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Polymethyl Methacrylate (Perspex type) Plastics; Crazing, Thermal and Mechanical Properties

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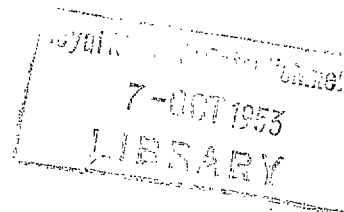
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Summary.—The report summarises the more practical aspects of the results of a long-term investigation of the basic physical and chemical properties of polymethyl methacrylate ('Perspex' type) plastic. Thermal, elastic, crazing, solvent absorption and mechanical properties are included and the effect of these on the service efficiency of a plastic structure is described.

Experimental evidence is given concerning the essential role of tensile stress and absorbed solvent in causing crazing and recommendations concerning means to reduce or avoid the incidence of crazing are included.

The basic thermal properties are compared with those of metals and the dangers of differential expansion in combined metal-plastic structures are noted, together with the serious effects of chilling of plastic structures during the 'hot-forming' operation. Details are given of appropriate heat treatments designed to remove casting and workshop strains without causing distortion.

The elastic behaviour of the plastic is explained on the basis of its long chain-like molecular structure and the change from a rigid glass-like type of mechanical behaviour to that of a rubber-like material with rise of temperature, such as in the hot-forming process, is described. The various strain components produced by mechanical stress, namely the instantaneously reversible, the long-range reversible 'creep' type and the irreversible 'viscous' type are examined. The low degree of 'permanent set' obtained even at hot-forming temperatures is explained.

Tensile, impact and flexural strengths, together with the effects of temperature, notch sensitivity, solvent and crazing on them, are given in detail.

References to the original reports of the investigations summarised are included in the text.

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1. *Introduction.*—Long-term investigations of the fundamental physical and chemical properties of polymethyl methacrylate 'Perspex' have been in progress at the Royal Aircraft Establishment for some time, and a certain amount of basic knowledge concerning the behaviour of the material has been gained, particularly with reference to 'crazing'. Some of the information obtained is of immediate practical interest, especially in view of the many developments now taking place in high-performance aircraft resulting in more exacting service demands on aircraft hood and canopy structures.

Brief reference was made to some of the results of these investigations in a symposium[1] held at the Royal Aircraft Establishment. More complete descriptions are now given below.

Although the investigations are still in progress it is believed that a report summarizing the more practical aspects of the experimental results so far obtained would be useful. A brief description is given of the more fundamental properties and molecular behaviour of the methacrylate polymer, in the light of these recent experimental studies. This is followed by an attempt to explain some of the features of the plastic such as:—

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[*] R.A.E. Report Chem. 454, received 30th December, 1949.

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(a) Crazing under mechanical stress, vapour action, cementing and the effect of heat treatment.

(b) Mechanical properties, such as elastic behaviour, creep.

(c) Other physical properties such as notch sensitivity and the effect of polishing on mechanical strength, thermal expansion, etc.

For the purposes of this report crazing may be described as surface failure resulting in fractures appearing in the surface of a sheet of the material. The fractures may be either randomly directed or orientated in a particular direction; they may vary from very fine to very coarse in size according to the conditions which produce them. In all cases crazing affects to a greater or less degree the visibility through a sheet of the material and tends to weaken the material mechanically.

It is appreciated that, in attempting to generalise from investigations that are still in progress, there is some risk of over simplification which may require modifications at later stages of the work.

Throughout this report reference is made to the original sources of detailed information when available.

1.1. *The Production of the Plastic.*—The fundamental process in the production of the plastic is polymerisation, that is, the conversion of material by heat-accelerated chemical reaction from a liquid state at ordinary temperatures, a state in which the molecules of the substance are small, to a solid state in which the molecules are exceedingly large. In the case of polymethyl methacrylate* this conversion of the ' monomer ' into the ' polymer ' is in effect an end-to-end attachment of momeric units to form exceedingly long ' chain-like ' molecules. The long chain molecular character has an all-important effect in determining the physical properties of the final material. Under normal conditions it is thought that these long molecules are randomly coiled and very much entangled with each other, a condition which also has an important influence on the mechanical properties of the polymer.

The conversion also involves a considerable decrease in volume which under certain conditions, may set up appreciable strains in the material.

Three types of the polymer were used in these investigations, *viz:*

(a) A type ' A ' which contained a residue of monomer and a plasticiser.

(b) A fully polmerised type ' B '. containing little or no monomer, but plasticised.

(c) A non-plasticised type ' C '.

Sheets of such materials are produced by first bulk-polymerising the monomer until it attains a syrupy consistency and then completing the polymerisation process while casting it at a moderate temperature between glass plates in order to obtain the required high degree of flatness of the finished sheets. A moderate temperature compatible with a not too lengthy processing time is used to ensure polymer of reasonably high molecular weight.

2. *Basic Properties.*—2.1. *General Behaviour.*—As a thermo-plastic material polymethyl methacrylate, according to the temperature at which it is used, behaves either as a hard brittle substance with good dimensional stability and high tensile strength or as a rubber-like material which has high deformability and is weak mechanically. Briefly this difference in behaviour is associated with the degree of hindrance to movement of one segment of a long chain molecule relative to other segments in the chain and to neighbouring molecules. Below a certain temperature this movement is very restricted, above it movement becomes possible. Due, however, to the long-chain nature of the molecules and to chain entanglements, little bodily movement of an entire molecule relative to its neighbours is possible either until much higher temperatures are reached in the case of lightly stressed material or until high stresses are reached for material at moderate temperatures.

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* This material, in the cast form, is marketed under the trade names of ' Perspex ' in the U.K. and ' Plexiglas ' and ' Lucite ' in the U.S.A.

The point on the temperature scale where the change in behaviour from that of a brittle to that of a rubber-like solid takes place has been designated the ' second-order transition temperature '. Unlike the melting point, which is a ' first-order ' transition temperature (or point where there is a change of phase), the second-order transition temperature is not well defined as the change is more gradual than melting. It does, however, correspond roughly with the softening points of a number of thermo-plastics determined by empirical methods. In comparing performances of thermo-plastics at a given temperature a knowledge of the second-order transition temperatures is of great value.

Ordinary operating temperatures lie below the second-order transition point for normal grades of polymethyl methacrylate; at these temperatures therefore the polymer behaves as a hard brittle solid. At ' forming ' or ' shaping ' temperatures (ca. 140 deg C) the polymer behaves as a rubber-like material since these temperatures are well above the transition point.

Certain materials compounded with or absorbed by the polymer (e.g., plasticisers, monomer or low molecular weight polymer, or solvent vapours), and which act as ' internal lubricants ', will lower the position of the transition point on the temperature scale. Imposing mechanical stress on the material will produce a similar result.

2.2. *Second-Order Transition Point.*—The second-order transition point for the various samples of polymethyl methacrylate examined was determined by measuring the volume increase in a test sample with temperature. A glass dilatometer containing a sample of about 1 gm of polymer and filled with mercury was used and was heated at a rate of about $\frac{1}{2}$ deg C per min. The increase in volume was plotted against temperature and it was found that the curve had two linear portions AB and BC of differing slope, as shown in Fig. 1. The temperature co-ordinate of the point of intersection (B) of the two lines represents the second-order transition temperature.

Determinations of the transition-point temperature were made on the three types A, B, and C of the polymer in the ' as received ' condition. However, on repeating the tests on the same test pieces higher values were obtained. After further investigation it was concluded that during the first heat run, polymerisation of residual monomer took place; this was an irreversible process as subsequent repeat tests gave constant values. Further check tests on fresh test samples which were given a preliminary heat treatment (heating in vacuo for eight hours at 100 deg C), together with tests on laboratory-produced plasticised and non-plasticised films confirmed these conclusions[2]. In the following table the experimental values obtained for the three types of material are shown.

TABLE 1

Sample	Second-Order Transition Temperature deg C	
	First Test	Repeat Tests
A	52	79
B	68	76
C	67	101

The smaller difference between the two values for sample B compared with those for the other samples indicates that the amount of residual monomer in type B material, as supplied, was small. The effect of plasticiser in lowering the transition temperature is seen by comparing the final values of samples A or B with that of C, the unplasticised material.

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The explanation given for these differences in the temperature-volume relationship is that during a rise in temperature the material expands, leading to increased freedom of movement of the molecular segments. Above a certain temperature region the freedom of movement becomes very large and the rate of change of volume with temperature is enhanced. The increased degree of movement, however, sets in at a lower temperature if there is an ' internal lubricant ' present (*e.g.,* plasticiser or monomer) or if external tensile forces are impressed on the material. The magnitude of the lowering of the transition temperature depends, within limits, upon the amount of the added substance present in the polymer.

2.3. *Solvent Absorption.*—It has been found that very many organic liquids dissolve the polymer or cause it to swell. The swelling action of a liquid or its vapour may continue until the material disperses in the liquid or it may cease before this stage is reached. [For example, a flat dumb-bell-shaped tensile test specimen $\frac{1}{16}$ in. thick was supported at each end above the free surface of benzene in an enclosed vessel at room temperature. After three days exposure to these conditions it was found that the central unsupported portion of the specimen had softened with absorption of benzene vapour to such an extent that it had sagged under its own weight until it touched the liquid and was then dissolved.

Experiments were performed[2] with the solvent benzene to determine the variation of solvent absorption with its vapour pressure on films of the polymer both plasticised and unplasticised, which had been polymerised in the laboratory at 60 deg C. Before starting the tests the films were heated at 100 deg C for six hours in vacuo to ensure complete polymerisation. They were suspended on calibrated quartz fibre spirals in sealed vessels into which solvent vapour at known pressures could be introduced. The vessels were maintained at a temperature of 35 deg C, and the vapour pressure was increased in steps, the sample being exposed for 24 hours before each increase in pressure. The increase in sample weight was noted by reading the extension of the quartz spiral. The vapour pressure was raised to as high a value as possible without severe deformation of the films taking place under their own weight. It was then decreased by similar steps.

Fig. 2 shows the results obtained. Examination of curve 1, which was obtained on unplasticised material, shows that no measurable absorption took place during the period of the experiment until the relative vapour pressure was raised to a critical value of over 90 per cent. At that pressure the absorption became very rapid, so rapid indeed that the individual points of the absorption curve could not be obtained. The addition of 8 per cent plasticiser (curve 2) however, reduces this critical value of the vapour pressure to 55 per cent, whilst 18 per cent plasticiser reduces it to 30 per cent (curve 3). Thus highly plasticised material has the least vapour resistance.

Similarly an examination of the desorption curves at the point where the pressure is reduced to zero shows that a quantity of the solvent is retained by the films and that this quantity is approximately inversely proportional to the amount of plasticiser contained by the polymer. That is, the unplasticised material retains the greatest amount of solvent and the sample with the highest plasticiser content retains the least.

Closer analytical examination of the amounts of solvent retained under these experimental conditions using benzene and other solvents suggests that the sum total of the number of retained solvent and plasticiser molecules in unit mass of polymer tends to be constant.

From the above experimental evidence it will be seen that the presence of plasticiser assists both the diffusion of solvent molecules into the polymer under absorption conditions and the escape of such molecules under desorption conditions. However, in every case an important fraction is retained.

Other experiments[2] showed that polymer films which were rapidly stretched when heated to the ' rubbery ' state (140 deg C approx.) and then cooled whilst stretched had a higher rate of vapour absorption than unstretched film.

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The explanation of the above behaviour is again based on the concept of molecular chain segment mobility. Essentially, at any given temperature, the ease of entry of vapour molecules is controlled by the initial mobility or energy of these segments. At a given temperature this mobility is least for non-plasticised material but increases in proportion to the amount of added plasticiser. Thus the non-plasticised material needs the highest initial vapour pressure in order to absorb appreciably during the period of the experiment. However, with entry of solvent the segment mobility is increased by the solvent swelling action and the rate of absorption of vapour begins to rise steeply. Conversely, during desorption at a given temperature, the mobility decreases progressively to a value such that a residue of solvent is trapped in the material and cannot readily diffuse out. Here again as the vapour pressure is reduced the non-plasticised material, other things being equal, reaches this degree of immobility first and, therefore, traps the greatest amount of solvent.

In a similar manner mechanically stretching the polymer when heated and then cooling it whilst in the stretched condition confers increased freedom for entry of solvent molecules and therefore increases the rate of vapour absorption by the polymer.

It will be appreciated from the above information that it is vitally important to keep the solvent vapour pressure to a minimum by providing the maximum degree of ventilation, during operations in which the material is unavoidably exposed to solvent vapours.

2.4. *Elastic Behaviour.*—When a high polymeric substance is subjected to a given mechanical stress it will suffer a deformation the extent of which will depend on the amount of stress, the rate of loading and the ambient temperature. In the case of the methacrylate polymer the deformation is related to the long-chain molecular structure of the material. First, the 'backbone' of the chain is made up of carbon atoms arranged in a staggered array and not in a straight line; consequently under mechanical stress the angles of the array and distances between the atoms may change. Secondly, the molecular chains are very much coiled up and entangled, and under stress the degree of coiling and entangling also may change. Thirdly, complete molecules under conditions of mechanical stress, may slip past their neighbours. The deformation under mechanical stress, therefore, may be resolved into three components:—

(a) A small instantaneous time-independent reversible component, designated 'ordinary elastic' deformation.

(b) A much larger reversible, non-instantaneous but time and temperature-dependent 'high elastic' component.

(c) A continuous time and temperature-dependent irreversible deformation due to a 'viscous' component.

Fig. 3 illustrates diagrammatically a strain-time curve for a hypothetical material containing the three components under a constant stress.

2.4.1. *Ordinary elastic deformation.*—Ordinary elastic deformation, characterised by being instantaneous and reversible on removal of the stress, is common to crystalline and glass-like solids. At constant temperature this deformation is, therefore, a function of stress alone.

To produce this kind of deformation in the case of a polymer of the long-chain molecular type, the chain molecule may be extended by stretching interatomic bonds and distorting the angle between individual atoms in the array (valency angles). However, the resistance to this type of deformation is very large and the polymer fails in tension before the deformation becomes appreciable. Ordinary elastic deformations, therefore, are always very small.

2.4.2. *High elastic deformation.*—Under appropriate temperature conditions the high elastic component can produce very large time-dependent, delayed, reversible deformations in long-chain type polymers, but, unlike viscous deformation, although it is delayed and takes time

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for completion, it has a finite limit and is reversible. It is, however, the characteristic property of rubber-like solids and is sometimes denoted as ' rubbery creep '. At constant temperature this deformation is, therefore, a function of stress and time.

The extremely long-chain-like molecules, which normally are randomly linked and coiled up, tend, under tensile conditions of stressing, to become more or less straightened out since the single primary bonds in the chain do not restrict rotation of chain segments about a bond. A small amount of uncoiling produces a large elongation. However, this movement is time-dependent because the resistance due to attractions between points along the chain and coinciding points on neighbouring chains has to be overcome. Similarly, these attractions delay recovery when the stress is removed and the molecules tend under thermal agitation, to revert to their coiled-up conditions. These hindrances to chain movement constitute an internal friction or damping force.

This high elastic behaviour which is based on a kinetic molecular mechanism therefore depends on two main factors; one is temperature, since molecular thermal agitation tends to assist the chain uncoiling process under tensile stress and recoiling—that is, deformation recovery—when the stress is removed, and the other an internal friction factor, which can be changed by modifying inter-chain attractions (*e.g.*, by plasticisation or by chemical alteration of the points of inter-chain attractions).

2.4.3. *Viscous deformation.*—Once the molecular chains have been more or less uncoiled and the stressing is continued, some of the molecules will tend to be dragged past others until failure in the material occurs. This deformation is irreversible and is a measure of the true viscosity of the system. Since the effect of heating is to increase the vibrational energy of the molecules, and thereby to assist in freeing them from the attractions of their neighbours, such viscous flow is in general very susceptible to changes of temperature.

Increasing the length of the polymer chains, however, increases the effective viscosity since it makes it more difficult for molecules to slip past each other. Therefore at a given temperature viscous deformation will differ, within limits, between polymers, due to variation in molecular chain length influencing other factors such as inter-molecular attractions, degree of chain entanglement, etc. In the case of commercial qualities of polymethyl methacrylate the chain molecules are very long and of the order of 20,000 monomer units. Thus, with such exceedingly long molecules the interchain attractive forces, although separately weak compared with the atomic forces within a chain, add up to an appreciable total over a long chain, so that bodily movement of a chain as a whole under stress is very restricted, the chain tending to break before movement takes place. Thus, at even moderately high temperatures, such as are used for forming operations on Perspex, little viscous flow takes place until relatively high stresses are reached. There is, therefore, little permanent set under normal hot-forming operations. During such operations the material is ' frozen ' into shape and subsequently, given sufficient time and a high enough temperature, it will tend to revert back to the original flat sheet.

However, as with other properties the relative contributions to a given deformation of the viscous and high elastic components will be modified by plasticiser content.

3. *Thermal Properties.*—3.1. *Coefficient of Linear Expansion and Heat Conductivity.*—The magnitude of the coefficient of thermal expansion of a material is closely related to the binding forces between, and to the weight of the atoms in its structure. For example, diamond, which has very strong binding forces between comparatively light atoms, has a low linear coefficient of thermal expansion (*viz.*, $1 \cdot 2 \times 10^{-6}$ per deg C) compared with metals ($10 - 30 \times 10^{-6}$ per deg C). The values for many organic solids are much higher than those for metals, particularly for thermoplastics, the actual values depending considerably on the plasticiser content. The filled thermosetting plastics, *e.g.*, the phenol- and urea-formaldehyde types have values falling between the above two groups. The following table of coefficients for different substances shows these differences in magnitude.

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TABLE 2

Coefficients of Linear Thermal Expansion (millionths/deg C)
and
Heat Conductivities (cal/sec/sq cm/deg C/cm)

Substance	Coefficient of expansion	Heat Conductivity	Substances	Coefficient of expansion	Heat conductivity
Diamond	1·2	0·33	*Thermoplastics*		
Graphite	8	0·01–0·03	Polyvinyl chloride	70–80	6×10^{-4}
Glass	9	0·002	Ebonite	80	4×10^{-4}
Steel	10–16	0·1	Polymethyl methacrylate	80–100	$3·5 \times 10^{-4}$
Aluminium	20–30	0·5	Celluloid and cellulose acetate	100–160	$3–9 \times 10^{-4}$
Duralumin	23–27	0·3–0·4	Polyethylene	200	7×10^{-4}
Lead	29	0·08	*Thermosetting Plastics*		
			Phenol- and urea-formaldehyde types, etc. (Filled)	25–50	$3–10 \times 10^{-4}$

On the other hand, the thermal conductivities of such materials as polymethyl methacrylate are very low compared with those of metals; the orders of quoted values are shown in the above table.

From the above it will be seen that the linear coefficient of expansion of the methacrylate polymer is about five to ten times that of steel and about five times that of Duralumin. Care is needed, therefore, to ensure adequate clearances between the plastic and metal members to allow for differential thermal expansion.

Fig. 4 shows the result of submitting a glass-Perspex combination to a low temperature. An $\frac{1}{8}$-in. thick Perspex sheet was laminated to $\frac{1}{4}$-in. glass sheet by an $\frac{1}{8}$-in. thick interlayer of polyvinyl butyral, a synthetic rubbery type of material. The laminate was cooled to − 40 deg C in a refrigerator and, because of the greater contraction of the Perspex compared with that of glass, the glass sheet was shattered.

3.2. *Heat Distortion.*—Heating followed by rapid cooling (chilling) of a sheet of the methacrylate should be avoided since strains are likely to be set up which may cause distortion, warping, or buckling, as well as assist crazing. The following experiment illustrates this point.

A strip of polymer was heated above 100 deg C and then removed rapidly from the oven and laid on a cold flat metal plate to cool. As the material cooled the ends of the strip began to rise until the whole strip became curved with the concave side upwards, only the centre portion of the strip being in contact with the plate. A second strip was heated in the same way but in this case the strip was laid on the metal plate and both were heated together. The plate, with the strip resting on it, was removed from the oven and allowed to cool down to room temperature and in this case the strip became concave downwards, that is, it arched so that only its ends were touching the plate. The explanation of both these results is based on the fact that if the polymer is cooled rapidly in the region of its second-order transition temperature it does not contract to the same extent as when it is cooled slowly over the same temperature range. In other words the rapidly cooled material tends to follow a curve such as CDE of Fig. 1 instead of curve CBA. Thus the lower face of the hot strip in the first experiment is brought into contact with the cold plate, cools more rapidly than the upper face and, therefore, does not contract to the same degree as the upper face. It is, therefore, extended and causes the ends of the strip to rise as the upper face, cooling at a slower rate, continues to contract. Conversely in the second experiment the hot strip is in contact with the hot plate and its lower face cools more slowly than the upper, the latter therefore does not contract to the same extent as the lower face and this causes the strip to become arched such that it is in contact with the plate only at its ends.

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Similarly if a flat sheet of the material is not uniformly heated it will suffer deformation of a similar type resulting in loss of flatness. For example, flat sheets held horizontally during a heating operation have shown a tendency to 'bow' so that only the central portions of the sheet support the whole sheet. This concentrated load caused local deformation which, when viewed on completing the cooling cycle, appeared as an optical distortion in the central portions of the sheet.

3.3. Heat Treatment.—For reasons given later (section 4.3) there are definite advantages to be gained by submitting sheets of the material to a heat treatment (Current Paper 18[3]) subsequent to the casting process. Again there is strong evidence that heat treatment (Current Paper 19[4]) of a completed structure at a temperature near the second order transition temperature followed by slow cooling to room temperature would materially improve the strength of the structure since this would relieve strains introduced during shaping and those due to fitting operations. To obtain the best results, the heating and cooling cycle must be related to the second-order transition temperature of the particular grade of material used. (*See* section 4.1.2.)

4. Crazing Properties.—**4.1. Nature of Crazing and General Conditions for its Development.**—During the investigations so far completed no crazing has been observed when the polymer is maintained at a temperature above its second-order transition temperature, that is, crazing has only been observed in the material when it is in its brittle glass-like condition.

The essential agents for producing crazing are:—

(a) *tensile stress*—crazing has not been observed under pure compression stresses, and (b) *solvent*—as a liquid or vapour, and crazing results under their combined action.

Again, two main conditions of the polymer may be distinguished which give rise to distinctive features in the production of crazing. They are :—

(i) *Normal condition*—(Type A material). As the material comes from the casting process.
(ii) *Heat-treated condition*—A condition produced by appropriate heating and cooling treatment given to the material subsequent to casting.

The main difference between these two conditions is that material in condition (i) comes from the casting process containing a residue of solvent (*viz.*, monomer, which is a solvent of the polymer) and random ordinary elastic strains, whilst in condition (ii) it is freed from both these elements by adequate time and temperature treatment, above the second-order transition temperature, followed by careful cooling so that thermally produced strains are not introduced into the material.

Further, while the combined residual solvent and random elastic strains contained by material in condition (i) are insufficient to produce crazing spontaneously (except possibly under prolonged storage conditions, weathering, sunlight, etc., in which one or other may become enhanced) the accentuation of either of them, *e.g.*, by exposure to solvent vapour alone or the application of tensile stress alone, can cause crazing. Condition (ii), however, requires the application of *both* tensile stress and solvent before crazing can be produced.

As an exception to the above there appear to be cases where a type of crazing is produced in material in condition (ii) under high tensile stress alone. The required stress, however, is very high and approaches closely to the ultimate strength of the material. This type of crazing may come within the category of rupture by tensile stresses of brittle solids in general. However, it awaits further study especially with regard to plasticised grades of the material, since in some ways the action of a plasticiser can be considered identical with that of a solvent.

4.2. Strains which Cause Crazing.—Since the material does not craze under compression stress and does so under tensile stress only when in the brittle condition the type of strain

necessary to produce crazing is the ordinary elastic strain common to glass-like solids, which involves stretching the interatomic bonds or distorting the angles between the individual atomic bonds.

It is necessary, however, for the ordinary elastic strain to rise above a certain minimum before crazing becomes evident, that is, there is a threshold value of the stress to start crazing. This conclusion is supported by the following experiments which illustrate also the extent to which heat treatment can increase this threshold stress. Tensile test specimens were cut from a sheet of material in the normal condition, and half of them were tested for tensile strength at room temperature without being heat treated, while the other half were heat-treated (24 hr at 100 deg C followed by slow cooling to room temperature) before being tested. The load during the tensile strength test at which crazing began to appear was noted in each case. Crazing began to appear at between 40 and 60 per cent of the failing stress for the specimens in the normal condition, even when the rate of stressing was varied from 1000 to 4000 lb/sq in./min, whilst for the heat treated specimens it did not appear until the stress had reached over 90 per cent of the ultimate. In addition the average failure strength of the latter was some 15 per cent above that of the normal material. The amount of crazing visible in the heat-treated material was very scanty and appeared to be initiated by small surface imperfections such as very slight scratches or barely visible notches in the test specimen.

Another series of tests[5] was made on non-heat-treated type A material in which flat dumb-bell-shaped test specimens were used, the central gauge portion of each being slightly tapered. Examination of the specimens after tensile testing to failure showed that the area crazed extended some distance up the tapered portion with a fairly well-defined boundary between the crazed and uncrazed portions. This result also indicated that a critical value of stress is necessary to start crazing.

The latter point was further examined[5] under bend test conditions at room temperature with the additional aim of determining the effect of time under load. A three-point loading system was used with flat-strip test specimens of type A material. The load was increased at the end of each period of 24 hr by an increment until crazing appeared. Here again, crazing did not appear until a critical stress was reached. If a duplicate sample was tested with a single load equal to that which had produced crazing in the previous test, where the loading was incremental, it crazed in the same manner. In a second series of tests the load was fixed at a value slightly less than that required to craze duplicate specimens in 24 hours, and the onset of crazing awaited. None was observed during the time of the test which was extended up to 100 hours.

It is concluded, therefore, that there is a minimum degree of molecular bond *strain* necessary before local rupture commences.

4.3. *Residual Strains from Casting Process.*—It is believed that the random strains present in the cast material arise during the casting process when carried out at moderate temperature. During the polymerisation process, which involves considerable volume reduction of the material the strains are set up (a) by non-uniform adhesion of the material to the glass surface of the cell in which the polymerisation takes place and (b), by the restriction imposed on reacting molecules, at a late stage of the polymerisation process, by fully formed neighbouring molecules. Towards the completion of this process, owing to increasing viscosity effects, diffusion of monomer becomes increasingly difficult so that to a certain extent the final chains to be formed are not randomly orientated but are restricted in their direction of growth by their neighbours with the result that they grow in a strained condition. Added to such strains are those due to the large thermal and density gradients set up in the thickness of the sheet during polymerisation and subsequent cooling.

Experiments[6] have shown that these residual strains can be relaxed by a short period of heat treatment at a temperature above the second-order transition temperature, the heat treatment being insufficiently prolonged to polymerise fully the residual monomer. . Such treated material

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does not craze when exposed to solvent alone. However, further prolonged heat treatment of such material at lower temperatures causes residual monomer to polymerise completely and the material may now craze when exposed to solvent alone, the extra polymerisation having created fresh strain in the material.

Strains can be reintroduced into a previously heat-treated material by local heating and chilling. Fig. 5 shows a photograph of holes drilled in a previously heat-treated strip of material. Heated metal rods were inserted in some of the holes (an inadvisable method of polishing holes). When cool the strip was treated with solvent and, as shown, the holes exposed to the heated rod exhibit heavy radial crazing whereas those not so exposed do not.

When tensile stress is applied to material containing these residual stresses, components of the internal stress lying in the direction of the applied stress assist the latter in crazing the material; they also tend to lower the ultimate tensile strength of the material. The above mentioned (section 4.2) tensile strength tests comparing heat-treated against non-heat-treated material, where a difference in ultimate strength was found, suggest that the removal of internal stresses contributes appreciably to this strength difference. Other tests show that the removal of residual monomer by heating will also increase the tensile strength of the material. Further study of this point is required.

4.4. *Crazing under Stress Alone.*—Crazing produced in normal material (*i.e.*, in material containing residual solvent, the monomer) by applying stress alone shows a somewhat similar pattern to that produced by applying combined stress and solvent vapour to heat-treated material.

The general direction of craze lines under stress alone tends to be perpendicular to the direction of the applied stress and to be located in the original surface of the cast sheet. Such crazing is absent in freshly cut or broken surfaces of the test specimens.

4.5. *Crazing with Solvent Alone.*—Exposing material in the normal condition to solvent vapour alone gives rise to a crazing pattern distinct in appearance from that caused by applying stress. The craze lines, although tending to form patterns in or near the original cast surfaces, are randomly oriented (*see* Figs. 6, 7 and 8).

This difference in appearance between craze patterns produced by solvent alone and those involving applied stress is very useful in locating causes of crazing in material which has been in service (*see* Figs. 6 to 11).

It is believed that the cause of solvent crazing lies in non-uniform solvent absorption; the rate of absorption of vapour by the polymer, as stated in section 2.3 above, is affected by strain in the material, a stretched film absorbing vapour at a greater rate than an unstretched film. This results in local plasticisation by the solvent vapour around strained chains which allows them to relax, thereby concentrating the stresses on neighbouring portions until the surface fails by fracturing; the fracture is visible as crazing. Experimental evidence[6] suggests that with very slow absorption of solvent vapour crazing does not occur, probably because of a more uniform absorption.

4.6 *Temperature Effect on Crazing.*—It is possible that the increased mobility of molecular segments conferred by absorbed solvent may be counteracted by decrease of temperature, since the latter tends to decrease molecular mobility. For example, in a separate investigation of the mechanical properties of type A material at low temperatures under bend test conditions, it was noticed that fractured specimens tended to exhibit crazing when tested at − 40 deg C but none at − 60 deg C. It is possible, therefore, that the ' threshold ' value of the stress necessary to cause crazing tends to rise as the temperature is lowered (that is, as the material hardens) until it approximates to the failing stress. As stated later, the Young's modulus, or the ' stiffness ', of the material increases with decreasing temperature and, as noted in section 4.2,

it is believed that a certain minimum degree of bond strain is necessary to initiate crazing. The tensile stress necessary to cause this minimum strain will therefore rise with decrease in temperature due to the increase in Young's modulus.

4.7. *Solvents which Cause Crazing*.—The number of solvents which are effective in causing crazing is large[6] and since there does not appear to be any common purely chemical property amongst them it is concluded that the solvent effect is a physical process of swelling or solution of the polymer. There is, however, a certain amount of evidence that the size of the solvent molecule may be a limiting factor, and that in a given homologous series of compounds the rate of absorption decreases with increased solvent molecular weight or size.

In some cases of crazing in structures under service conditions the source of the solvent was initially difficult to trace but was finally tracked down to unsuspected materials in the vicinity of the structure. Various synthetic materials such as rubber, sealing compounds, polishes, etc., can cause trouble in this way, particularly if heated. Fig. 9 shows a photograph of a portion of an aircraft nose near which cabin heater piping was located. The crazing shown is attributed to evolution of organic vapours generated by heat from the piping system.

4.8. *Crazing under Combined Tensile Stress and Solvent Vapour*.—All grades of polymer so far examined, whether heat treated or not, tend to craze when exposed to solvent vapour whilst under tensile stress. Alternatively, crazing will result if the stress is applied some time after exposure to vapour, the solvent having diffused into the material.

The pattern of craze lines produced under these conditions shows an important difference from that described in a previous section. The lines always tend to lie in a direction perpendicular to that of the tensile stress. Typical examples are shown in the photographs of Figs. 6, 7 and 8. Examples of this type of crazing have appeared in formed structures which have been exposed to high concentrations of solvent vapour owing to lack of adequate ventilation (*e.g.*, vapour from cold setting cements used in fabricating structures). Fig. 10 shows a photograph of a portion of an aircraft hood which had contracted differentially, when exposed to low temperature, on to the metal framework so that large tensile stresses were set up which caused crazing[1]. In this particular case, besides coarse crazing taking place in the surface covered with cement at the cemented joint, finer vapour crazing appears some distance away where there is comparatively sharper curvature of the hood. As previously explained, absorption of vapour takes place to a greater extent in a given time in those portions which receive the greater degree of stretching such as occurs when ' hot-forming ' a structure. It will be appreciated that in this case the tensile stress developed in the material some considerable period after exposure to solvent.

Ordinary elastic stresses caused by force-fitting a hood to a metal frame or one shell to another in a double-shell hood, or by clamping pressures applied during cementing operations, have provided the necessary stress to produce crazing in the presence of solvent.

The mechanism of this type of crazing is similar to that described in a previous section in that the absorbed solvent assists the stress in breaking up the surface by its non-uniform softening action on the material. Initially the onset of crazing tends to relax the surface and thus to relieve the stresses, but if the applied stress is maintained crazing leads to complete failure. For example, a section of material was removed from the affected part of a hood showing coarse crazing similar to that illustrated in Fig. 10; examination of its cross-section showed that the coarse crazing had penetrated to a depth of one third of the thickness near the portion of the structure which had completely fractured under test. Fig. 11 shows how crazing penetrates into the bulk of the material.

4.9. *Effect of Crazing on Strength*.—In a later section, 5.10, experiments are described in which the effect of scratches on impact and flexural strength was investigated. The results

show that there was an appreciable loss in strength when the scratches were orientated in a direction parallel to the surface which was in tension and perpendicular to the direction of the tensile stress. Craze lines such as those shown in Fig. 8 have a similar effect locally on the strength of the material.

4.10. *Removal of Crazing.*—Attempts to remove crazing from a structure by applying heat over restricted portions are of doubtful value from the point of view of the strength of the material, although vision through the crazed area may be improved. The action of heat in expanding the material locally causes the fissures to close up and remain closed when the material is cooled. Experimental evidence suggests, however, that the resulting adhesion between the walls of the fracture has low resistance to tensile stress. Samples which were crazed by bending and then heated to remove the craze lines tended to exhibit the same pattern of crazing when again stressed by bending. Added to this is the danger that heating a structure locally may itself induce random stresses in the material.

Similarly, the painting of crazed portions with a solvent to smooth out scratches will provide solvent for crazing when the material is subsequently stressed in tension.

4.11. *Removal of Absorbed Solvent.*—Once the material has absorbed solvent its complete removal by diffusion at ordinary temperatures is very slow, as will be appreciated from the details described in section 2.3. Only heating would speed up the diffusion process. A heat annealing process given to a fabricated structure after cementing would materially assist dispersal of cement solvents.

4.12. *Removal of Ordinary Elastic Strains by Heat Treatment.*—In the same way as heat treatment removes casting strains in normal material, so it can be applied to remove ordinary elastic strains introduced in forming, fabricating or mounting a structure. If the material is heated for sufficient time near the second-order transition temperature, ordinary elastic strains in a structure are replaced by the high elastic strains which in themselves do not cause crazing in the presence of vapour even when the material is again at normal temperature.

4.12.1. *Heat treatment of flat sheets.*—The recommended treatment[3] for flat sheets is to heat the material at 140 deg C for a period of time (t minutes) depending on the sheet thickness (x in.), given by the formula:—

$$t = 10 + 80x$$

The heat treatment at this temperature polymerises the residual monomer reasonably quickly.

The material is then either cooled very slowly and uniformly, or preferably cooled quickly, to a certain annealing temperature T_a, which varies according to the plasticiser content, by transferring the sheet from the 140 deg C oven on to a flat glass plate contained in an oven maintained at the temperature T_a. It is then kept at this annealing temperature for a definite period of time, after which the supported sheet may be allowed to cool to room temperature under normal conditions.

For unplasticised material T_a is 93 to 96 deg C and the minimum annealing time 3 hr, for 5 per cent plasticised material the figures are 80 to 82 deg C and 4 hr, and for 8 per cent plasticised material they are 73 to 75 deg C and 4 hr.

4.12.2. *Heat treatment of formed structures.*—Since the degree of strain retained in a formed structure depends on the efficiency of the forming operation, maintenance of correct temperature, etc., and the uniformity and rate of cooling after forming, it cannot be known precisely and the choice of annealing temperature must be a somewhat arbitrary one. Again the degree of distortion resulting from heat treatment subsequent to hot forming will vary with this

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unknown degree of strain. The annealing temperature however should be as high as possible without causing serious distortion but should be below the second-order transition temperature (section 2.2) for the grade of material used, since, unlike the case of the treatment of flat sheet, the material cannot easily be uniformly supported.

In addition, any metal framework which is part of the structure and the attachment of which may unavoidably produce strain in the material, should be fitted as far as possible to the structure prior to the annealing treatment. The treatment will also reduce these added strains.

From the experimental data so far obtained[4] the annealing temperature for formed structures should be between 65 deg C minimum and 70 deg C maximum for material containing 5 per cent plasticiser and between 84 deg C and 87 deg C for unplasticised material. The annealing time in each case is not less than 3 hours.

It is important to note that the heat treatment will materially assist in removing any cement solvent retained in the structure, and for maximum benefit any enclosed spaces in the structure likely to collect solvent vapour, so liberated by heat, should be swept with air preheated to the oven temperature.

4.13. *Cements and Crazing.*—In order to get a joint strength in the material as high as possible it is necessary to employ a solvent for the material as a component of the cement and thereby ensure that the surfaces to be joined are properly wetted and temporarily slightly softened. Subsequent tensile stressing of the joint however, is liable to cause crazing unless the solvent is completely removed (*see* Fig. 10). As stated previously, the complete removal of absorbed solvent is difficult at ordinary temperatures. However, since the monomer of methyl methacrylate is a solvent for the solid polymer, such a solvent could be rendered ineffective in inducing crazing by converting it into the solid polymeric condition in the joint. Such a cement is under development commercially. It has two further possible advantages:—

(a) It is in the form of ' dough ' and can, therefore, be used to fill gaps, making unnecessary the use of excessive clamping pressures to close gaps when cementing the material.

(b) The monomer (the solvent in this case) can be polymerised by ultra-violet light from special lamps assisted by light activated material in the dough. Thus excessive local heating is avoided.

For complete success, the polymerisation process must be such that the cement is fully polymerised and that the mechanical strength of the cement in a gap approximates to that of the material being cemented.

Submitting a structure, after jointing, to heat treatment such as annealing or hot forming, would materially assist in dispersing cement solvent and in relieving strains in dough joints.

4.14. *Avoidance of Crazing.*—From the above it will be seen that wherever possible the following measures should be taken:—

(a) Avoid the use of solvents. Where they must be used, as much ventilation as possible should be provided to keep their vapour pressure low.

(b) Avoid introducing ordinary elastic strains wherever possible, for example, by eliminating—

(i) Force-fitting of a structure in metal framework or of one part of a plastic structure in another part. Where possible buffering material such as rubber should be used to relieve such stresses.

(ii) Excessive clamping pressures during cementing, *e.g.*, to close gaps between parts to be joined.

(iii) Local heating of the material.

(iv) Inadequate clearances for thermal expansion.

(c) Heat anneal the structure whenever possible before putting it into service.

4.15. *Test for Adequacy of Heat Treatment.*—A quick method of checking whether a sample of material has been adequately heat treated to remove casting strains and residual monomer is being sought. On the samples so far examined, it has been found that immersing a portion of the sample without stressing it in benzene for a few minutes, and then allowing the solvent to evaporate, develops crazing in normal material. It is believed, however, that the absence of crazing under this test only indicates that casting stresses are below the minimum necessary to start crazing and does not indicate the absence of residual solvent (monomer).

5. *Mechanical Properties.*—**5.1.** *Extensibility and Temperature.*—Reference has been made in section 2.1 to the change in properties of Perspex with change in temperature, *viz.*, the change from a hard brittle to a rubber-like solid as the temperature is increased. This change is very evident in the elastic behaviour of the material at different temperatures. A curve relating stiffness or Young's modulus (E), with temperature Fig. 12, shows the considerable temperature susceptibility of the material. At room temperature and below, the modulus is of the order of $0 \cdot 3$ to $0 \cdot 5 \times 10^6$ lb/sq in. (*cf.* steel 30×10^6 lb/sq in.). As the temperature is raised to about 50 deg C there is a slow fall in E, but between 50 deg and 100 deg C the fall becomes very rapid and at about 140 deg C the value of the modulus drops to that of soft rubber *viz.*, 100 to 200 lb/sq in.

The actual value of the modulus at any given temperature and the shape of the curve are again influenced by additions to the polymer such as plasticisers and solvents.

The large decrease in stiffness with increasing temperature is considered to be due to the effect of heat on the material in facilitating the uncoiling process of the long-chain molecules. Conversely, decreasing the thermal energy of the chains by lowering the temperature will increase the restrictions on the uncoiling process. However, since the amount of the uncoiling, under a given stress, is dependent on the time under stress, the measured value of the modulus depends upon the rate of stressing.

5.2. *Yield Point and Ultimate Elongation.*—The curves in Fig. 13 showing tensile stress-strain relationships, at various temperatures and under normal rates of loading, reveal that as the temperature is increased the maximum stress at the yield point progressively decreases. Similarly, Fig. 14, a plot of ultimate elongation as ordinate against temperature, shows a curve having a sharp elbow in the temperature region of 50 to 70 deg C. Below this temperature region the ultimate extension is low and the mechanism of deformation is mainly that of ordinary elastic deformation. For example, in a study of the strength of bolted joints in Perspex[7], it is reported that tensile tests, at room temperature and below and at normal rates of loading using Type A material, resulted in brittle failures with no measurable permanent deformation of the specimen or the bolt holes, except in the case of a few specimens which failed at exceptionally high stresses. In the case of the latter specimens, the material flowed in line with the bolts, the holes being elongated some 20 per cent. It is assumed that these few high results are probably due to the test specimens being particularly free from scratches or slight notches which usually initiate failure.

Similarly flat dumb-bell-type tensile test pieces when tested at room temperature showed no ' necking ' in the region of the fracture.

As the temperature is increased above 50 deg C, however, extension of the high-elastic type becomes more evident resulting in a progressively lower yield point and greater ultimate extension.

It will be noted that these major changes in elastic behaviour with temperature occur in the region of the second-order transition temperature for the material.

5.3. *Extensibility and Heat Treatment.*—Determinations of Young's modulus in bending were made at room temperature on Type A material before and after the heat treatment previously

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described, in which it is believed internal strains are eliminated and residual monomer is fully polymerised. In both cases, before testing, the specimens were allowed to come to moisture equilibrium with the room humidity conditions. The results indicate that the modulus was increased some 10 to 20 per cent by the heat treatment.

5.4. *Reversibility of Deformations.*—At low and room temperature conditions, that is with the material in the brittle condition, the deformations under mechanical stress obtained at the usual laboratory rate of stressing are small, except for excessively high stresses (*see* section 5.2), and are of the practically instantaneous reversible type due to the ordinary elastic mechanism.

At higher temperatures, however, the rubber-like elastic behaviour makes the material highly suitable for hot shaping or forming processes. At these higher temperatures, under comparatively light pressures, sheets of the material can be blown or pressed to complicated curvatures and then frozen into the curved shape by cooling. It is important to note, however, that the deformation at shaping temperatures (approx. 140 to 150 deg C) and under light stresses, involves little or no viscous flow of the material which would lead to permanent set. Much higher temperatures or stresses or longer times are needed to produce permanent set and at these higher temperatures there is danger of a certain amount of polymer degradation (conversion of polymer back to monomer) and gas evolution leading to bubble formation in the material. On the other hand if the shaping temperature is too low, higher stresses are needed to shape the material and these introduce into the polymer appreciable ordinary elastic stresses which cannot be fully ' frozen in ' by cooling. Therefore, when the shaped article is cooled and released from the constraints of the former or shaper it tends to spring back, causing distortions in shape which may in the presence of solvent vapour cause crazing. Fig. 15 shows a strip sample of material which was heated below the usual forming temperatures and bent into a V-shape under high stress in a vice. It was allowed to cool, still held in the vice, and when cool, solvent was applied to the inside of the bend but no crazing appeared. However on releasing the material from the vice and again applying solvent to the inside surface of the bend crazing appeared. This result is due, it is believed, to tension stresses developing on the inside of the bend because of instantaneous elastic recovery of the strip as a whole on releasing it from the vice.

The following experiment illustrates the high degree of reversibility of deformations produced at the usual shaping temperatures. A long strip of the material was heated in an oven at 140 deg C and whilst hot was twisted so that several turns were produced along its length. The strip was cooled to room temperature whilst held in the twisted condition and then released. No appreciable untwisting was observed. However, on replacing the sample in the oven it began slowly to untwist. When the strip was placed in an oven at 150 deg C, the untwisting became rapid and continued until finally little or no twist remained in the strip.

It is to be noted, therefore, that articles shaped from heated polymer sheet have an inherent tendency, due to the reversibility of deformation, to return to the sheet form rapidly at high temperatures, but so very slowly at normal temperatures as to be negligible. The plasticiser content of the material will, however, affect the temperature at which the rate of recovery becomes appreciable.

5.5. *Tensile and Shear Strengths and Temperature.*—Investigations have shown that the tensile strength of the polymer is sensitive to temperature changes. For example, the tensile strength value increases steadily as the temperature is lowered, its value at -60 deg C being about twice the value at room temperature. Further, at about 70 deg C the yield stress decreases to below half of the value of the tensile strength at room temperature. Similar results were obtained for shear strengths.

5.6. *Tensile Strength and Heat Treatment.*—Heat treatment, of the kind previously described, applied to tensile test specimens of Type A material caused an appreciable increase in strength of the order of 10 to 20 per cent, together with a decrease in scatter of the results.

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5.7. *Tensile Strength and Time under Stress.*—Studies by Chasman[8] of the time for the polymer to fracture at room temperature under various tensile stresses gave a linear relation between the logarithm of the stress and the logarithm of the time to fracture. Taking 1,000 hours as the long-time limit it was found that the long-time failing stress was of the order of 45 per cent of the stress which caused failure under normal laboratory rates of loading.

5.8. *Tensile Strength and Solvent Absorption.*—A series of tensile strength tests was made on Type A material after the test specimens were exposed at room temperature for increasing periods of time to an atmosphere saturated with benzene vapour. The specimens were placed in a sealed container over a free surface of benzene for a given time and they were then removed, exposed to the free air of the laboratory for an equal length of time and then tested for tensile strength. The time of exposure to vapour and room conditions was progressively increased and the relation between percentage strength and time of exposure is shown in Fig. 16. The strength of unexposed control specimens was taken as 100 per cent.

A portion of the batch of test specimens was given the pre-heat treatment previously described (section 4.2), similarly exposed to solvent vapour and strength tested. The result, also shown in Fig. 16, reveals a considerable increase in resistance to vapour as indicated by a smaller percentage loss in strength with time of exposure. The explanation of this result is again based on the fact that the heat treatment removes elastic strains and residual monomer, both of which assist the absorption of solvent vapour by the material.

In a further series of tensile tests the specimens were similarly exposed to benzene vapour but for one hour only. Before being tested they were exposed to room conditions, to allow desorption of vapour to take place, for various periods of time. The curves of Fig. 17 show the results. From Curve A it will be seen that even after 168 hours exposure to room conditions material $\frac{3}{16}$-in. thick in the 'as received' condition recovered only $\frac{1}{3}$ of the loss in tensile strength incurred by the one hour exposure to benzene vapour. The asymptotical trend of Curve A suggests that there is likely to be a permanent loss in strength of some 10 to 20 per cent, due probably to crazing. A comparison of Curves A and B in Fig. 17 shows the greater resistance to solvent vapour of heat-treated material.

5.9. *Impact Strength, Velocity of Impact and Temperature.*—Studies of impact strength of the polymer, measured by the usual methods and at various temperatures, show little change of strength with temperature in the range — 60 to + 40 deg C, where the material is in a brittle condition, that is, where there is relatively small change of Young's modulus, E, with temperature. However, above 50 deg C where E begins to decrease rapidly the impact strength starts to increase with rise of temperature. Since the usual impact strength-test measures the amount of energy to cause failure rather than the maximum stress, the energy of deformation up to the breaking point is proportional to the square of the maximum stress and inversely proportional to the Young's modulus. Therefore a hard material having a high value of E, other things being equal, will have a lower impact strength than a material having a lower value of E. However, since E may involve time deformations, that is, E is dependent on rate of stressing, a material may have a higher or lower impact strength according to the velocity of impact.

Haward studied[9], at room temperature, the energy needed to fracture a sheet of the methacrylate polymer, using falling weights. His results indicate that the energy necessary to cause failure varies with the velocity of impact such that in the range of velocities used (300 to 3,000 cm/sec approximately) the energy rose to a maximum and then rapidly decreased to low values at the high velocities. The scale of this peak effect, however, depended on the size of the test piece. At the higher velocities, where the initiation of vibrational stress is important and where the energy to fracture is low, damage to the specimen is small and is confined to the immediate neighbourhood of the point of impact resulting in small Y or star cracks. On the other hand impact failure at low velocities tended to give long cracks.

5.10. *Impact and Flexural Strength and Notch Sensitivity. The Effect of Surface Scratches.*—At normal and low temperature the material has little resistance to crack propagation so that once a crack has started little extra energy is necessary to complete the failure. Observation has shown that, in service, failure usually starts at minute cracks or notches, *e.g.*, under large stress concentrations occurring at notches on the sides of bolt holes. Fig. 18 shows failure in tensile test specimens, at the unpolished bolt holes and not within the gauge length of the specimen. It was found, however, that enlarging the unpolished hole as shown in the figure eliminated this failure. This result, however, needs confirmation by detailed investigation covering different sheet thicknesses and hole sizes.

Investigations by Bartoe[10] of the effect of surface scratches on impact and flexural strength in which the surface was scratched by sanding in a direction perpendicular to the long dimension of the Charpy and bend-test specimen ($\frac{1}{2} \times \frac{1}{2}$ in. section), showed that the impact strength of the scratched specimen was approximately half and the maximum flexural strength 70 per cent of that of the polished specimen for a depth of scratch of approximately 0·02 inch. The curves giving these strengths against depth of scratch are L-shaped indicating a very rapid drop in strength with scratch depth up to a depth of approximately 0·020 in. followed by a rapid change to a relatively flat portion of curve over the range 0·025 to 0·1 in. of depth.

5.11. *Impact and Flexural Strength of Hot-Formed Material.*—Some experiments by Rogowsky[11] on the change in impact and bending strengths at room temperature of Perspex which had been stretched at forming temperature and then carefully cooled in the stretched condition showed that both characteristics are affected by the stretching process. The unnotched impact strength, at room temperature (*see* Fig. 19), rose to approximately 25 per cent above that of the unstretched material as the percentage stretch was increased from 0 to 25, the direction of stretch being in a direction parallel to the long dimension of the test bar.

Over a similar range and direction of stretching the bend strength at room temperature rose by about 20 per cent for 25 per cent stretch (Fig. 19). For higher percentages of stretch the rate of increase in bend strength with percentage stretch was less than for impact strength. Where the direction of stretching was perpendicular to the long dimension of the test bar the impact strength value decreased with degree of stretch. The rate of change of impact strength with percentage stretch, however, was less than for the case where the direction of stretch is parallel to the long dimension of the test bar.

The bend strength values showed no change with percentage stretch for a direction of stretching perpendicular to the test bar.

The probable explanation of this improvement in strength of the stretched material lies in the tendency, at high temperatures where the chain molecules are most mobile, for the tensile stress to orientate the chain molecules, to a limited degree, in the direction of the stress. The applied stress, being maintained during cooling, that is, as molecular mobility decreases, causes the orientation to remain until it becomes fixed at the lower temperature. In this way the much stronger primary forces within a molecule contribute more to the tensile strength of the material in the direction of their orientation than when they are randomly arranged. In the latter case the strength of the material in a given direction is more dependent upon the weaker secondary forces between the molecules. In some other high polymer substances, which show regions of crystallinity and which are suitable for forming synthetic fibres, molecular orientation produced by stretching and setting processes can appreciably enhance the tensile strength of the fibre.

5.12. *Polishing Bolt Holes and Edges.*—From the test results described in section 5.10 the need for polishing all edges and bolt holes in a structure is evident.

The following methods have been used for polishing bolt holes:—

    (i) All twist drills are maintained in as sharp a condition as possible and reserved for use with this material only. (It is known that a cutting edge, formed by breaking a sheet of glass and using the broken edge can be used to cut the material so that an optical finish to the cut surface is obtained.)

During drilling at a low rate of feed, the drill is kept as cool as possible. Overheating during drilling has been known to render the material ' sticky ', degrade the polymer back to monomer (a solvent) and cause crazing under stress. The initial pilot hole is drilled with a standard drill 1/32 or 1/64 in. diameter undersize; a final drilling then brings the hole up to size.

If the drilling is carried out with reasonable care little final polishing is required.

The final polishing is performed with a wooden mandrel which is appreciably smaller than the bolt hole, and slotted for a portion of its length to receive a piece of soft cloth. Two of the edges of the cloth are cut to taper towards the end of the mandrel for easy insertion in the holes. The cloth is moistened with the polishing medium, and brief application under light pressure produces a good finish.

    (ii) Another method of polishing holes has been developed[10] which is preferable, since it is quick and easily applied as a production method.

In this case special twist drills and counter-sinks are used and during the drilling operation the drill is continously flooded with the liquid polishing medium.

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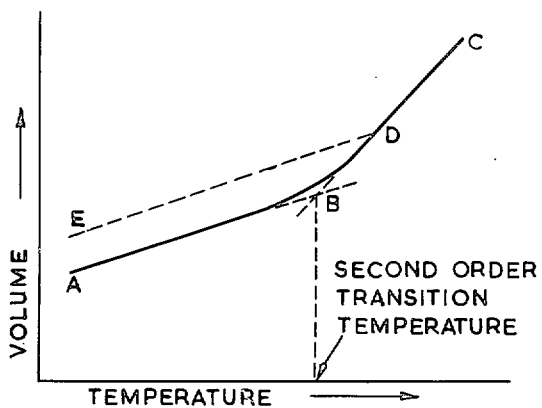
FIG. 1 (section 2.2).   Thermal expansion.
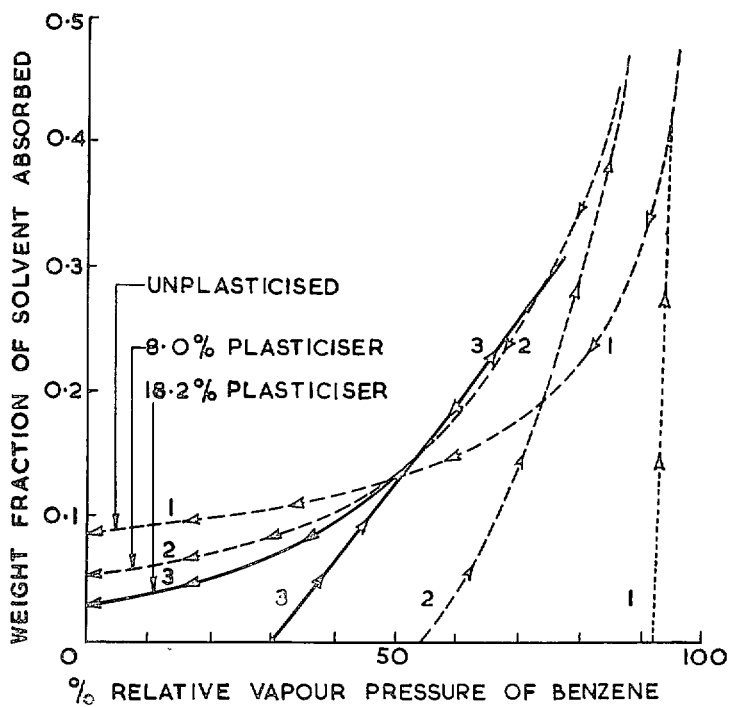
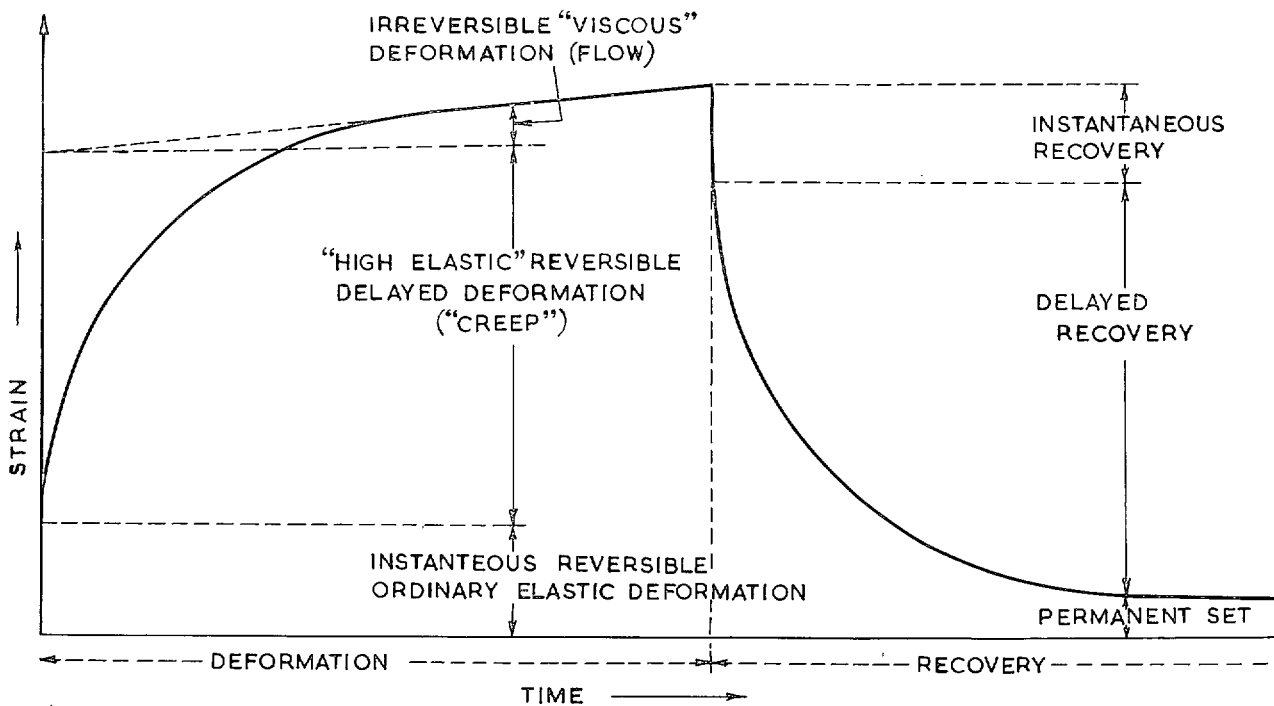
FIG. 2 (section 2.3).   Solvent absorption.

FIG. 3 (section 2.4).   Strain-time diagram at constant stress.
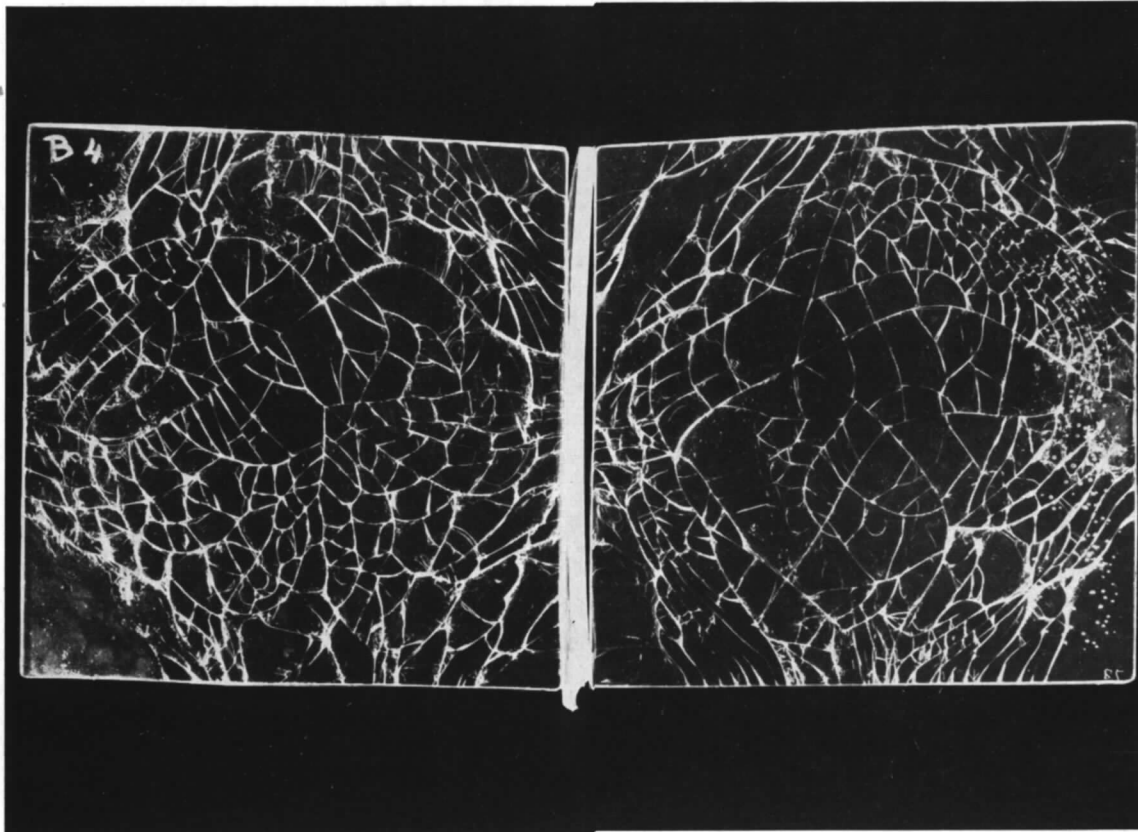
19

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FIG. 4 (section 3.1). Perspex-vinal-glass laminate. Failure of glass at low temperature (due to glass-Perspex differential contraction, at a temperature of −40 deg C).
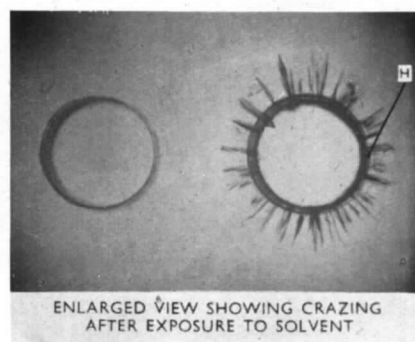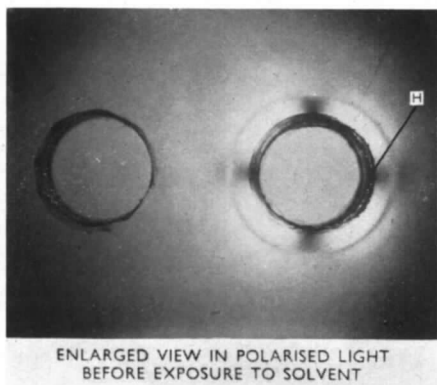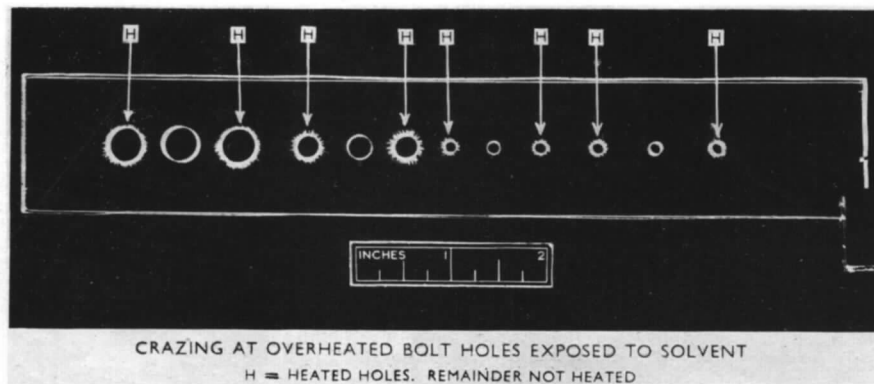
CRAZING AT OVERHEATED BOLT HOLES EXPOSED TO SOLVENT

H = HEATED HOLES. REMAINDER NOT HEATED

ENLARGED VIEW IN POLARISED LIGHT
BEFORE EXPOSURE TO SOLVENT

ENLARGED VIEW SHOWING CRAZING
AFTER EXPOSURE TO SOLVENT

FIG. 5 (section 4.3).   Examples of crazing.

CONDITION 'AS CAST'
RANDOM PATTERN CRAZING
DUE TO SOLVENT ALONE

HEAT TREATED CONDITION
DIRECTIONAL PATTERN DUE
TO STRESS AND SOLVENT

FIG. 6 (section 4.5).   Examples of crazing.

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HEAT TREATED CONDITION
DIRECTIONAL CRAZING

'AS CAST' CONDITION
RANDOM CRAZING

ENLARGED VIEWS OF CRAZING

a. HEAT TREATED AND CRAZED WITH SOLVENT WHILST
   STRESSED IN TORSION
b. TWO THIRDS HEAT TREATED (H) REMAINDER 'AS CAST',
   CRAZED WITH SOLVENT AND TORSIONAL STRESS
c. TWO THIRDS HEAT TREATED (H) REMAINDER 'AS CAST',
   CRAZED WITH SOLVENT ALONE
d. PORTIONS HEAT TREATED (H) REMAINDER 'AS CAST',
   CRAZED WITH SOLVENT ALONE

FIG. 7 (section 4.5). Examples of crazing.

'AS CAST' CONDITION. CRAZING DUE TO SAWING OPERATION

CRAZING DUE TO FINGER-PRINT
ON HEAT-TREATED MATERIAL
UNDER TENSILE STRESS

FIG. 8 (section 4.5). Examples of crazing.

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FIG. 9 (section 4.7). Crazed aircraft nose.

DOUBLE SHELL HOOD. FAILURE UNDER PRESSURE TEST AT LOW TEMPERATURE

DOUBLE SHELL HOOD. CRAZING PRODUCED BY LOW TEMPERATURE TEST
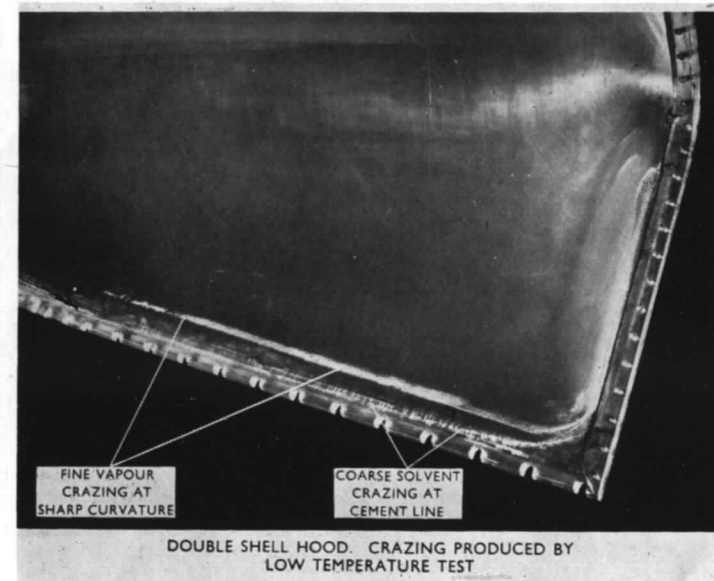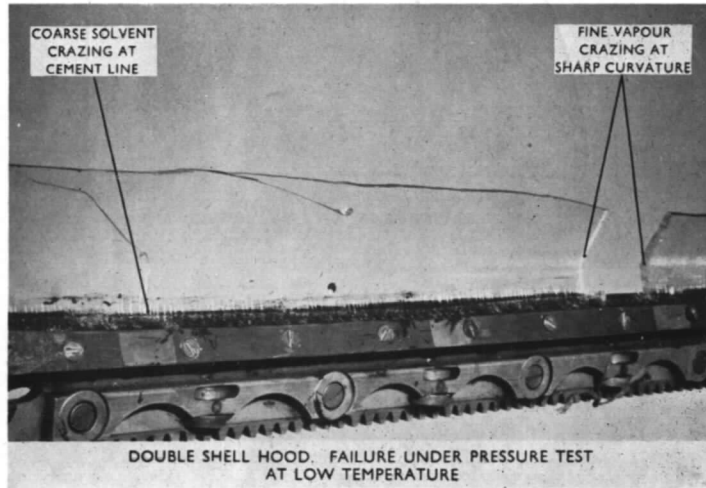
FIG. 10 (section 4.8). Examples of crazing in structures.

| MAGNIFIED FRONT VIEW | FRONT VIEW | MAGNIFIED SIDE VIEW |
| (SHOWING DIRECTION OF CRAZE LINES) | | (SHOWING DEPTH OF PENETRATION OF CRAZING) |
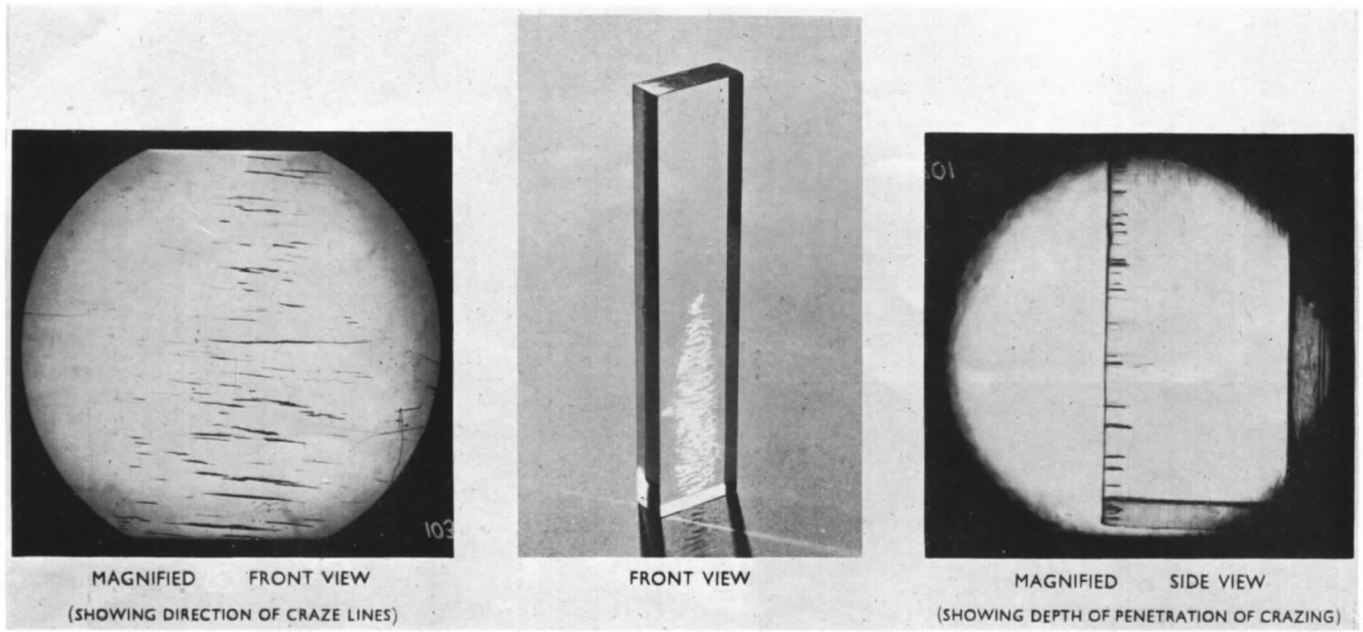
FIG. 11 (section 4.8).   Directional crazing of tension face.   Combined bending stress and solvent.
(Heat-treated sample, benzene solvent applied only to the central portion of sample face.)
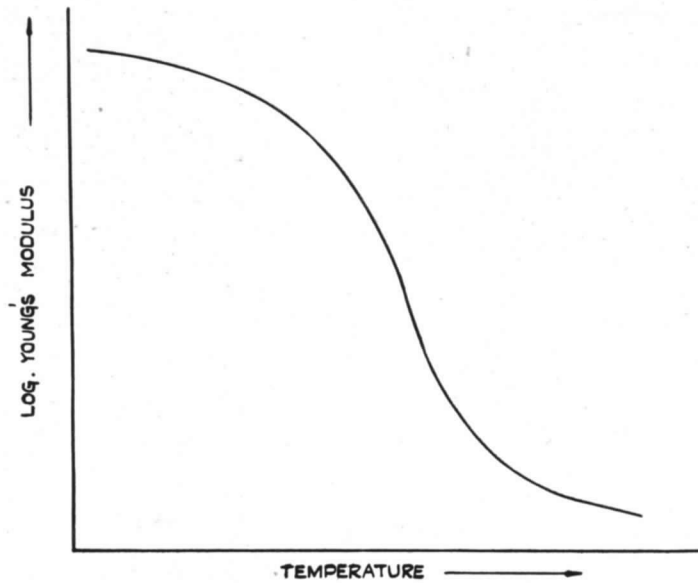
FIG. 12 (section 5.1).   " Stiffness " and temperature.

24
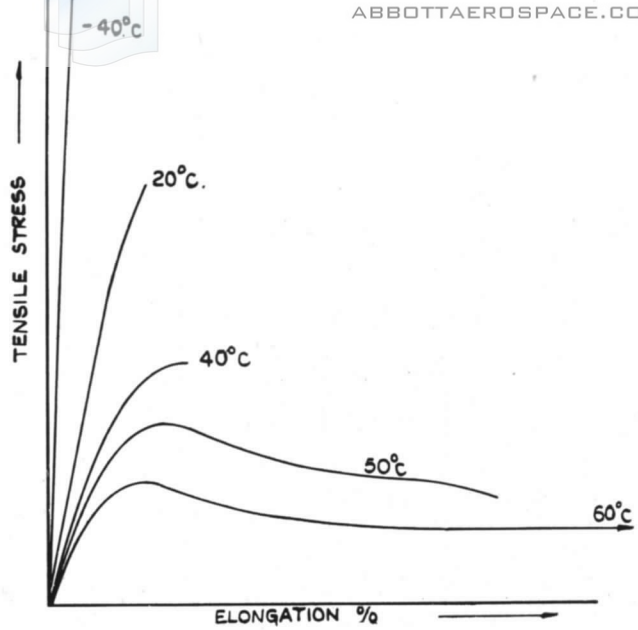
FIG. 13 (section 5.2). Tensile stress, elongation and
temperature (Carswell and Nason).
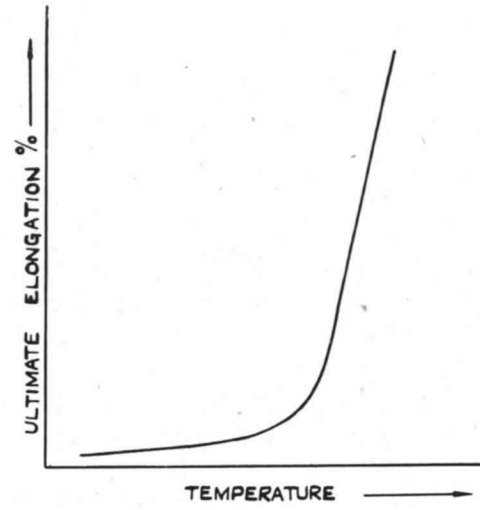
FIG. 14 (section 5.2). Ultimate elongation and
temperature.

25
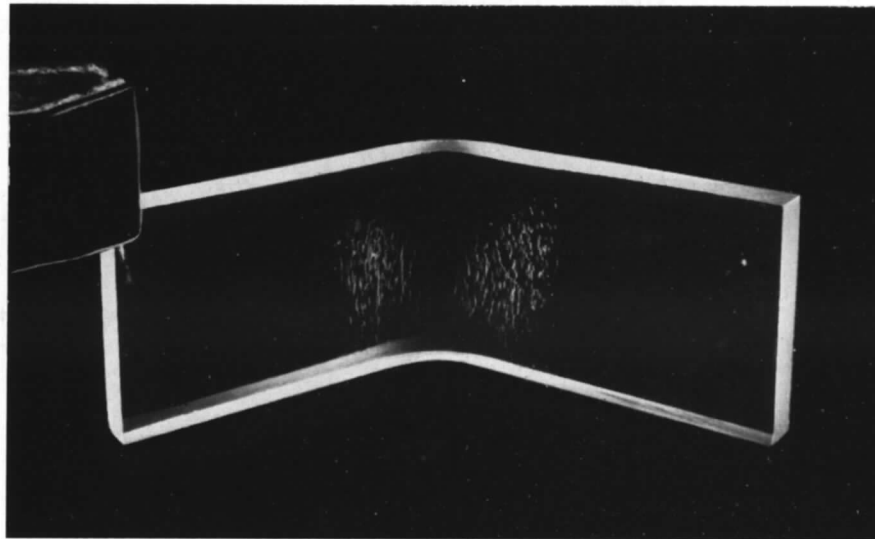
FIG. 15 (section 5.4). Crazing due to forming at too low forming temperature
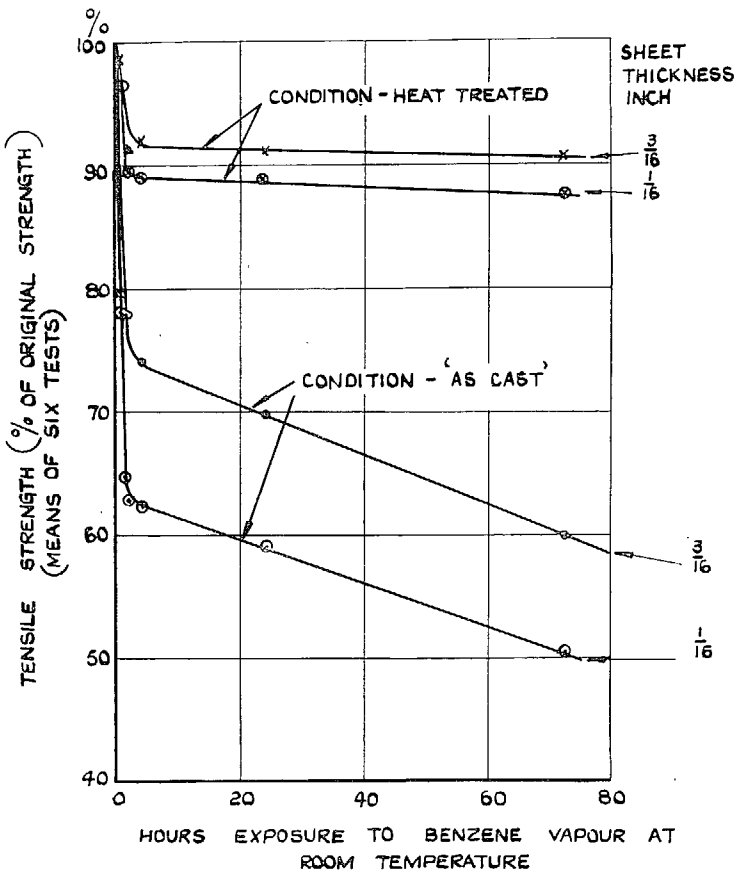(Stress and solvent crazing in heat-treated material).

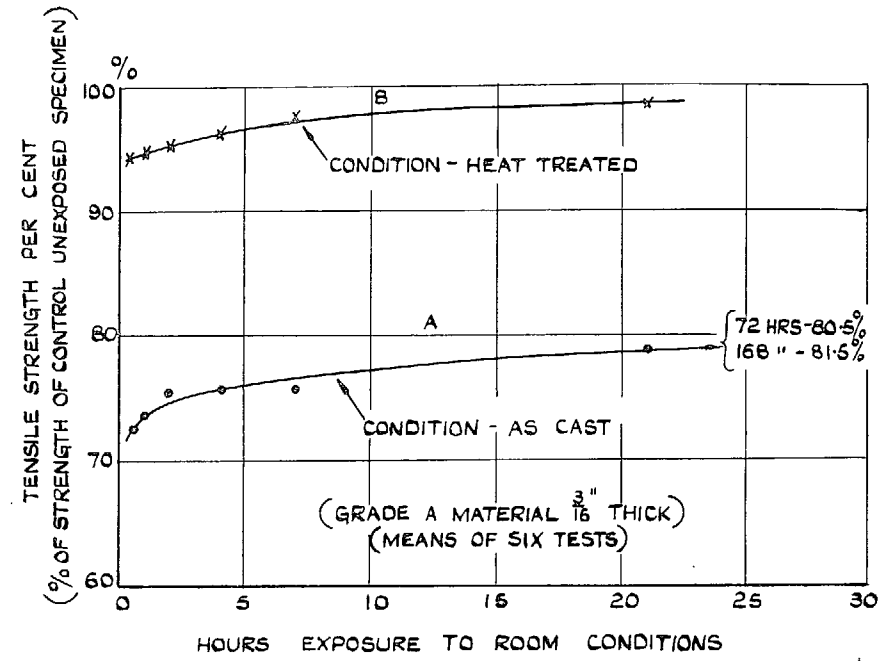FIG. 16 (section 5.8). Loss of tensile strength with exposure to solvent vapour.

FIG. 17 (section 5.8). Recovery in tensile strength with exposure to room conditions after 1 hr in benzene vapour.

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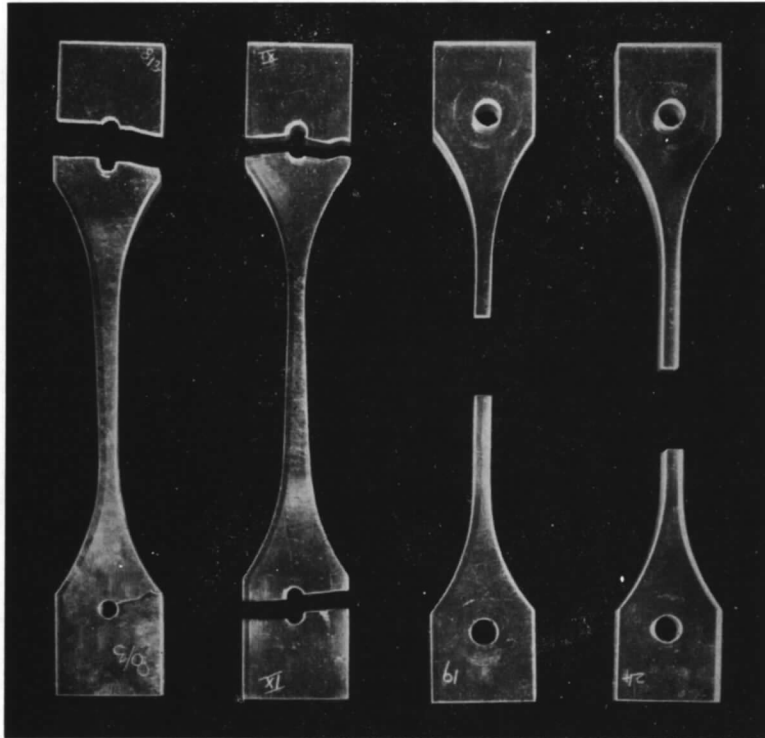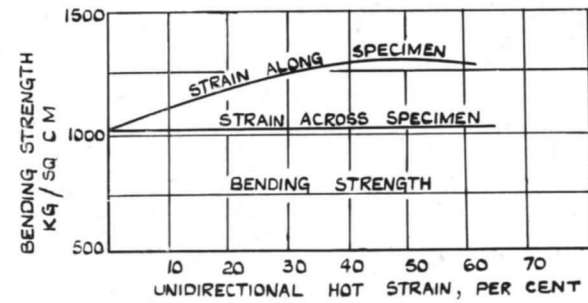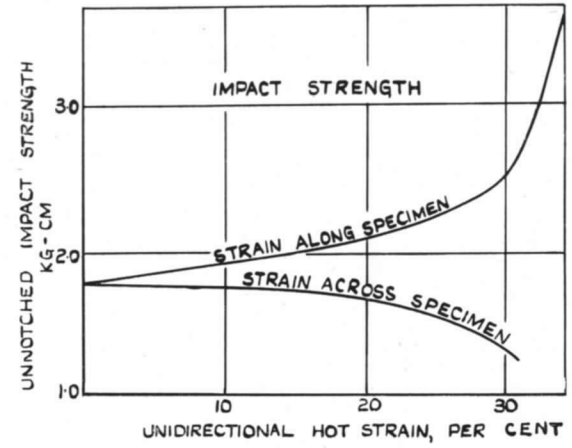
FIG. 18 (section 5.10).   Bolt hole failure.

FIG. 19 (section 5.11).   The influence of hot forming on mechanical strength (Rogowsky)[11].

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