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Mechanical Testing and Structural Characterization of Hydrostatically Extruded Polymers. I. Effects of Hydrostatic Extrusion on Subsequent Mechanical Behavior *

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Crystalline and amorphous polymers were hydrostatically extruded at room temperature with pressures up to 4 kilobars. Polymers studied include polyethylene, polypropylene, nylon, polyacetal, polyvinylchloride, ABS-co-polymer, polymethylmethacrylate and polycarbonate. Within the range of reduction percentages studied, 20-85%, the extention showed higher flow stress and lower elongation than the starting materials except PMMA: Fourfold increase in elongation with essentially unchanged flow stress was observed with the amorphous polymers. Dimensional stability of the crystalline extrusion at room temperature and also at 100°C decreased with an increasing reduction percentage and reached a minimum at 60% reduction, followed by an increase with higher reductions. On the other hand, with the amorphous polymers, the higher the reduction percentage, the poorer the dimensional stability. A linear relation was established between the extrusion pressure and the extrusion ratio. The polymers were also tested for compression , bending, specific gravity and hardnees, and correlation among the test results was discussed under assumption of a possible structural change due to hydrostatc extrusion.

1. Introduction

Conventional as well as hydrostatic extrusion of polymers in solid state at room temperature has been extensively studied and some improvements in mechanical properties of extrudates are reported.[1]-[3] In the field of metalworking, the hydrostatic extrusion has proved practical and useful, especially for brittle materials.[4] On the other hand, tensile testings on metals as well as polymers have been performed to study the effects of pressure on the mechanical behavior of those materials under hydrostatic pressure. As compared with metals, it is now known that the properties of polymers are considerably affected by pressure environment.[5]-[12] Taking notice of that point, the present authors have studied the hydrostatic extrusion[13]-[15] of solid-state polymers as well as deformation mechanisms operative at extrusion. In the case of polymers it seemed that distinction should be made between crystalline and amorphous phases when the mechanism of deformation is studied; consequently crystalline and amorphous polymers were both employed for study. Hydrostatic extrusion is potentially an effective measure for forming amorphous or brittle polymers which are hard to extrude.

In th present paper, report is made on observations made recently, including a success in extruding polymethylmethacrylate (PMMA) which has been considered difficult to extrude at room temperature.

2. Experimental

2.1 Materials. Crystalline polymers studied include polyethylene, HIZEX 5000 B (PE); polypropylene, J 105 G(PP); nylon 6, Nylon 1030B(Ny-6); and polyacetal,Zuracon M 25(POM), while amorphous polymers of Torex G 1 (PMMA); polycarbonate, Panlight K 1300(PC); polyvinylchloride, Shinetsuchemichals RG 8(PVC) and acryronitrile-butadiene-styrene co-polymer, 21 NP(ABS) are used as test materials. The samples were machined to nosed billets with adequate dimensions from a commercial stock,which had been manufactured by conventional method of extruding at temperature.

2.2 Extrusion method. Figure 1 is a schematic representation of the hydrostatic-extrusion device comprising a piston-cylinder system. High-pressure container made of 18-Ni maraging steel had a bore diameter of 25.4 mm and was 310 mm in diameter. The die half-angle was chosen to be 10, 20 or 45 degrees. Power for extrusion was provided by an Amsler-type universal testing machine, which effected hydrostatic extrusion of crystalline and amorphous polymers with piston speeds of 1.5 and 1 mm/s, respectively. Castor oil was used as the pressure medium, the samples being extruded at room temperature(34-28°C). Only the billets of PMMA were rubber-coated prior to extrusion, no other polymers being coated. The reduction percentage of area (R) is defined by the following equation:

$$R = [(D^2 - D_o^2)/D^2] \times 100 \ (\%),$$

where D and d_o are original diameter of the billet and outlet radius of the die resprct-

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ively.

2.3 Recovery of dimension.

Recovery percentage of dimension is defined by the following equation:

$$\gamma_i = [(D_i - d_0)/ d_0] \times 100 \ (\%),$$

$$i = S, \ R, \ T$$

where d_0 and D_i are radii of the die outlet and the extrudates, respectively, D_S being sample radius immediately after extruding ; D_R after dimensional stability is reached at room temperature, and D_T at about 100° C in an air oven.

2.4 Measurement of the mechanical propertis of extrudates.

Stress-strain curves of the extrudates at room temperature, 20-25 °C, were mainly obtained by using TENSILON UTM-1 of Toyo-Baldwin Co. for the polymers with crosshead speed of 10 mm/min. Compression and bending tests were also made to supplement the tensile tests with crosshead speed of 5 mm/min . Figure 2 shows a configuration of the test specimen.

2.5 Other tests.

Hardness and specific gravity were measured for the original as well as the extrudates by using a Rockwell hardness tester and displacement method respectively. The latter employs a precision balance of direct reading sensitivty of 0.1

mg. Results of hardness tests for crystalline and amorphous polymers were represented in $H_R R$ and $H_R M$ scale, respectively. Liquid used for the specific-gravity measurement was water purified by ion exchange for PMMA and absolute alcohol for other polymers.

3. Results and discussions

3.1 Extrusion condition.

Table 1 lists the processing limit for each polymer. As is evident from the table, the largest percentage of reduction in area was obtained near the half die-angle of 20 degrees, which is best represented by rubber-coated PMMA. In this report, therefore, discussions on the experimental result will be made on those data which were obtained by the use of a die having its half angle of 20 degrees. Polyethylene and polypropylene extrudates had smooth surface up to a large reduction percentage, 80 or 85%, irrespective of the die angle. Working with Ny-6 was limited at the reduction percentage of 80%: the extrudates with reduction percentage of 85 % no longer had smooth surface as is exemplified by an appearance of the extrudates shown in Figure 3. Extrusion of POM was limited at the reduction percentage of about 70%. As mentioned above, the hydrostatic extrusion of crystalline polymers was feasible up to the reduction percentage of 85%. The limit

Fig.1 Schematic representation of the hydrostatic extrusion apparatus

Fig.2 Dimension of test specimen

Table 1 Extrusion limit

o excellent ⊙ good △ poor ✕ failure

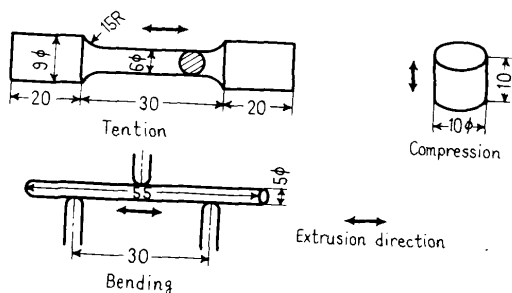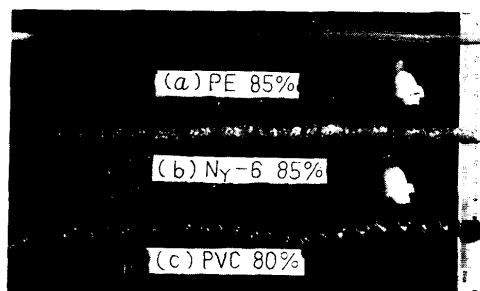| α°	R%	PE	PP	Ny-6	PA	PVC	ABS	PMMA	PC
10	20	O	O	O		O	O	O	
	30						O	✕	
	40	O	O	O		O	O		
	60	O	O	O		O	O	✕	
	80	O	O	⊙		✕	△		
	85	O	O	✕					
20	20	O	O	O	O	O	O	O	O
	30							O	O
	40	O	O	O		O		O	O
	50				O			O	O
	60	O	O	O		O	O	O	O
	70				O	O	△	✕	✕
	80	O	O	O	△	✕	✕		
	85	O	O	✕	✕				
45	20	O	O	O		O	O	✕	
	40	O	O			O			
	60	O	O	O		O	O	✕	
	80	O	O	△		✕	△	✕	
	85	⊙	✕	✕			✕		

Fig.3 Photographs of typical examples of hydrostatically extruded samples

of processing for the amorphous polymers, on the other hand, was 70% at the maximum in terms of reduction percentage. As shown in Figure 3 (C), the extrudates of PVC at R=80% as well as those of ABS and PC at R=70% became spiral-looking about the direction of extrusion. Attempts were also made to extrude unsheathed PMMA at room temperature without success: they shattered on passing through the die. This means there is a need to consider the effect of pressure medium around the billet material. The PMMA billet of successful extrusion was sheathed in a thin rubber-film. It should be noted that even a material as brittle as PMMA can be successfully extruded at room temperature up to the reduction percentage of at least 65 % by the use of rubber-coating on the billets. As mentioned above, there is a considerable difference between the proccessabilities of crystalline and amorphous polymers. The conventional[2](3) as well as hydrostatic extrusion yielded similar results for the other polymers than PMMA. It was of particular interest that a polymer as brittle as PMMA could be successfully extruded at room temperature. On the subject of the effects of hydrostatic pressure on the mechanical behavior of polymers tensile tests under hydrostatic pressure have been conducted for varied polymers by a number of researchers and quite a few reports are available. It is well established that materials which behave in brittle manner, when tested under high pressure, undergo brittle-to-ductile transition[6]-(12) at a certain pressure level. When fine cracks are present on the surface of billets in unsheathed samples, the medium penetrates into the cracks with the same pressure as the surroundings. In sheathed samples, on the contrary, most probably the cracks are closed up preventing the pressure medium from penetrating into them. For this reason, it is considered that even brittle materials can be successfully extruded under pressure environment. As for the possible deformation in structure which occurred due to the processing, the mechanism of deformations can be considered to consist of two processes, which will be discussed later in connection with the other mechanical characteristics. Penetration of pressure medium into the billet materials during extrusion was found to be negligible.

3.2 Extrusion pressure. Figure 4 shows the relation obtained between the muximum extrusion pressure, P_{max} ,and the extrusion ratio for the materials tested. As is evident from the figure, the extrusion pressure increases almost linearly with the extrusion ratio. Generally, when there is no friction between and container, the following relation holds between the mean pressure, P_a, and the extrusion ratio:

$$P_a = \bar{\sigma} \{(1+B)/B\}(R'^{-B}- 1) \quad \text{----}(1)^{(16)}$$

where $\bar{\sigma}$ is the yield stress in compression and $B = \mu \cot \alpha$, μ being friction between the die and billet. The value of μ in hydrostatic extrusion being 0.01-0.05 is smaller than that in conventional extrusion.
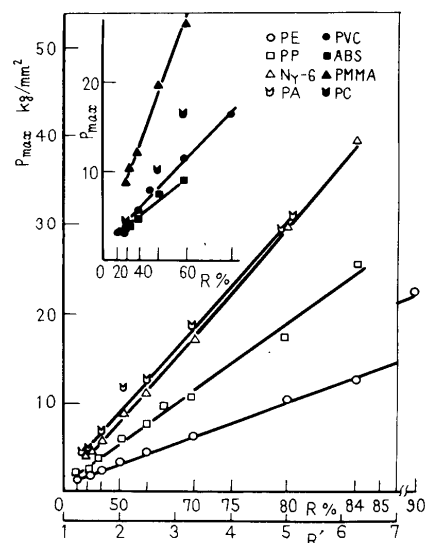
Johnson and Pugh gave the following experimental formula:

Fig.4 Relation of extrusion pressure vs. extrusion ratio R'(or reduction percentage of area, R.)

Table 2 Values of coefficient "a" in extrusion-pressure vs. extrusion-ratio relationship

Polymer	PE	PP	Ny-6	PA	PVC	ABS	PMMA	PC
a	2.5	4.7	7.4	7.3	6.5	5.5	17	11.2

$$P_a / \bar{\sigma} = a \ln R' + b \quad \text{------}(2)$$

using the constants a and b. In the case of no strain hardening or small μ, a linear relationship holds between P_a and $\ln R'$.

Unlike the formulas mentioned above the present authors obtained a relation of $P_{max} \propto R'$ but no linearity between P_{max} and $\ln R'$: this is considered to be due to the marked strain hardening of the billet materials during processing. In the present experiment, the extrusion pressure can be written as $P_{max} = a (R' - 1) + b$, where b is considered to be due to the friction between piston and container. Table 2 shows the values of "a" experimentally determined for various polymers.

3.3 Thermal recovery. It is known that the die swell of polymers is larger than that of metals. Figures 5 and 6 show the relation between the recovery, γ , and the reduction percentage, R. The recoveries of crystalline and amorphous polymers are indicated to be quite different from each other. The recovery of amorphous polymres increases with an increasing reduction percentage. , while that of crystalline ones first increase with an increasing R up to 60%, and then decrease. The recovery of crystalline polymers at room temperature is larger than that of amorphous ones, but the tendency is reversed in thermal recovery. The curve designated by γ_{max} in the figure shows the extreme degree of recovery where the extrudate reassumes its original shape and dimensions. It is observed that the ABS extrudate, when heat-treated, almost completely recovers up

to its original billet-size. The recovery of PE is larger than other crystalline polymers. Point which special attention should be paid to is the extremely small amount of thermal recovery for POM and PC when compared with other polymers. Moreover, as mentioned before the recovery takes its maximum value in the neighborhood of R = 60% except for ABS, PC and POM.

In the course of extreme deformation by hydrostatic extrusion, it seems that a new molecular conformation is constructed, and as touched upon before, a deformation mechanism of the following two steps is considered:
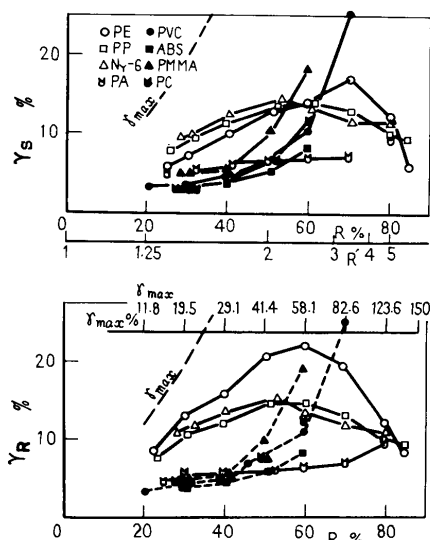
Fig.5 Relation between recovery percentage and reduction percentage. Curve γ_{max} plots the complete recovery up to virgin-billet size. Inelastic recovery (a) right after extrusion and (b) when stabilized at room temperature
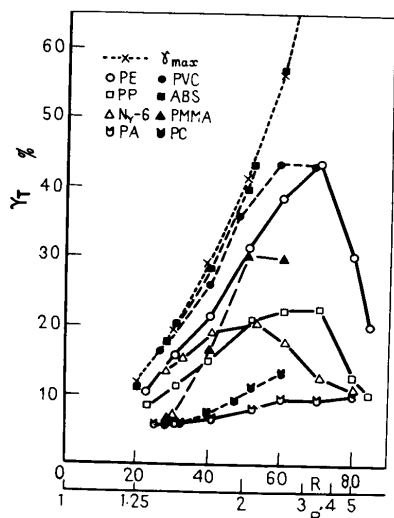

Fig.6 Relation between thermal recovery percentage and reduction percentage when kept in oven at 100 ± 3 °C

First, small as the recovery of amorphous polymers is at room temperature, their thermal recovery is larger than those of crystalline polymers. This is explained as follows: In the deformation range up to approximately R = 60% the deformation mechanism of the extrusion process is considered to be primarily due to the reorientation of those molecular chains which are entangled within the amorphous areas; the chains become elongated in the direction of extrusion.

On the other hand, the distortion of the molecular chains within the crystalline areas is restricted to elastic deformation plus some movements as a whole inside the area. Therefore, the recovery up to R=60% is large by thermal relation. The second step in the deformation during extrusion, which is operative at above R=60%, occurs primarily in the crystalline areas. Namely, the intermolecular slip as well as pulling out of the tie-molecules out of the crystals occurs, resulting in the untying of the molecular chain in the crystalline areas. As a result, fine crystals are formed and the molecular chains realigned in the direction of extrusion build up a new structure. Amorphous polymers, on the other hand, can not be soundly extruded over R=60-70% at room temperature due to the existence of a little or no crystalline areas. Consequently, spiral extrudates result due to partial breaking of noncrystalline molecular chains, or catastrophic crashing due to overall destruction of molecular chains. As above mentioned, the thermal recovery of crystalline polymers deformed beyond R = 60% may not occur any more due to the formation of the stable structure.

The above-mentioned mechanism of deformation will be definitely established only by the direct observation of micro-structures with an electron microscope. This will be done in the forthcoming report. According to Maeda et al.[3], however, from observations of PP with optical microscope, the above-mentioned mechanism can be established to some degree.

3.4 Mechanical properties of the extrudates. Mechanical properties in tension of the extrudates by hydrostatic processing have been already reported in part. Figures 7 (a)-(f) show nominal tensile stress-strain curves of the virgin samples as well as the extrudates with various reduction percentages tested at room temperature. Figure 7(a) shows that of PE; the effect of the variation in die angle is also shown. As shown, no difference in tensile behavior due to variation in die angle can be observed without the range of scatter, a similar result being obtained with other polymers and in other types of testing. It is a common phenomenon with crystalline polymers that flow stress increases while the elongation percentage decreases with an increasing reduction percentage of area. There is not very much change in behavior with regard to yielding in tension up to R = 80%, but an extreme increase in yield point is seen when R=80%. The Ny-6 extrudate with R=60% already broke down while still in the elastic region without yielding. An increase in the flow stress of the extrudate with R = 80% was as

much as 3-fold for PE and 5-fold for Ny-6 when compared with the virgin sample. The flow stress of amorphous-polymer extrudates also increases with an increasing reduction percentage as was the case with the crystalline counterparts. The yield point of ABS scarcely changes from the virgin sample when R = 20 %, but increases when R = 60%, little change in yield point was observed for PVC and PMMA extrudates over the whole range of reduction percentages. Of greatest interest was the mechanical behavior of PMMA extrudates. When tested in tension virgin samples broke within the elastic limit without being plastically deformed In the extrudates, however, when a post-yield elongation at the reduction percentage was small as **R** = 20 % , the elongation reached 40 percent for R=50%.

Namely, the elongation of PMMA extrudates increased with an increasing reduction percentage. The behavior is unique among the polymers tested, and a possible structural change responsible for the ductility is unknown at present.

Stress-strain behaviors in tension and in compression of metals are said to be similar to each other, with regard to yield point and subsequent behavior, but with polymers the situation is quite different from metals. To compare the results of tensile tests with those of compressive ones, typical examples of true-stress-strain curves are shown in Figures 8 (a)-(d) with tensile data on the upper side and compression ones on the down side. As is clearly shown, mechanical behavior of crystalline polymers is quite different from that of metals, showing
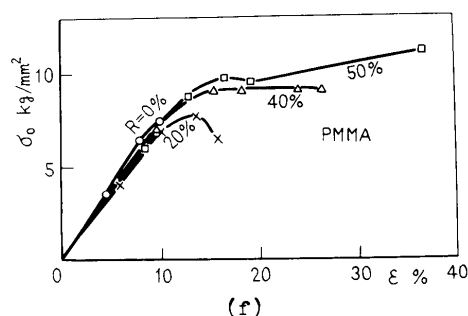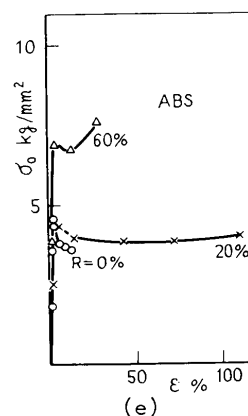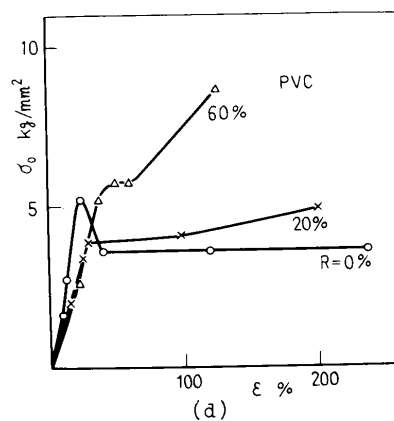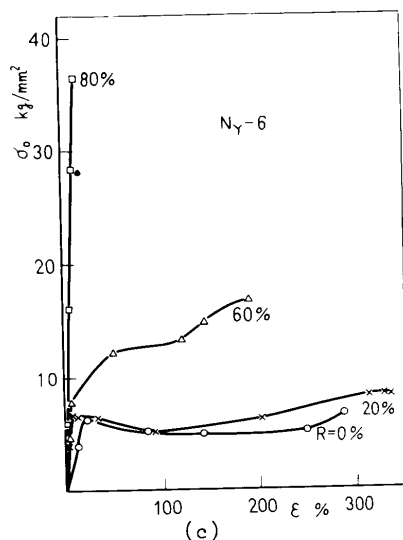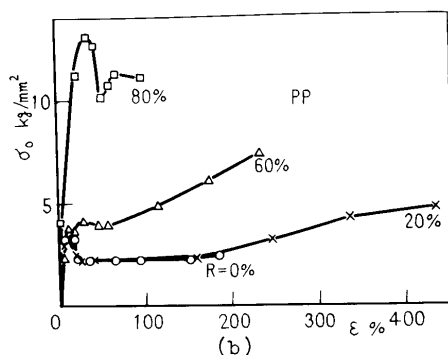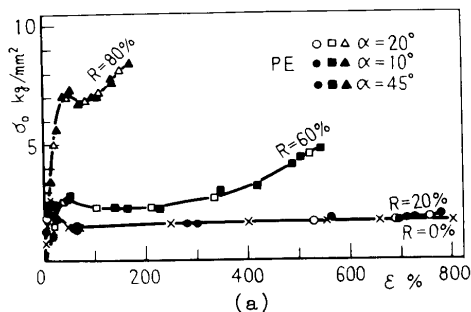

Fig. 7 Nominal stress-strain curves in tension of virgin samples and extrudates with various reduction percentages

completely different characteristics in tension from those in compression. For amorphous polymers, however, as shown in Fig. 8 (c) and (d), the overall shape of the stress-strain curve is different but the behaviors up to the yield point are comparatively similar to each other: especially, slope of the curves in elastic region of PMMA is nearly equal in tension to that in compression. The flow stress in compression for all extrudates of polymers used in the study became smaller than that of their virgin counterparts: the maximum values of compressive flow stress for PE, PP, and any one of Ny-6, PVC or ABS were 2.8, 4.8 and 6.7 Kg/mm^2, respectively. While the stress for PMMA had a large value of 11 Kg/mm^2. The dependence of flow stress in compression on reduction percentage cannot be expressed in a single word because it is also dependent in a complicated way on the amount of strain, ε.

Figure 9 shows the relation between yield stress in compression, σ_Y, — peak values of the stress-strain curves with the exception for PE where the stress value at $\varepsilon = 0.1$ was taken — and reduction percentage,

R. Except for minor variance with each polymer the general tendency is that the yield stress decreases once and then increases with an increasing R. The minimum yield point in compression is assumed at R = 60% for crystalline polymers except for Ny-6, and at R=20% for amorphous polymers. There is a change in deformation characteristics peculiar to the compression test at around R=60%. Table 3 shows the value of elastic modulus obtained from bending test.[17],[18] As is evident from the table, the elastic modulus increases with an increasing R. The rate of increase, however, is different be-

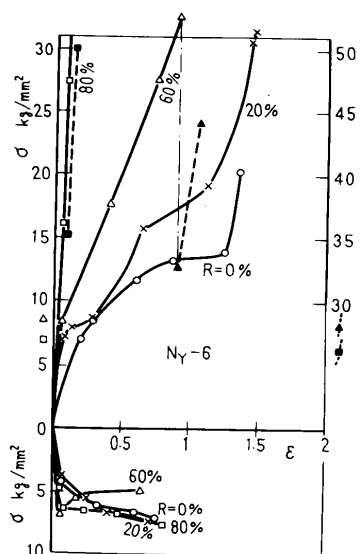Table 3 Elastic modulus estimated from bending test (kg/mm^2)

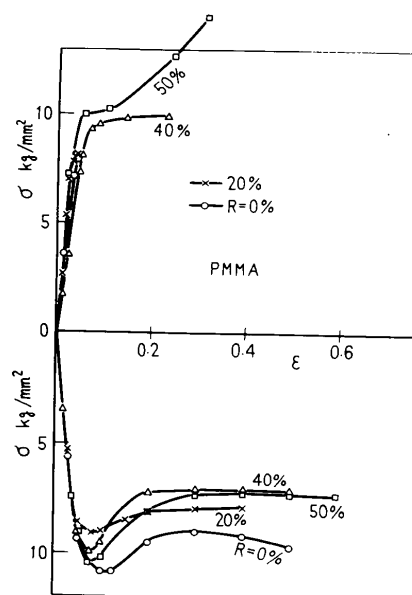| $\alpha°$	R%	PE	PP	Ny-6	PVC	ABS	PMMA
20	0	76.8	166.1	98.5	268.8	205.5	
	40	77.1	162.9	104.0	312.5	252.7	
	60	79.2	182.4	204.4	337.0	281.8	
	80	107.2	264.8	303.0			
	85	163.1	296.1				

(a)

(b)

(c)
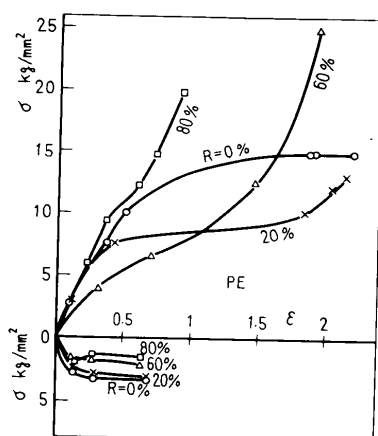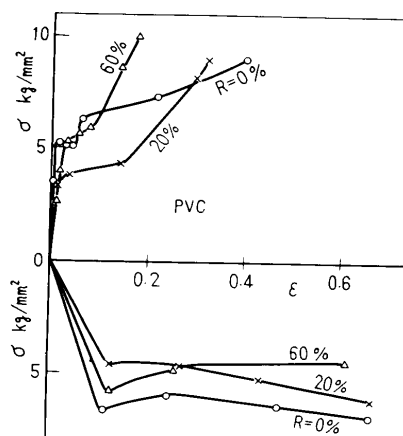
(d)

Fig. 8 True stress-strain curves in tention or compression of virgin samples and extrudates with various reduction percentages

tween the crystalline and the amorphous polymers. The rate increases almost linearly with R for amorphous polymers of ABS and PVC, and shows an extreme increase at R = 40% for Ny-6, and at R = 60% for PE or PP. It is interesting to note that the mechanical properties of crystalline polymers undergo a rapid change at a reduction percentage where a peak is observed in their thermal recovery. As is mentioned before, this is considered to be due to the change in structure in accordance with the proposed mechanism of deformation in two steps.

3.5 Hardness test. There is no conclusive definition of hardness for polymers yet. In order to investigate the effect of hydrostatic extrusion on the hardness of extrudates, however, the measured values by conventional tests are listed and compared with each other in Table 4. For each reduction percentage the hardness of cross section is listed at top and that of side surface at bottom. The hardness values of each polymer decrease once and increase with an incressing R. There is a slight difference in hardness between the cross section and the side surface, but no systematic rule has been obtained for judging which is harder. The difference in hardness can be attributed to friction between die and billet during extrusion process and subsequent temperature gradient. Hardness of the extrudates for other polymers than listed, except for Ny-6, is smaller than that of virgin material. The hardness values have their minimum at maximum of their thermal recovery aforementioned, and this is also considered to be due to the change in structure.

3.6 Specific gravity. It is considered that specific of crystalline polymers depends upon crystallinity as well as the change in structure. Specific gravity of amorphous polymers, on the other hand, may have no relevance to the structure. No remarkable change in specific gravity was observed between the virgin samples and respective extrudates, irrespective of the kind of polymers.

Table 5 shows the effect of reduction percentage on the specific gravity of various polymers. For amorphous polymers, the values of the specific gravity tend to increase with the reduction percentage. The values of the specific gravity of crystalline polymers do not show systematic dependence on reduction percentage except that they all have their minimum values at R=60%. However, for PE and PP extrudates with R=80%, especially for those successfully extruded hydrostatically with R=85%, it is observed that the specific gravity increases with R. This may be considered to be due to the change in structure aforementioned. It is considered that the decrease in specific gravity is attributable to the release of crystalline region, while the increase in specific gravity with an increase in reduction percentage takes place because of the construction of a new structure due to the reorientation of molecular chain or semi-crystalline region.

Summing up the present experimental study, it was a most significant achievement that the hydrostatic extrusion of PMMA, a brittle polymer, was successfully performed by sheathing PMMA with rubber at ambient temperature without back pressure. The hydrostatic extrudates of PMMA became ductile to some degree.

The estimation of extrusion limit and extrudates properties for various polymers can be done by classifying them into crystalline and amorphous polymers. The success in hydrostatic extrusion for brittle polymers such as PMMA suggests certain extrudability of thermo-setting resines. The method of hydrostatic extrusion is an effective means for forming and in many cases improving the mechanical properties of polymers and should be studied furthermore in future.

Table 4 Values of hardness for virgin and extrudates (cross section in top, side surface in bottom)

Scale		$H_R R$			$H_R M$		
$a°$	$R\%$	PE	PP	Ny-6	PVC	ABS	PMMA
20	0	131 105	105 93	81 115	122 121	101 89	88 78
	20	91 92	79 76	72 103	89 78	74 71	63 58
	40						66 61
	50						74 62
	60	50 63	73 63	90 111	95 68	93 81	
	80	66 82	98 87	93 117			

Fig.9 Relation between yield stress in compression and reduction percentage

Table 5 Specific gravities of virgin and extrudates

$a°$	$R\%$	PE	PP	Ny-6	PVC	ABS	PMMA
20	0	0.951	0.907	1.140	1.484	1.042	1.200
	20	0.952	0.904	1.139	1.473	1.042	1.193
	40	0.948	0.902		1.474		1.184
	50						1.185
	60	0.949	0.899	1.135	1.470	1.047	
	80	0.950	0.897	1.138			
	85	0.964	0.901				

Testing temperature (16°C for Ny-6 and PMMA, 18°C for other polymers)

4. Conclusions

The present authors attempted to hydrostatically extrude various polymers at ambient temperature. As the first report of this study, processability of polymers and the effect of hydrostatic extrusion on the mechanical properties are presented. It is concluded that the method of hydrostatic extrusion is an effective means for forming thermo-plastic resins. The major results of the study may be summarized as follows:

(1) The hydrostatic extrusion of PMMA, which is a brittle polymer, is successfully performed by sheathing the polymer with rubber up to 60% reduction percentage. Various properties of the PMMA extrudates are almost similar to those of other amorphous polymers. For PMMA extrudates the flow stress in tension as well as the elongation increases with an increasing reduction percentage.

(2) Extrusion pressure, expressed by its peak value during the process, is almost linearly proportional to extrusion ratio for all polymers studied.

(3) The upper limit of reduction percentage, R, for hydrostatic extrusion at ambient temperature is R = 80-85 % in crystalline polymers, and R = 60-70% in amorphous polymers. These limits for amorphous polymers closely coincide with the peak value in recovery for crystalline ones, suggesting that different mechanisms are operative in deformation above and below the critical value of reduction percentage.

(4) Inelastic recovery is large for crystalline polymers, PE etc., under R = 60 %, while it is almost constant for amorphous polymers irrespective of R, with few exceptions. On the other hand, thermal recovery of amorphous polymers is larger than that of crystalline ones: especially, at temperature ABS extrudates recovery to the original dimension of billets before extrusion.

(5) In general, it seems that dimensional accuracy of extrusion for amorphous polymers is poor, because of a large recovery. The accuracy of extrusion for PC and PMMA, however, seems to be comparatively good.

(6) The accuracy of extrusion, as is determined from the thermal recovery testing, is better for higher reduction percentage, that is, for larger extrusion pressure, with few exceptions.

(7) Deformation mechanism, upper limit in reduction percentage, mechanical properties, and molecular structure for various extrudates can best be studied by classifying them into crystalline and amorphous polymers. Deformation mechanism can best be understood by assuming it to consist of two separate steps, one primarily for deforming amorphous region and the other for crystalline one. To prove the proposed deformation mechanism, however, it is necessary to conduct a micrographic study of the extrudares. These investigations will be reported on in the next paper.

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