent manner whereas the true stress at fracture first increases but then begins to decrease with ever increasing amounts of cold work. Tensile strength increases with cold work

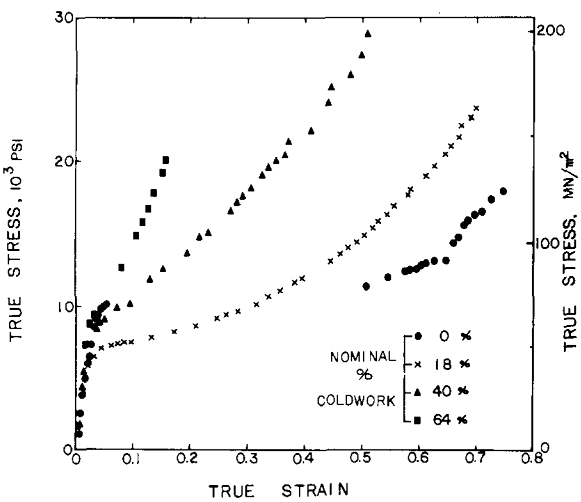

Fig. 2. Tensile true stress - true strain curves of PC for four levels of nominal per cent cold work by extrusion.

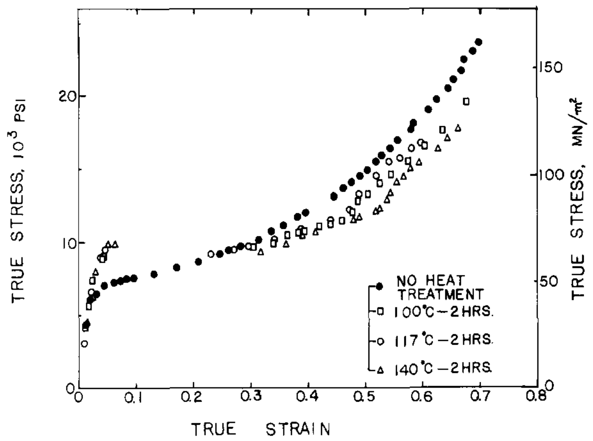

Fig. 3. Tensile true stress - true strain curves of PC cold worked 18% by extrusion then subjected to various thermal treatments.

3. Tensile true stress - true strain behavior of heat treated specimens

Figures 3 - 5 show the influence of heat treating the extrudates that had experienced 18, 40 and 64% cold work respectively. In all cases, heat treating raises the yield stress while lowering the tensile strength. Reference to Table 2 displays the findings more explicity.

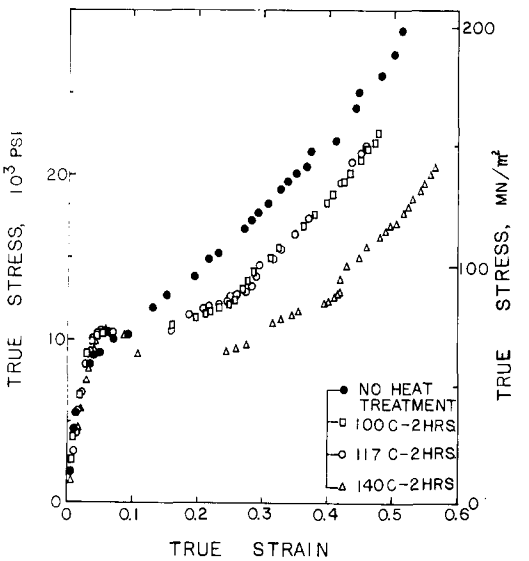

Fig. 4. Tensile true stress - true strain curves of PC cold worked 40% by extrusion then subjected to various thermal treatments.

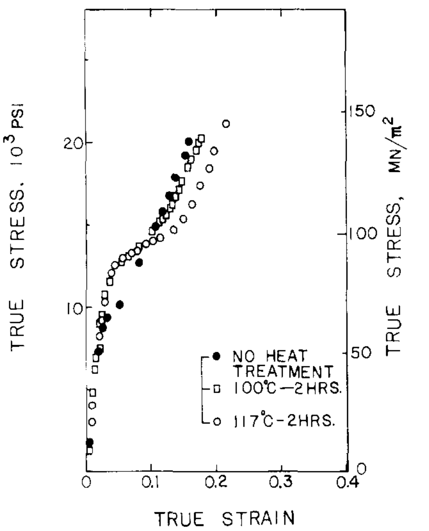

Fig. 5. Tensile true stress - true strain curves of PC cold worked 64% by extrusion then subjected to various thermal treatments.

Heat treating in general also tends to lower the elastic modulus and the true stress at fracture compared with the non-heat treated extrudate. No general pattern was observed regarding the influence of heat treament on the true strain at fracture.

4. Neck formation

For any specimen that displayed a sudden tendency to form a sharp localized neck, it was not possible to transfer from extensometer to micrometer readings in a manner that permitted a continuous monitoring of strain information. This is reflected on the stress - strain curves by a fairly large jump in strain before a smooth continuation of the curve proceeds. On Fig. 2 this phenomenon may be associated with the curve describing the "as-received" material; note that there are no points between a strain of about 0.05 and of 0.50. Similar observations pertain to Figs. 3 and 4 with all the specimens that were heat treated.

It would seem reasonable to conclude that heat treating the initially cold worked specimens tends to alter the structure in a manner that approaches the "as-received" material and, therefore, one would expect a reversion to an abrupt and localized neck which is characteristic of the non-cold worked material. Thus, in operations where PC is used and localized necking is detrimental, the use of a particular mechanical - heat treating history will prove desirable.

CONCLUSIONS

Within the limited range of mechanical - thermal treatments used in this exploratory study, there is little doubt that the mechanical behavior of PC can be altered to produce definite and controllable changes in yield stress, stress and strain at fracture, the tendency to avoid local necking, and tensile strength. Although the trends may differ, similar treatments have been used for years to control mechanical properties of metallic solids. It is obvious that more extensive studies must be pursued before the observations presented might be considered as showing typical behavior for other polymers; we are currently pursuing such studies.

APPENDIX

Engineers have traditionally differentiated between the yield stress and ultimate tensile strength in metals but many workers in polymers confuse these terms and a designer may be caught unawares when looking up polymer strength data from the literature.

The common definitions of yield strength (S_y) and tensile strength (S_u) of ductile metals are illustrated in Fig. 6, with reference to a load/extension (or nominal stress - nominal strain) curve for an annealed low carbon steel. For all practical purposes, 'yield strength', 'elastic limit' and 'limit of proportionality' are given by the same stress S_y, where the associated strain is most often less than 0.2% or so. There is essentially no change in cross-sectional area between O and Y, so that nominal stress and 'true' stress are the same at yield.

The maximum load point U, at which an unstable neck initiates, gives the ultimate tensile strength (or tensile strength) S_u. The associated strain is quite considerable, say 20%, and there is a marked but uniform reduction in cross-sectional area between Y and U; the true stress at ultimate is thus greater than S_u. The unstable neck at U *always* leads to fracture in the region where this neck first develops.

The flat portion of the curve at Y is really a series of ripples in the load trace, with the associated propagation of Lüders bands. Depending on the material and testing arrangement, a stress spike can sometimes occur at Y, giving an upper and lower yield point. For

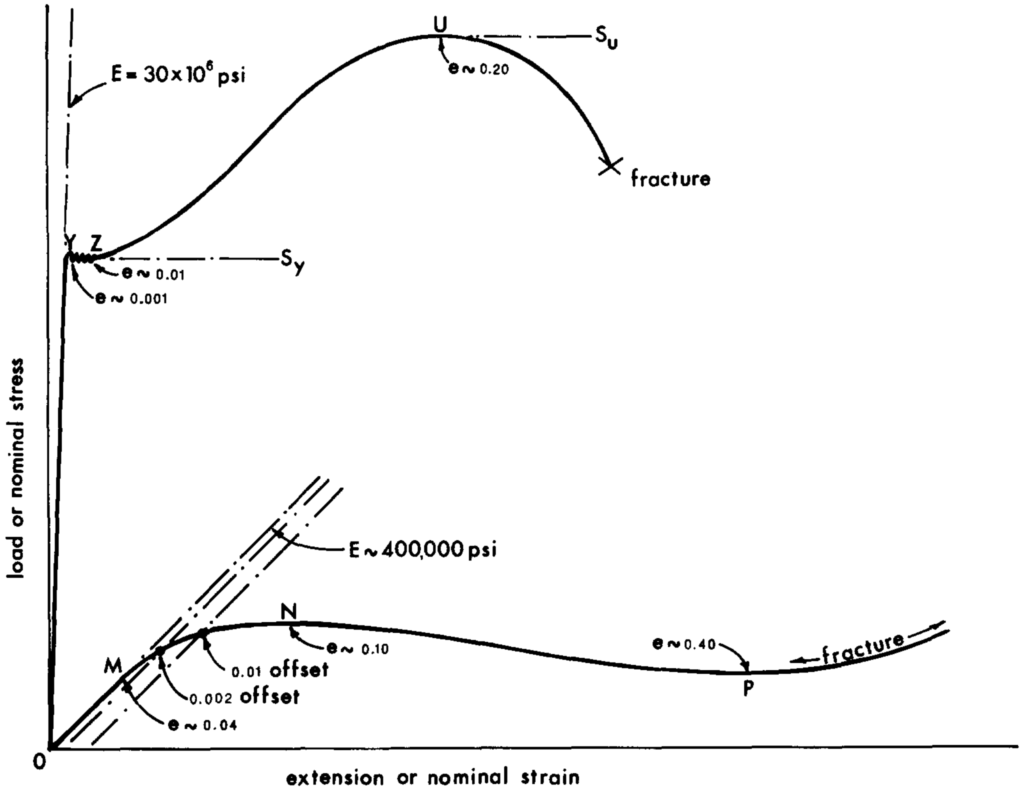

Fig. 6. Nominal stress - strain curves for a polymer that displays stable neck propagation ("cold drawing") as compared with an annealed plain low carbon steel which exhibits a pronounced yield point.

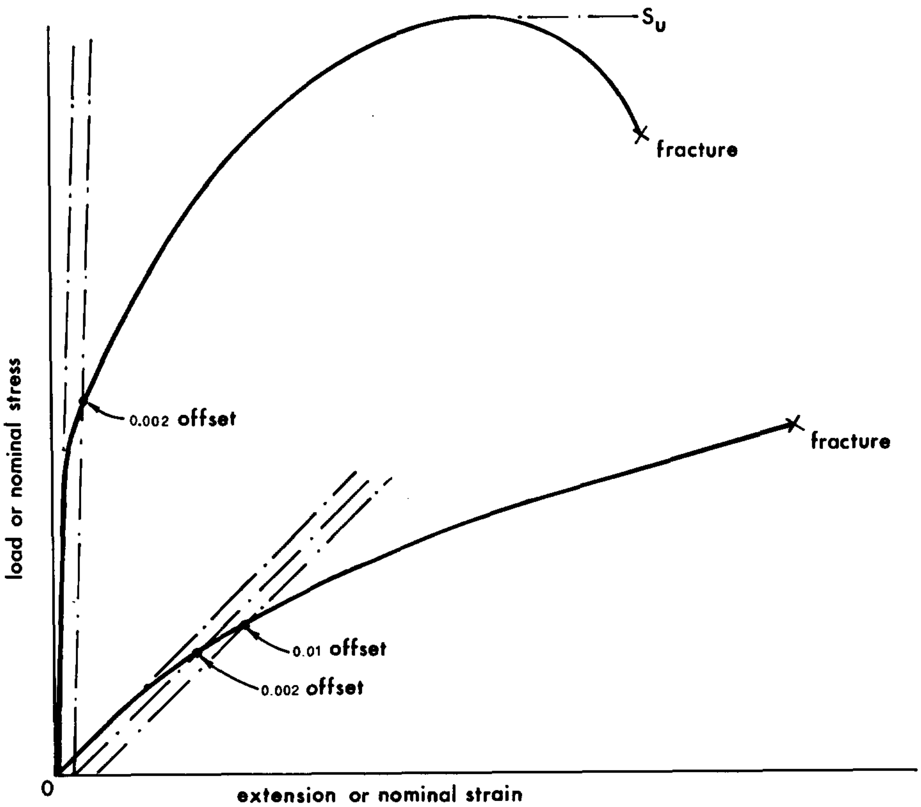

Fig. 7. Nominal stress - strain curve for a polymer that does not display localized necking (*i.e.* does not "cold draw") as compared with a ductile metal which does not exhibit a pronounced yield point.

design purposes, S_y as shown in Fig. 6 is usually the important strength parameter.

Other metals display nominal stress -strain curves as shown in Fig. 7, where there is a gradual transition from elastic to plastic behavior. The flat region at Y of Fig. 6 is not in evidence and the yield point is defined by an offset (proof) method. The associated yield strain is still of the order of 0.2% or so.

The deformation behavior of ductile polymers is characterized by much larger strains than ductile metals, and the Young's moduli are also much lower. Many polymers also display the feature of what is called "cold drawing", which mechanically is the propagation of a stable neck along the tensile testpiece.

A typical load - extension (or nominal stress - strain) plot for a polymer, such as polyethylene that 'draws', is shown in the lower half of Fig. 6. The precise behavior can be affected by viscoelasticity and anelasticity, but for practical engineering design, the following description is adequate*.

There is a departure from linearity at M, (where the strain may be some 1%), and the load curve rises to a local maximum at N (where the strain may be 10%) at which point the stable neck initiates. The load then falls as the neck reduces in cross-sectional area, until stability is reached and the neck propagates along the testpiece at the essentially constant load P. Subsequently, after the neck has propagated the length of the test bar, the load increases again and fracture eventually ensues under rising load, akin to failure in brittle materials. The particular polymer fracture load may be less than or greater than the load at N, depending on the interaction of the geometry of the propagated neck and the original shoulders of the testpiece.

After the local load maximum at N, measurements and definitions of strain in terms of *length*, such as the nominal strain given by $(l-l_o)/l_o$ or the 'draw ratio' l/l_o, are quite meaningless because the reduction is non-uniform. Clearly, *any* value is possible depending on the reference gage length (the percentage elongation in tensile tests of metals is likewise meaningless without reference to the starting gage length). It is most sensible beyond N to measure the strain in terms of 'percentage reduction of area' $(A_o-A)/A_o$, or true strain, $\epsilon = \ln (A_o/A) = 2 \ln (D_o/D)$. Then during most of the stable neck propagation, changes in true stress and true strain are minor until the neck has propagated to the shoulders. It is worth noting that, depending on the 'suddenness' of the initial neck formation, it may be very difficult experimentally to obtain points between N and P. This is pointed out in this paper in the section entitled "Neck formation".

The region NP and its growth of *one* stable neck corresponds with the region YZ on the low carbon steel diagram where there are many local maxima and minima in the load, corresponding to the propagation of many Lüders bands. For a detailed explanation of mechanical instability the reader may consult Vincent [10] or McClintock and Argon [11].

Polymers which do not 'draw' have continuously rising load - extension (nominal stress - strain curves), similar to Fig. 7 for metals, but the strains are larger and the moduli smaller.

The deformations and strains at N and P in ductile polymers which draw are much greater than those at Y and Z. Also the range of strain between M and N is extremely large compared with the corresponding region for ductile metals which occur near Y. The point at which permanent deformation sets in is somewhere between M and N. The curvature over a large range of strains between M and N and the local maximum in load at N has led some workers to call N the ultimate tensile strength for polymers. Reference to Fig. 6 shows that this is erroneous, if we mean that ultimate tensile strength is followed by an unstable neck and fracture as is the case with ductile metals*. Again, it is clear that N and P do not represent upper and lower yield points in the traditional sense.

Other workers identify N as the local yield point, and the similarity of events between N and P, and Y and Z, makes such an approach justified. However, the strains at N are much bigger than at Y and from a design point of

* As strain rates are increased, the tendency to "draw" is decreased. Also, the load - extension (nominal stress - strain) behavior shown in Fig. 6 does not mean that the true stress - true strain behavior will necessarily display a drop after point N (see, *e.g.*, references 3 and 9).

* A point such as N *may*, however, indicate the maximum *load* and in that context the use of "tensile strength" is consistent with a long standing definition.

view, M may be more meaningful as a limiting strain; even then the deformations are greater than traditional metal yield strains.

The principal objection to using N as a yield value, however, relates to those load - extension curves, as shown in Fig. 7, that show *no* load maximum. It is impossible to have a consistent definition of yield unless one resorts to an offset method. Though the offset used is arbitrary, it does have the merit of consistency once a particular value is chosen.

REFERENCES

1 G. Gruenwald, Mod. Plastics, 38 (1960) 137.
2 L.J. Broutman and R.S. Patil, Soc. Plastics Engrs., 28th Ann. Tech. Conf., New York, 1970, p. 20.
3 R.M. Caddell, T. Bates, Jr. and G.S.Y. Yeh, Mater. Sci. Eng., 9 (1972) 223.
4 P.H. Rothschild and B. Maxwell, J. Appl. Polymer Sci., V, 16 (1961) 311.
5 A. Buckley and H.A. Long, Polymer Eng. Sci., 9 (1969) 664.
6 C.S. Lee, R.M. Caddell and G.S.Y. Yeh, Mater. Sci. Eng., 10 (1972) 241.
7 L.J. Broutman and S. Kalpakjian, Soc. Plastics Engrs. J., 25 (1969) 46.
8 H.L. Li, P.J. Koch, D.C. Prevorsek and H.J. Oswald, J. Macromol. Sci., B4 (3) (1970) 687.
9 R. Raghava, R.M. Caddell, L. Buege and A.G. Atkins, J. Macromol. Sci. B6(4) (1972) 655.
10 P.I. Vincent, Polymer, 1 (1960) 7.
11 F.A. McClintock and A.S. Argon (eds.), Mechanical Behavior of Materials, Addison-Wesley, 1966, p. 311.