THE RELATION BETWEEN CHEMICAL STRUCTURE AND MECHANICAL BEHAVIOUR OF PHENOLIC RESINS

High-speed shearing of paper-based phenolic laminates

by

Keith Leslie Watson, B.Sc., A.R.I.C.

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SUMMARY

A wide range of electrical and electronic components are produced by punching from paper-based phenolic laminates. The inherent brittleness of these materials often leads to various defects around the punched edges. Plasticisation of the resin may be used to overcome this problem but industrial methods are largely based on empirical observations and there is a need for a greater understanding of the fundamental principles involved. There is also a need for information about which phenolic starting materials, readily capable of commercial synthesis, may be used in manufacturing laminates which are easily punched.

An investigation into these problems has begun by instrumenting a power-press, such as might be used in commercial practice. A technique has been developed to enable the stress/strain characteristics of a laminate to be observed over a wide range of temperatures during the punching process.

This technique has been used with a series of commercial materials to provide background information about industrial practice against which information from experimental materials may be examined. The effect of processing variables introduced in preparing laminates from a given resin/paper system has been investigated to preclude the unanticipated

influence of such variables in comparing different resin compositions. This preliminary work has shown that punching temperature is of primary importance but that the type of base-paper used is also important. Processing variables show surprisingly little effect provided that resin content and laminate thickness are held constant.

A comparison of laminates based on different papers, but otherwise similar, has shown that, of the papers in common use, bleached kraft is the most suitable for demonstrating resin effects.

Work with different resins has suggested that, apart from cross-link frequency, the presence of hydrogen bonds may influence their brittle behaviour. Further work has been suggested to investigate this observation.

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CHAPTER 1.

THE PROBLEM

1.1. Long term view.

The work described in this thesis represents the first stage of an extended investigation into the effect of the structure of phenolic resins on their mechanical properties.

The specific area covered by this part of the work is the effect of resin structure on the punching properties of paper-based phenolic laminates. The fundamental basis for this lies in the need for manufacturing synthetic starting materials for phenolic resins because of the increasing difficulty in obtaining coal tar products. It is hoped that this project, taken as a whole, will help to show which phenolic starting materials, readily capable of synthesis, may be used in manufacturing paper-based laminates which are easily punched.

Apart from such politic considerations, laminate manufacturers are likely to be interested in any attempt to gain further understanding of the punching process which, for them, presents many real day-to-day problems.

As will be seen, the present work has not gone very far towards answering the first question but has

laid down a technique which is likely to enable this to be done. It has certainly provided some further understanding of the way in which commercially available laminates behave. As a result of this, commercial support for the project has been extended for a further three years. Without undue optimism it could be predicted that this period might well provide some of the answers to the primary question.

1.2. Statement of the problem.

The reinforcement of brittle solids with natural fibres is a long established technique. The ancient Egyptians added chopped straw to clay for making bricks and the Mayas and Incas incorporated vegetable fibres into pottery. In both cases it seems likely that the reason for this was to prevent cracking during the shrinkage of the clay as it hardened. The crack stopping properties of the reinforcing filler during use appears to have been an incidental benefit.

Both advantages are apparent in the reinforcement of phenolic resins with cellulose fibres. This technique enables a wide range of mouldings to be prepared under high temperature and pressure conditions and to enable these to withstand the demands put upon them in service.

Laminates may be prepared by impregnating paper with phenolic resin and hot pressing a pack of impregnated sheets to give a consolidated board. Such

paper-based laminates are used in the electronic and electrical industries for making a wide range of components, notably printed circuit base boards.

Although the basic process for manufacturing paper-based phenolic laminates is simple there is a considerable number of variables which need to be controlled to enable satisfactory materials to be produced with reproducible properties.

There is a wide range of phenolic resins used in the production of laminates. Such resins are made by the chemical condensation of phenol and formaldehyde, usually in the presence of a catalyst. For electrical grade laminates the presence of electrolytes in the finished product is undesirable and ammonia or barium hydroxide, which can easily be removed as an insoluble salt, are often used as catalysts.

The nature of the phenol used is dependent upon its source. Phenol itself may be either synthetic or natural. Natural phenol is obtained by the distillation of coal tar and is available in various degrees of purity. Substituted phenols such as the cresols and xylenols are also produced by coal tar distillation but synthetic methods are now being introduced.

The formaldehyde is normally used as formalin which is an aqueous solution of formaldehyde (often about 37% HCHO w/w) usually containing methanol to

stabilise it against the precipitation of formaldehyde polymers. Higher aldehydes are sometimes used and paraformaldehyde can be useful when the presence of water is undesirable.

In a typical industrial process for resins used in laminating (resoles) the reactants are mixed together and heated to reflux until the formaldehyde has combined with the phenol. The reactions involved and the products obtained depend upon the nature of the reactants, the catalyst and the conditions employed. This has been discussed in a large number of text books and papers and some of those relevant to the present work will be referred to later. The next stage of the process involves vacuum distillation during which water, and sometimes other low molecular weight materials, are removed and the molecular weight of the resin is increased. Water is a product of the reaction and as it is removed by distillation the reaction is forced towards yielding a high molecular weight product. When the resin has reached the required molecular weight it is dissolved in a suitable solvent (often industrial methylated spirits) and the solids content and/or viscosity of the solution adjusted as necessary. The resin solution is now ready to be brought in contact with the paper.

The papers used are many and varied. They generally contain no size or adhesive and tend to

consist of pure cellulose held together by jackstraw arrangement with some degree of hydrogen bonding (semi-chemical bonding).

Natural kraft papers are made from ground soft wood pulp with minimal mechanical and chemical treatment. They contain only slightly modified cellulose together with natural resins (lignins) and consist of long, strong fibres which are somewhat impervious and give strong laminates with poorer electrical properties.

Bleached kraft, alpha cellulose and cotton linter constitute the main types of white papers used. Cotton linter fibres have a natural tubular structure. Bleached kraft and alpha cellulose papers are made from highly treated cellulose from which lignins and other non-celluloses are removed. The fibres are somewhat degraded having a more or less open cell structure and an irregular rod-like appearance. Thus these papers have lower strength and higher capability for absorbing resin and give better electrical properties.

Further factors influencing the properties of the finished laminate are introduced when the paper and resin are brought together. The paper, in roll form, is unwound to pass through the resin solution. This stage partly determines the resin content of the impregnated paper. Resin content depends primarily upon the type of paper and the nature of the resin

solution. However it will also depend on such factors as the speed of the paper through the solution, whether the paper is totally immersed or wetted on one side only and the presence of "doctor rolls" to remove excess resin after the paper emerges from the solution.

The solvent is then removed by passing the paper through a hot-air oven. Residence time and temperature are obviously important. Conditions may be adjusted merely to remove the solvent or, in addition, possibly to provide some further advancement of the resin. There is also the possibility of some resin loss from the paper at this stage if the molecular weight is not sufficiently high.

The dried impregnated paper is now cut into sheets which are assembled into packs. The sheets may be alternatively crossed to minimise any effect due to fibre orientation in the base paper. The packs are now pressed between stainless steel sheets or "press cauls" at high temperature. Typical pressing conditions for a laminate 1/16 in thick might be 1000 lbf/in^2 for 1 hour at 150^{o}C.* In this way laminates may be prepared up to 10 in thick but

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* The units used throughout this thesis are those in normal technological use in this country and the U.S.A. when discussing a particular point.

punching stock is usually about 1/16 in thick.

It is clear that there is a large number of variables arising from the choice of resin and paper and from the selection of impregnating, drying and pressing conditions. However, the story is not yet complete since a further important factor, related to those above, lies in the interaction between resin and paper fibres.

This can be resolved into four components:

1) physical wetting of the fibres by the resin,
2) removal of air from around and inside the fibres,
3) chemical bonding between resin and fibres, and
4) filling of voids between fibres with excess resin.

The proportion of resin usually lies between 30% and 50% by weight and that of voids is usually less than 5% by volume.

Wetting is controlled by the absorption of the paper and the viscosity and hydrophilicity of the resin. The more complete the wetting, the more brittle is the laminate and the better the electrical properties because of the reduction in water absorption. Less wetting gives a stronger, tougher and more water absorptive laminate which has poorer electrical properties. The closer the relationship between fibre and resin (e.g. with a paper having high resin absorptive properties and using a low viscosity aqueous resin solution) the more homogeneous the

laminate. In this case the changes in composition and properties at the interfaces between resin and fibre are minimal. This results in poor ability to absorb vibrations or shock loads, and hence in poor punching properties and a highly brittle nature.

Many hydroxyl groups are present on the surface of the cellulose. These may react with some resins but not with others. Hence hydrophilic resins will wet the fibres whereas hydrophobic resins will not. It may prove advantageous to subject the paper to several different impregnations; for example, the paper may first be impregnated with a small amount of a hydrophilic resin which will give good wetting, and subsequently the paper may be impregnated with a larger amount of hydrophobic resin to build up the desired properties.

One of the most useful methods of making electrical components from paper-based phenolic laminates in sheet form is by punching. This may either involve the piercing of holes, the blanking of individual components or a combinatinn of both. Some of the technological aspects of punching techniques, tool design and the design of punched components will be briefly discussed later. The main disadvantage of the method lies in the inherent brittleness of the laminates themselves which can lead to various defects around the punched edges.

As will be seen later, these defects often appear to originate from the inability of these materials, under unfavourable conditions, to resist the propagation of cracks.

There are several methods of reducing this brittle behaviour by modifying the resin. Cured phenolic resins may possess a three-dimensional network structure in which the constituent molecules are cross-linked by primary chemical bonds. These are permanent in nature and their removal would result in destruction of the resin. They are partly responsible for the rigid, brittle nature of cured resins but secondary bonds of an electrostatic nature may also be present. In any case, the nature of the backbone structure is likely to lead to rigidity on steric grounds. Brittleness may be reduced by heating or by plasticisation. This may be due to reduction of secondary forces, the reduction of steric effects or possibly a combination of both although the mechanism is uncertain.

The brittle nature of laminates is often overcome in production by hot-punching the sheet stock. This usually provides sufficient "ductility" to enable satisfactory components to be produced although overheating must be avoided since this will lead to further embrittlement. Apart from economic disadvantages, accurate registration of punched holes

can be difficult because of thermal expansion and contraction of the material during this heating and cooling cycle. These and other difficulties make it desirable to devise cold-punching, or at least low punching temperature laminates. This may be achieved by the addition of external plasticisers to the resin, but over a period of time the plasticiser may migrate to the surface of the sheet and be lost. Alternatively, a variety of modifications may be introduced into the final cured structure of the resin leading to permanent internal plasticisation.

The complexity of the situation is quite obvious. Partly because of this and partly because of the understandable reluctance of industry to release manpower, equipment and time for research, the approach to methods of improving punching quality has been largely empirical. It, therefore, seemed an appropriate task in a Technological University, to attempt this project with a view to setting the problem on a more fundamental basis.

The objective can therefore probably be best summarised as follows :
to obtain a greater understanding of the punching of paper-based phenolic laminates by reference to structural features of the finished material, the paper fibre and especially to the resin.

1.3. Approach to the problem.

It should be emphasised that this thesis is only concerned with the punching characteristics of laminates. Other properties were not examined unless they were necessary to help in the interpretation of punching data.

It was first necessary to establish a technique whereby the punching characteristics of a laminate could be evaluated over a wide range of punching temperatures. This was achieved by instrumenting a power press, such as might be used in industrial practice, to enable stress/strain characteristics to be observed during the punching process. Facilities were provided for preheating the test-pieces and maintaining them at the required temperature until immediately before the punching operation. Apart from the shape of the stress/strain curves, materials were characterised by stress at break, strain at break, time to break and an independent visual assessment of punching quality.

The test procedure was established by reference to a commercially available medium punching temperature laminate. The effect of delay between removal of the laminate from the heat source and the punching operation was examined. The effect of heating time and the onset of embrittlement at a punching temperature in excess of that recommended were also studied. The general

effect of punching temperature was examined using this material and a proprietary cold-punching grade. In the light of observations of other workers a hypothetical fracture process was suggested to explain the shape of the stress/strain curves obtained.

A series of commercial materials was then examined in order to obtain a background picture of punching characteristics obtained under conditions which typified those encountered in industrial practice. These results were somewhat marred by scatter.

Before any work could begin on the evaluation of the type of resin employed it was necessary to establish the effect of some of the variables encountered during the impregnating, drying and pressing stages of laminate manufacture. Part of this work involved the preparation of two laminates almost identical in all respects other than the type of paper used. The differences between these materials suggested the value of re-examining the commercial series with reference to the type of paper from which they were made. The manufacturers of the commercial materials co-operated by supplying the necessary information. Much of the scatter of the previous results was explained by 'grouping' of the materials according to paper type.

In order to find which paper was most suitable

for emphasising resin effects four laminates made from the same resin but different papers were tested over a wide temperature range.

In conclusion, four laminates were examined in which different resins were based on the same paper.

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CHAPTER 2.

LITERATURE SURVEY

The literature survey carried out in connection with this work presented some problems. There were many publications on aspects of empirical technology, especially articles about the design of tools and punched components, preheating techniques and patents covering resins formulated for good punching properties. On the other hand there were comparatively few publications relating to more fundamental studies. From discussion with people involved in the industry this appeared to reflect the general state of knowledge in the field.

This chapter will therefore review the literature somewhat selectively. It would be tedious to refer to all the publications found relating to the empirical technology so only those of particular relevance will be cited. Other publications, of marginal relevance, are listed in Appendix 1 for completeness.

Six papers were written about the work described in this thesis and will be referred to in due course. Copies of these papers have been placed in the pocket inside the back cover.

2.1. Empirical technology.

2.1.1. Design considerations arising from the nature of the process.

The punching process is essentially one of high-speed shearing. The external forces involved are illustrated in Figure 1 (taken from Hojo[35]).

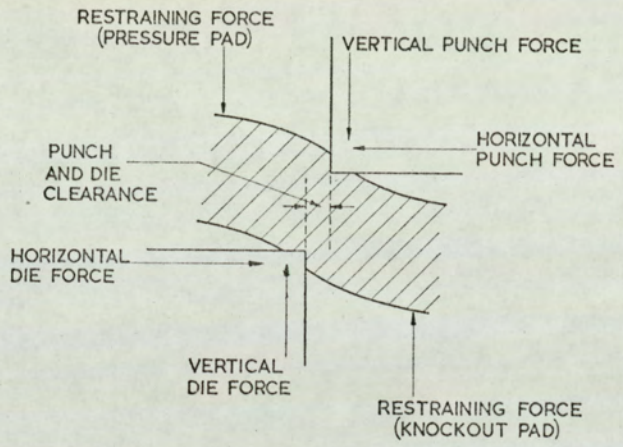

FIGURE 1. EXTERNAL FORCES INVOLVED IN THE PUNCHING PROCESS.

Basically the tool-set consists of a punch and die. A force is provided by the punch and restraint of the material by the die. The combination of vertical and horizontal forces caused by the punch and die result in shear stresses in the region of clearance between the punch and die. The tool-set is usually provided with a combined pressure pad/stripper plate to hold the laminate firmly during punching and during the withdrawal of the punch. Occasionally a knockout pad

is used to apply an upward force to the blank but this is unusual. Minimal punch and die clearance together with the restraining forces supplied by the pressure pad and knockout pad tend to give 'pure' shear in the clearance region resulting in clean punched components. Although exaggerated in Figure 1, it can be seen that the laminate flexes during the punching process. Relaxation occurs after removal of the tool. Consequently a pierced hole will be slightly smaller than the punch which produced it. As a result of this the material will 'bind' onto the punch during withdrawal. It is, therefore, necessary to ensure that clearance between punch and stripper plate is small to avoid delamination on withdrawal.

Practical considerations in designing punched components and tool-sets for their production have been briefly discussed by Learmonth and Watson[1]. There have been many publications discussing aspects of the workshop technology involved but these are beyond the scope of the present work and are listed in Appendix 1.

2.1.2. Preheating techniques.

Because of the importance of heating laminates to the correct temperature before punching, preheating techniques will now be considered in some detail.

Where hot-punched precision parts are required, accurate temperature control must be achieved in order

to maintain accurate compensation for cooling contraction after punching. Hot-punching material is usually preheated at 40° - 140°C, the exact temperature and preheating time depending upon the grade of material and intricacy and quality requirements of the final product. Stel, Jacobs and Shriek[2] found that preheating for 5-10 min at 130° - 140°C gave the best results in their experiments. Frerichmann[3] and Chen[4] found 10-20 min gave the best results over the same temperature range for the material which they used. (Learmonth and Watson[5] found that for a medium punching temperature material (80° - 100°C) heating times of 1, 10 and 30 min gave similar results at 55°, 90° and 125°C. At 160°C, 1 min was insufficient whereas 20 min resulted in significant overcure.)

Laminates may be heated using hot plates, infra red lamps, oil baths or hot-air ovens. If a hot plate is used only the lower surface of the material is heated and contact is seldom even. Infra red lamps heat only the upper surface and temperature control may be difficult. The use of an oil bath necessitates a subsequent degreasing operation which is time-consuming and can result in removal of plasticiser from the laminate. Hot-air ovens provide good temperature control and are clean in operation but, as with all these methods, suffer from the

disadvantage that the heated material must be carried from the heat source to the press. This results in cooling of the material which, together with further cooling during the punching process, sometimes necessitates reheating with consequent danger of embrittlement. In instrumented punching experiments Radovsky, Kendall and McHerron[6] showed that laminates became cool within seconds to give results approximating to those of an unheated material. (Learmonth and Watson[5] found that for a medium temperature punching material heated at the correct temperature (90°C) for 10 min, a delay of 10 s at room temperature could be tolerated with little change in punching characteristics, but after 30 s significant deterioration occurred. After 200 s delay the material gave results approximating to those of an unheated material.)

All these difficulties may be overcome by attaching a suitable heater to the press itself, through which the strip material may be fed. Such a device may be heated in any convenient way, but one particular method[7,8,9,10] has several advantages. The material is fed through an air-heated guideway, the exhaust air both heating the tools and keeping them free from swarf. The stock is heated to the required temperature once only so that blistering and overcuring are avoided. The method is clean and

continuous and output is considerably improved.

2.2. Resins for punching laminates.

2.2.1. Commercial resins.

One of the longest established techniques for plasticising phenolic resins for punching laminates involves the addition of esters such as dibutyl phthalate, tricresyl phosphate and ethyl abietate[11]. The main disadvantage of this technique is that such esters, being physically dispersed in the cured resin, are liable to migrate to the laminate surface and to be lost from the system although there is the possibility that ethyl abietate might react into the resin structure.

Cashew Nut Shell Liquid (C.N.S.L.) has also been employed as a plasticiser for over 20 years[12] and is still in use[13]. This material contains phenolic constituents which possess long linear unsaturated hydrocarbon side-chains. Thus the side-chains, having the plasticising properties, are permanently bonded into the resin structure by means of the phenol group. Plasticisation with C.N.S.L. will be discussed later in more detail.

The use of natural oils is a popular and long established method of plasticisation[14,15,16]. These materials have presumably found their way into the laminate industry through surface coating technology where some of them are used as drying oils. Many are

rich in glycerides of unsaturated fatty acids and, as in the case of C.N.S.L., therefore provide unsaturated hydrocarbon chains. There appears to be some uncertainty as to whether the oils are chemically bonded into the resin structure, but one method claims that by using epoxidised oils[16] permanent bonding may be achieved by reaction at the phenolic hydroxyl group or, in the case of resoles, at the methylol groups.

A further way of introducing long chain hydrocarbons has been to incorporate fatty acids[17] into the resin structure. It has been suggested that oleamide is capable of reacting into the chemical structure[18] leading to permanent plasticisation. Polyamides, such as that based on ethylene diamine and dilinoleic acid[19], offer further possibilities.

Phenethyl phenol and phenisopropyl phenol may also be used as plasticisers[20]. These may be prepared by reacting styrene or alpha methyl styrene with a phenol in the presence of sulphuric acid. It is interesting to note that the same company which patented this method later patented a phenolic resin made from styrene, phenol and a vegetable drying oil[21].

This discussion of the patent literature has been brief and gives a greatly simplified picture. Nevertheless, the point is still quite clear. If these examples are representative of commercial practice, then the most widely adopted method of

plasticisation of phenolic laminates for punching applications is by incorporating hydrocarbon chains (usually unsaturated) into the resin structure.

2.2.2. Published experimental work.

There appears to have been little published experimental work on the effect of resin composition on punching properties.

Freeman and Traynor[22,23] plasticised phenolic resins by introducing substituents into the phenol molecule which, they suggested, prevented the close approach of polar centres by steric hindrance with consequent reduction in hydrogen bonding. They reasoned that since the phenol molecule is planar, a substituent which is out of plane to the greatest extent should create the maximum interference to the close approach of the planes and thus of the polar hydroxyl groups attached to these planes. They found that, by incorporating meta-isopropyl phenol into the resin, effective plasticisation was achieved.

Sprengling and Traynor[24] incorporated nitrile rubber into phenolic resins resulting in improvement of their cold-punching properties. They suggested a reduction in hydrogen bonding resulting from the presence of a flexible chain 'diluent' and by the elimination of phenolic hydroxyl groups by chemical reaction between phenolic ortho-methylol groups and carbon-carbon double bonds in the nitrile rubber.

Some attention has been paid to the use of saturated hydrocarbon chains as plasticisers for phenolic resins. Brookes[25] prepared waxphenols by alkylating phenol with chlorinated paraffins and then prepared resins by condensation of the waxphenol and phenol with formaldehyde. Laminates made from these resins gave good cold-punching laminates. Doroshenko, Korshak and Sergeev[26] made phenolic resins from 1,6-bis(p-hydroxyphenyl)hexane, 1,8-bis(p-hydroxyphenyl)octane and 1,10-bis(p-hydroxyphenyl)decane. They found that their impact strength and flexural strength increased as the number of methylene groups between the phenolic nuclei. Although they did not punch laminates made from these resins they must have been aware of possible cold-punching applications since they referred to the work of Brookes.

Nakano[27] suggested that, by varying the initial reaction temperature in preparing a resin, punching characteristics could be altered. He found that a resin reacted initially at 70°C gave a laminate which required less punching load and less work to punch than laminates prepared from resins reacted at 40° and 100°C. His arguments about resin structure were somewhat nebulous and it is difficult to draw any useful conclusions. As will be seen later, however, his technique for measuring punching characteristics was of great interest in the present work.

The only real conclusion that can be drawn from the published experimental work is that there are suggestions that a reduction in hydrogen bonding may be partly responsible for good cold-punching properties.

2.3. Punching tests.

It is clear, both from the literature and from discussion with people involved in the commercial manufacture of laminates, that there is no satisfactory method of evaluating punching quality. The reasnn for this seems to lie in the complicated behaviour of phenolic laminates during the punching process. As will be seen later, this behaviour can lead to a variety of defects in a punched component. However, attempts have been made to devise punching tests and these are now examined.

2.3.1. Standard tests.

Standard methods of assessing punching quality exist in Germany, the United States of America and in Great Britain.

The German Standard DIN 53 488[28] employs a carefully specified die-set which produces a test-piece having nine diamond-shaped holes with apices spaced progressively closer together. The shortest distance remaining uncracked divided by the nominal thickness of the material forms the basis of the evaluation. Either preheated or cold test-pieces

may be used.

The American method is given in ASTM Standard D 617-44[29]. A standard die-set is again employed and test-pieces are punched at room temperature and at 135°C. A separate numerical rating is assigned to each punched test-piece in respect of quality of edges, surfaces and holes. Ratings are assigned by reference to a prescribed set of standards. The average of the three values constitutes the measure of punching quality. A hardness test provides a control for uniformity of punching quality.

The British Standard 2076 : 1954[30] contains a piercing test in which a standard pattern, consisting of a series of squares, circles and diamonds spaced at various distances apart, is punched in a paper-based thermosetting laminate not exceeding 3/32 in in thickness. A blanking test is included in which a 1 in diameter blank is punched from material not exceeding 1/8 in. The quality of the punched test-piece is assessed visually. No quantitative assessment is specified. In British Standard 1137 : 1966[31] an optional punching test involves the piercing of a 1/4 in diameter hole in paper-based phenolic laminates not exceeding 1/8 in in thickness. Assessment is again visual and qualitative. It is laid down that the British Standard tests shall be carried out according to the manufacturer's

recommendations.

It should be noted that the German test is the only one that gives a quantitative assessment not dependent upon the judgement of the operator.

The "Gramophone Company Test" is used in India[32] and in this country. The test is based upon the tool pattern specified in British Standard 2076 : 1954 and a numerical value is assigned to the test-piece depending upon the presence of cracks between the various shapes of pierced holes. This test is really a more complicated version of the German Standard.

2.3.2. Special techniques.

There have been several attempts to examine the punching characteristics of paper-based phenolic laminates by rather more quantitative and objective techniques than described in Section 2.3.1.

Stel, Jacobs and Shriek[2] reported that they had examined the connection between the hardness of laminated plastics and the quality of components punched from them. They concluded that the hardness test provided a good method of assessing punching quality althoughthe correlation which they produced was not convincing.

Radovsky, Kendall and McHerron[6] described a technique in which strain gauges were attached to the punch. Forces involved in punching laminates were plotted against time using an oscilloscope. The

method was proposed as a potential technique for measuring ease of punching and for obtaining a 'machinability index' for a given material. Different materials gave different punching curves. Warming the laminates gave smoother curves which showed less punching force and less binding of the punch on the material. The method was envisaged as a quantitative non-operator controlled test which could be used on a standard industry-wide basis.

In a later paper Radovsky[33] considered progress in defining a punching quality test. 'Round Robin' punching tests with various tool-sets had been carried out using the ASTM Standard tool-set as a control. A needle penetration test of the Vicat type, apparently similar to that used by Stel, Jacobs and Shriek, had been examined together with the strain gauge method noted above. No real correlation was observed however. 'Round Robin' testing with the German Standard tool-set gave fair correlation with cold-punched but not with hot-punched samples. The results were compared with those obtained from punching oscillograms using an instrumented German Standard tool-set but the latter only provided values for peak force. Work had started towards a mathematical analysis of punching oscillograms. Radovsky's paper discussed the work of the NEMA/ASTM/IPC/EIA Steering Committee on Punchability, the purpose of which was to examine and

evaluate possible methods of determining punching quality and to make recommendations to the NEMA Test Facility at the University of Delaware. The NEMA Laboratory had the responsibility of fully developing and finalising the ultimate test method. The University of Delaware/NEMA report of March 1967[34] concluded that the German Standard was the best method yet available although the tool-set needed to be kept in good condition for significant results to be obtained. It suggested the possibility of simplification of the tool-set to give a pass/fail test. In discussing future work, the report began "If the problem of punchability has sufficient importance to merit further work .....". It was not clear whether this reflected lack of general interest in the work done so far or a lack of conclusive results for the efforts made.

There certainly seems to be the feeling among some workers in this country that some simplification is needed. Complications have arisen because of the number and variety of tests used. One well known Company making very high quality laminates uses three tests based on visual assessment but these do not correlate well.

Several attempts have been made to examine the punching properties of phenolic laminates by reference to their stress/strain characteristics during the punching process using instrumented power presses.

Hojo[35] and Frerichmann[3] studied the punching process by examining sections of test-pieces throughout the sheared zone by arresting the punch at various penetrations. They also examined the corresponding stress/strain properties. They both came to similar conclusions about the fracture process but this will be discussed in more detail later. Chen[4] described what appeared to be the same work as Frerichmann giving a more detailed description of the apparatus but made no reference to the fracture mechanism proposed by Frerichmann. Nakano[27] attempted an examination of the effect of degree of cure of phenolic resins on punching characteristics of their laminates. He came to similar conclusions to those of Hojo and Frerichmann about the fracture process by reference to inflections which he had observed in the stress/strain curves (see Section 3.1.1.). He made no reference to the appearance of the punched edges.

It seemed reasonable to conclude that any study of the factors influencing punching characteristics should not be entirely dependent upon visual assessment. The best chance of success appeared to lie in the more fundamental approach, involving the measurement of stress/strain characteristics, supported by a simple visual assessment of punching quality.

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CHAPTER 3.

EQUIPMENT AND PROCEDURE FOR DETERMINING PUNCHING CHARACTERISTICS.

3.1. Development of instrumented power press.

3.1.1. Practical considerations in measuring punch penetration.

The direct measurement of stress/strain characteristics during the punching process seemed preferable to the use of the partial penetration techniques used by Hojo[35] and Frerichmann[3]. Such techniques appeared unattractive because the rapid deceleration and reversal of the punch before complete penetration was not representative of commercial practice and may have introduced strain rate effects.

Nakano's method[27] seemed to offer the best approach and preliminary experiments indicated that the movement of the punch was responsible for the inflections which he observed in his load/penetration curves. This will be discussed later in some detail but the point is illustrated in Figure 19 (p. 61).

Neither Radovsky, Kendall and McHerron[6], Radovsky[33] nor the University of Delaware/NEMA report[34] mentioned any attempts to measure punch penetration.

Hojo[35] used the bottom face of the press ram as the reference point for his punch penetration measurements. This took no account of the deflection of the load transducer nor of any distortion of other

components between the press ram and punch face. Presumably as a result of this, he reported no inflections such as were seen by Nakano.

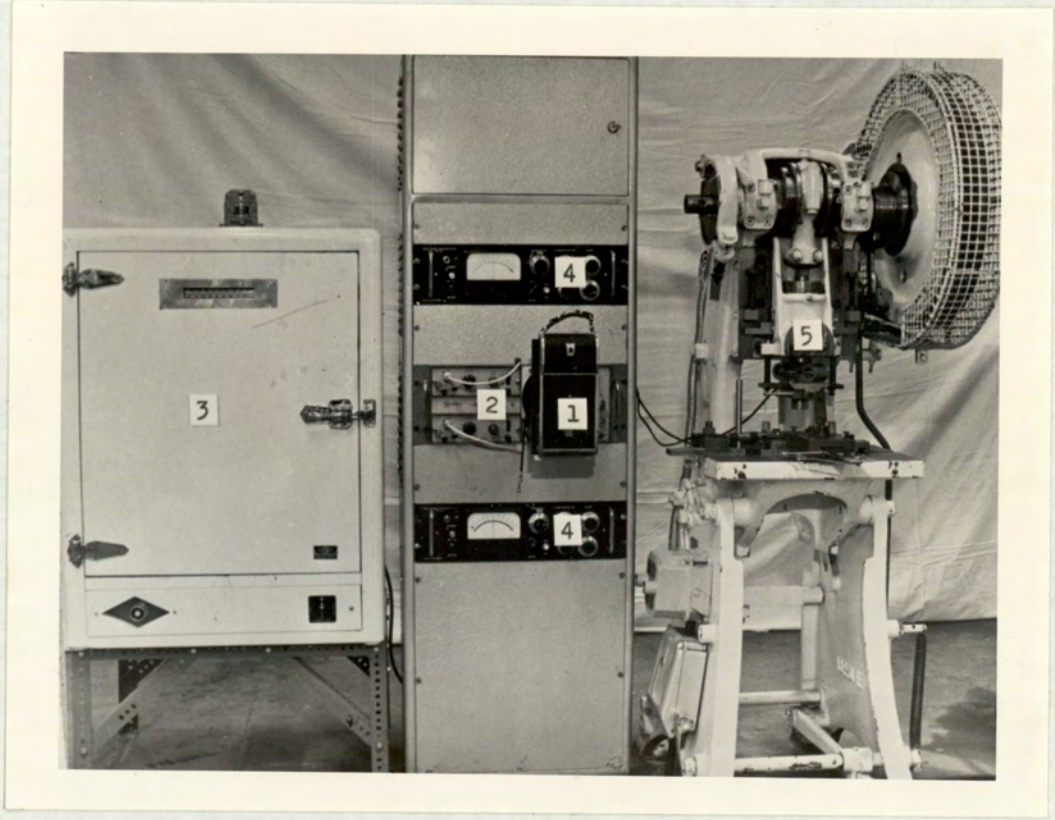
Frerichmann[3] and Chen[4] apparently describing the same work, did not offer sufficient information regarding their method of measuring punch penetration for comment to be made. However, Chen implied that the penetration values used were calculated rather than measured. It is perhaps significant that the force/penetration curves which they obtained were markedly similar to the stress/time curves obtained in the work discussed in this thesis. It appears that, by assuming the sinusoidal penetration/time relationship expected with a crank operated machine, they by-passed the strain/time irregularities which, as indicated earlier, are responsible for the significant inflections in the stress/strain curves.

Therefore, it seemed that Nakano's approach came closest to obtaining true force/penetration curves for the punching process. Nevertheless he still mounted the armature of his penetration transducer to the bolster plate supporting his punch. This did not preclude the possibility of slight distortion of the bolster plate influencing penetration measurement.

From the outset it was clearly necessary to fix the reference point for punch penetration measurement directly to the punch itself.

3.1.2. Description of the instrumented power press.

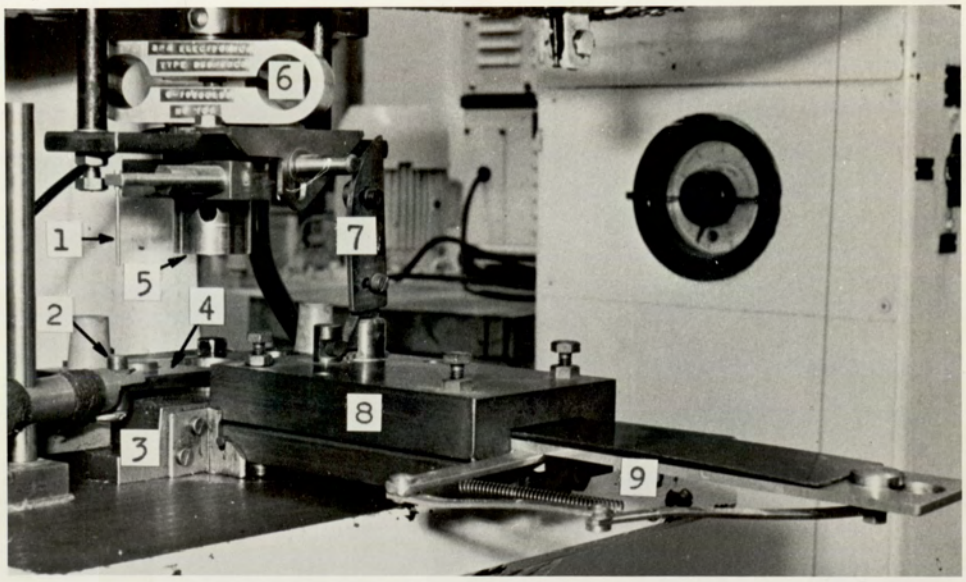
A photograph of the power press with its ancilliary equipment is shown in Figure 2.



1. Oscilloscope camera.
2. Double-beam oscilloscope.
3. Hot-air oven.
4. Transducer meters.
5. Power press.

FIGURE 2. INSTRUMENTED POWER PRESS

Figure 3 shows the press table layout.



1. Displacement transducer armature.
2. Displacement transducer.
3. Die block.
4. Stripper plate/compression pad.
5. Punch.
6. Load transducer.
7. Heating block trigger.
8. Heating block.
9. Heating block spring mechanism.

FIGURE 3. PRESS TABLE LAYOUT

The press was a commercially available crank operated machine of 6 tons capacity. (All the major items of equipment used in the experimental work are listed in Appendix 4.)

A circular punch was used which was 1.502 in in diameter and the clearance between punch and die was less than 0.001 in on the radius. A combined compression pad and stripper plate was used to hold the laminate firmly in place both during punch penetration and punch withdrawal. The clearance between the plate and punch was 0.009 in on the radius. The plate was driven directly by the press ram, through rubber buffers, to avoid superimposing its operating load on the measured punching load.

Two differential-inductance displacement transducers were used to measure punching load and punch penetration. These devices consisted of two coils mounted side by side on the same axis along which ran an armature. A transducer meter provided an a.c. signal in one coil which was induced in the second coil via the armature. The amplitude of the induced signal was proportional to the penetration of the armature in the second coil. This signal was returned to the meter and displayed as the movement of a needle over the meter scale. The signal could also be rectified, filtered and displayed on a cathode ray oscilloscope. The meter also provided a calibration signal equivalent to 100% full scale deflection (F.S.D.).

Punching load was measured against time by means of a load transducer mounted between the punch and the

press ram. The transducer was a proof ring incorporating one of the displacement transducers. As the proof ring deflected the armature moved relative to the coils. The output of the transducer meter used in conjunction with the transducer was fed into one channel of a double-beam oscilloscope.

Punch penetration was measured against time by means of the other displacement transducer used in conjunction with a second meter. The transducer armature was mounted on a support arm clamped directly to the punch and the transducer itself was clamped to the press table. The displacement output was fed into the other channel of the oscilloscope.

In operation the oscilloscope was triggered by the signal from the displacement transducer meter and a photographic record was obtained using a Polaroid oscilloscope camera.

3.1.3. Instrument calibration.

Load transducer.

The load transducer was calibrated against a standard proof ring using a 10 ton hydraulic press.

The standard proof ring was provided with a dial gauge and with calibration data giving the relationship between dial gauge deflection and true load. This data is plotted in Figure 4.

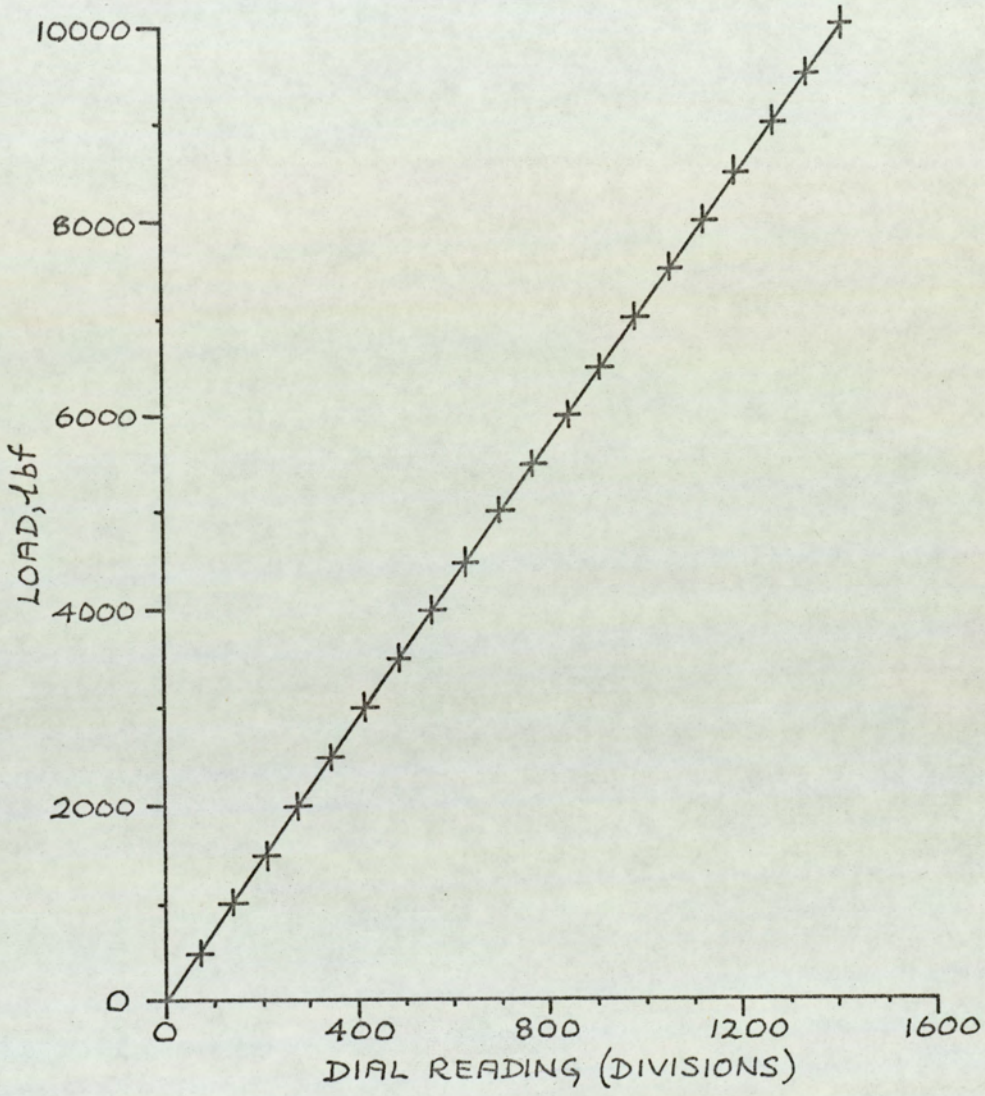


FIGURE 4. CALIBRATION GRAPH FOR PROOF RING.

Transducer meter readings are tabulated with corresponding proof ring dial gauge deflections in Table 1.

TRANSDUCER METER READING, % OF F.S.D.	PROOF RING DIAL READING, DIVISIONS	LOAD, lbf.
12.4	162	1180
22.4	306	2220
32.2	442	3200
43.8	604	4360
53.8	744	5340
64.0	896	6380
74.8	1050	7440
85.0	1192	8440
95.8	1346	9520
100.0	1408	9920

TABLE 1. LOAD TRANSDUCER CALIBRATION DATA

The load values are taken from the calibration data.

Figure 5 (p. 37) shows transducer meter readings plotted against load. From this it may be seen that 100% full scale deflection (F.S.D.) of the meter represented 9940 lbf and that the relationship was linear over the range employed.

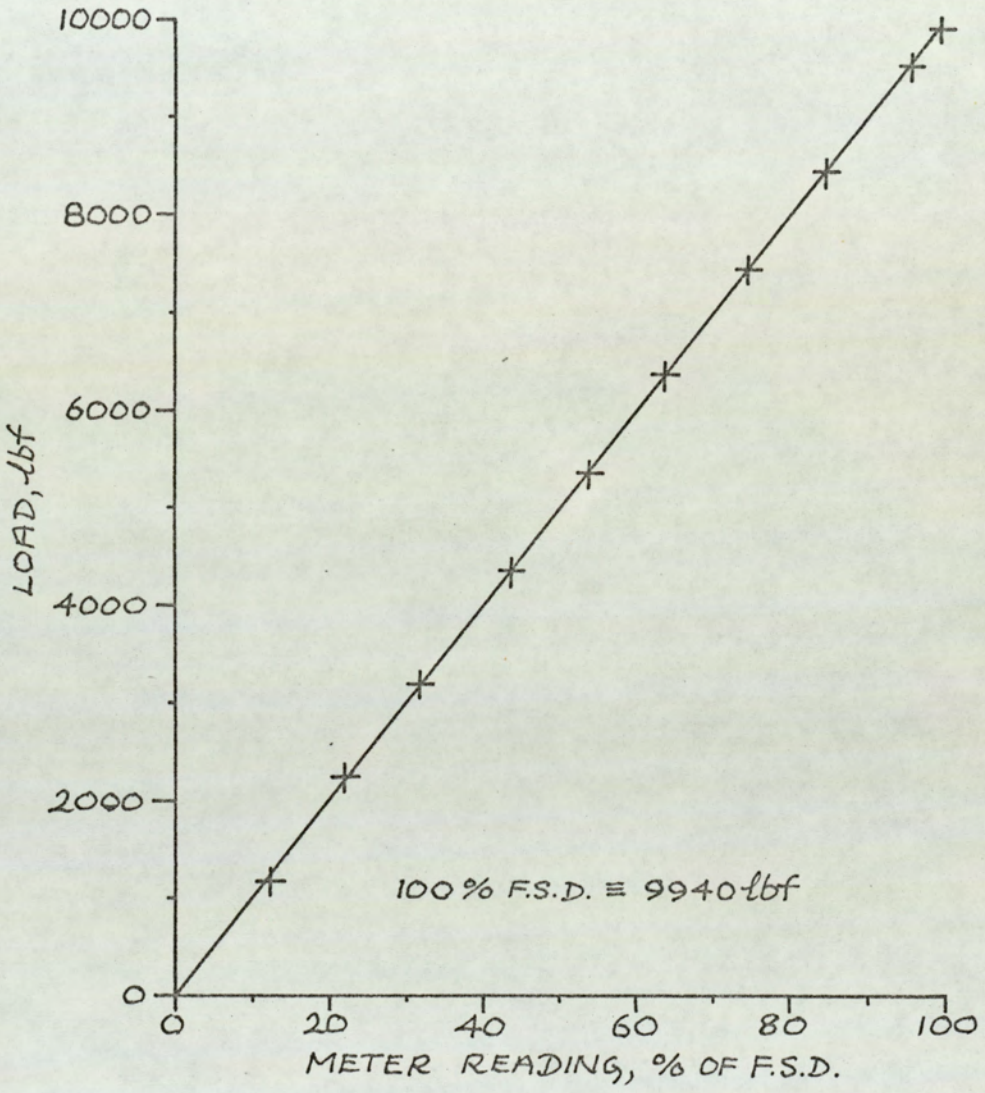


FIGURE 5. CALIBRATION GRAPH FOR LOAD TRANSDUCER.

Penetration transducer.

The penetration transducer was calibrated in its operating position on the press using a dial gauge clamped to the press table. Transducer meter readings

are plotted against dial gauge readings in Figure 6.

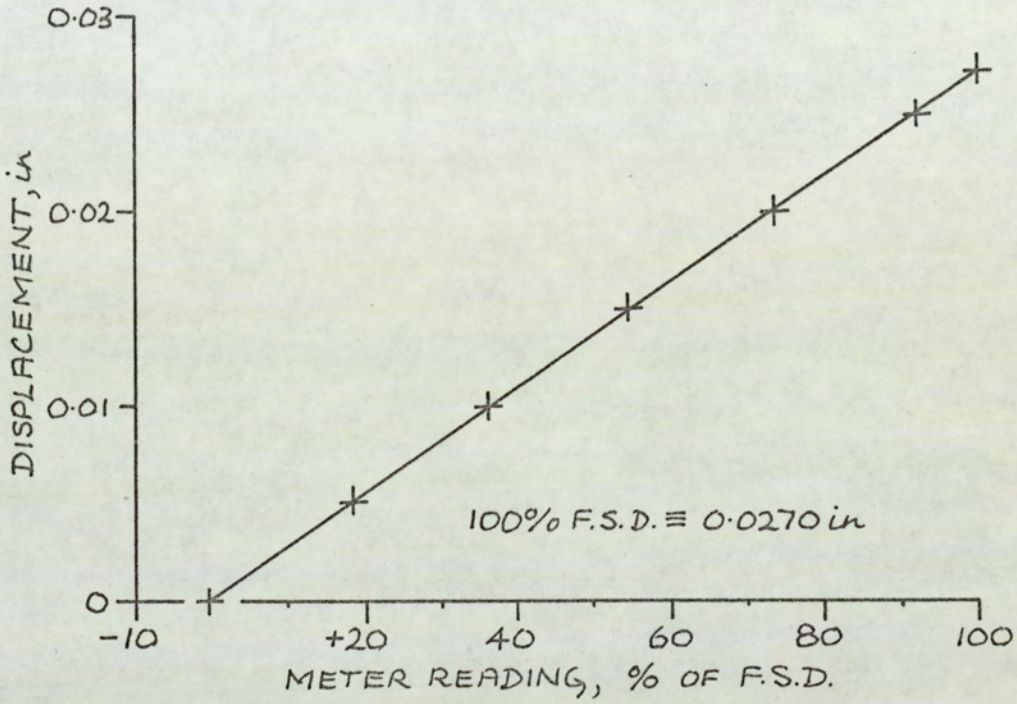


FIGURE 6. CALIBRATION GRAPH FOR PENETRATION TRANSDUCER.

From this it may be seen that 100% full scale deflection (F.S.D.) of the meter represented 0.0270 in displacement of the punch. The relationship was linear over the range employed.

Time calibration.

The oscilloscope was provided with facilities to enable mains frequency to be displayed as a square wave and this was used as the basis for time calibration. The 20 ms peak to peak trace was divided by 0.4, using the time base speed adjustment, to enable two peaks to be displayed on the screen in one sweep. This gave a

peak to peak calibration trace of 8 ms.

3.1.4. Preheating technique.

Since it seemed likely that punching temperature would be an important factor in this work then some careful thought was given to the method to be used for preheating the test-pieces. It was clearly essential that the temperature of the material should be closely controlled until immediately before the punching operation.

The only method described in Section 2.1.2. which seemed capable of achieving this conveniently was by using an air-heated guideway. The difficulty seemed to be in achieving the same degree of temperature control as provided by a hot-air oven.

A compromise was therefore effected by using a heating block which could be maintained at the correct temperature in a hot-air oven until shortly before the test. A rectangular slot through the block contained the test-piece. The block served to maintain the laminate at the test temperature from the time it was removed from the oven until the punching operation. A trigger and spring mechanism activated by the press ram ensured that the test-piece was projected into the tool-set within 0.2 s of the punching operation. The heating block and its trigger and spring mechanism may be seen in Figure 3 (p. 32).

3.2. Visual assessment of punching quality.

At the beginning of the work punching quality was simply assessed by the general visual appearance of each pierced hole. Points, from 0 to 6, were awarded for each test-piece by reference to a set of standards (see Figure 7).

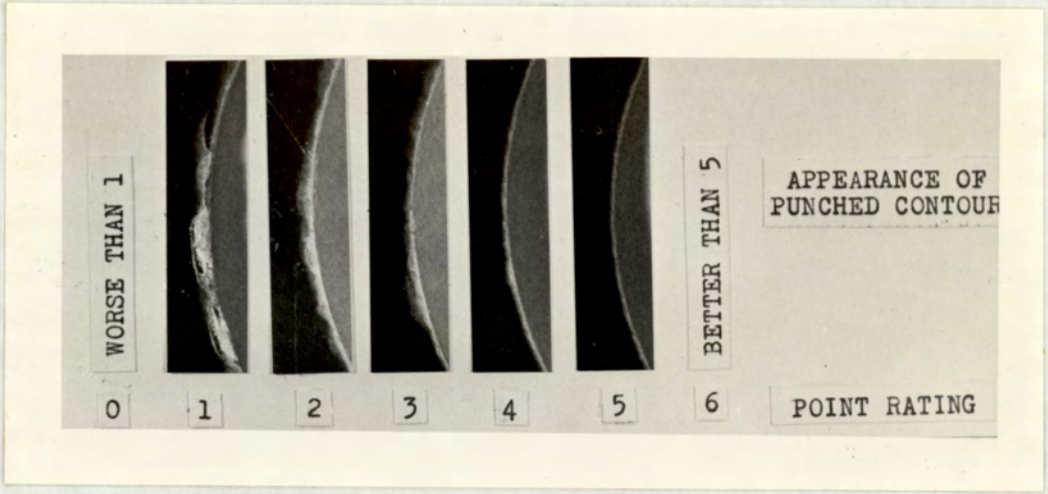
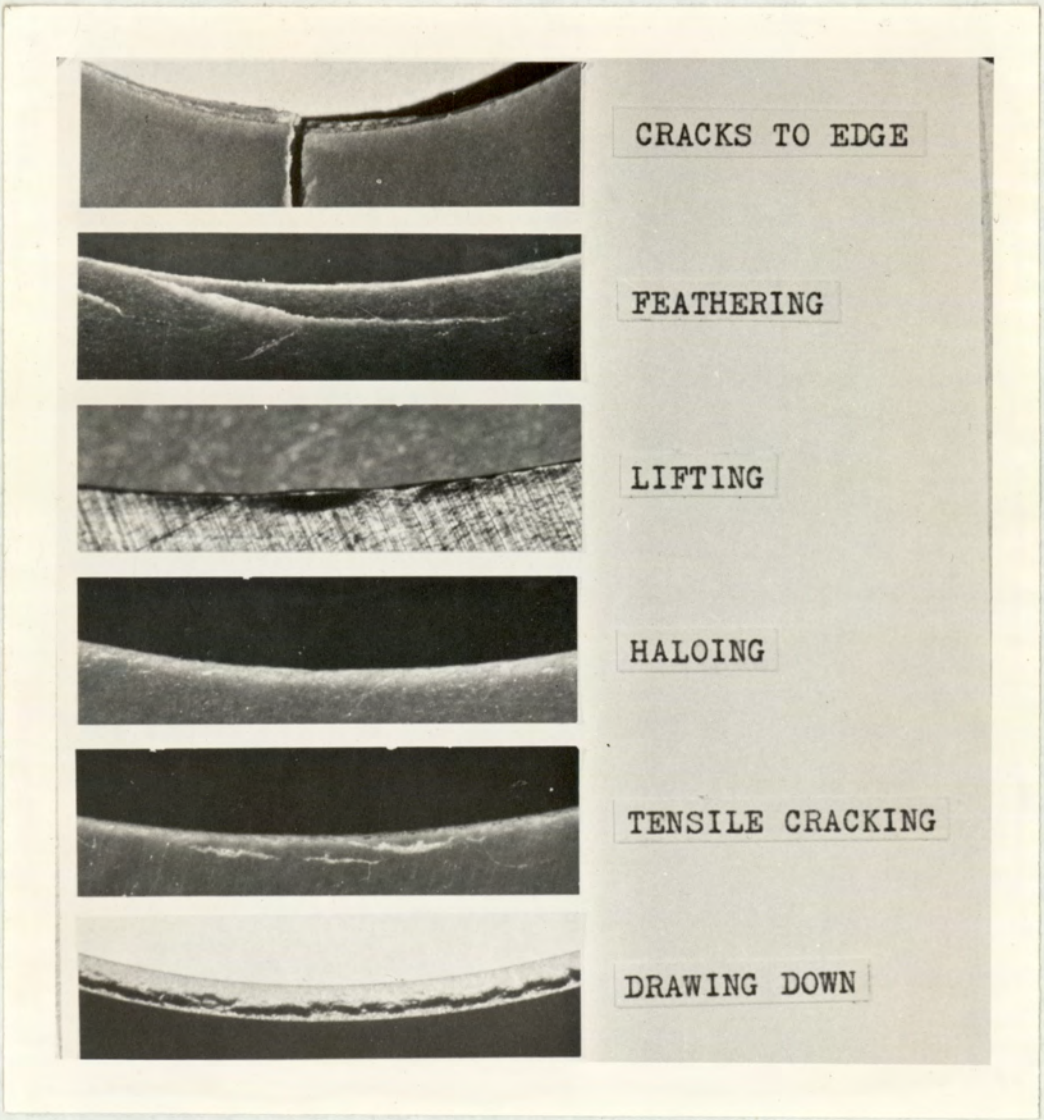


FIGURE 7. POINT RATING FOR VISUAL ASSESSMENT OF PUNCHING QUALITY.

Each test involved the use of five test-pieces and the total number of points scored by these represented the punching quality (P.Q.) of the material at that test temperature. As a rough guide P.Q. values of 10, 15, 20 and 25 were regarded as bad, poor, good and excellent respectively.

This approach had the great advantage of simplicity but as the work progressed it was sometimes

helpful to attempt to classify the types of defects seen in the test-pieces. The type of defects are shown in Figure 8. Their origin will be discussed in Section 9.4.1.



The scale may be judged from the diameter of the pierced hole ($1\frac{1}{2}$ in) and the laminate thickness (1/16 in nominal).

FIGURE 8. TYPE OF DEFECTS OBSERVED.

3.3. Determination of stress/strain characteristics.

The technique for obtaining the photographic records for the five test-pieces under each set of experimental conditions is now outlined. The derivation of the stress/strain curve from average stress/time and strain/time plots obtained from the photographs is illustrated by an example.

3.3.1. Experimental technique.

This section presents an outline of the test procedure finally adopted. Detailed operating instructions are not given here although these have been prepared for the benefit of future users of the equipment[36].

The transducer meters and oscilloscope were switched on to allow 15 min warming time before use.

Under the standard test conditions the test-piece (which measured 4 in x 2 in x 1/16 in (nominal)), was placed in the heating block 10 min before the punching operation.

5 min before punching the meters were zeroed and their calibration signals adjusted to 100% F.S.D. The load meter was zeroed internally but the penetration meter was zeroed by moving the punch by using a tommy bar through a hole provided in the press crank-shaft.

The press flywheel was switched on 90 s before punching.

When the press ram was at rest the penetration armature was completely withdrawn from the transducer. Although this was not harmful to the meter because of a built-in protective circuit, the manufacturers recommended reducing such a period as far as possible. The transducer meter was therefore not set to read punch displacement until 35 s before punching. (The load meter could, of course, be set to read with no such problems.)

5 s later the heating block was removed from the oven and fixed onto the locating slots in the tool-set and the spring mechanism was fitted.

The camera shutter was opened and the test-piece punched after having been in the heating block for 10 min. The empty heating block was then replaced in the oven and the press switched off.

The penetration transducer was zeroed and, by triggering the oscilloscope externally, zero baselines were superimposed on the oscilloscope traces already photographed. Similarly, F.S.D. calibration lines were also photographed.

The 8 ms square wave time calibration pulse was recorded and the electronics switched off.

The polaroid film was developed. An example of a photographic record is shown in Figure 9.

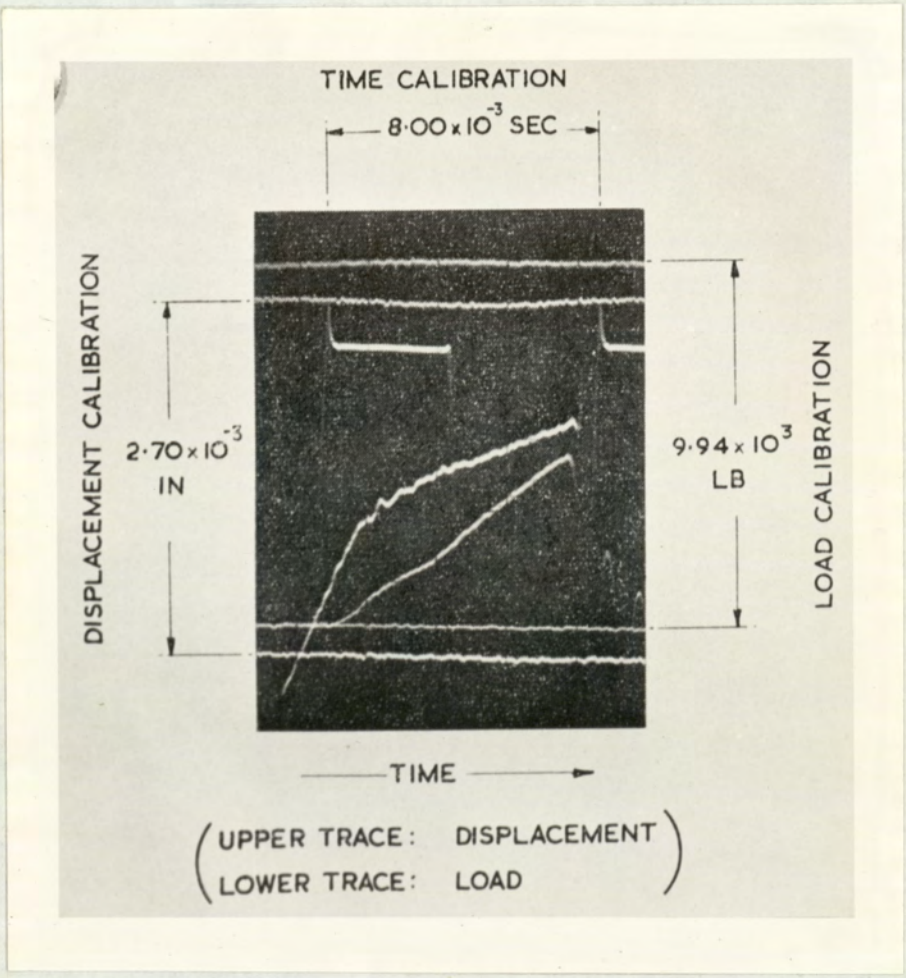


FIGURE 9. EXAMPLE OF OSCILLOSCOPE RECORD.

The test-piece was examined for assessment of the punching quality and the thickness of the test-piece measured with a micrometer. The average of four thickness values, taken at equal distances round the circumference of the pierced hole, was noted.

3.3.2. Example of derivation of stress/strain characteristics.

The method of deriving stress/strain characteristics from the five photographic records is now illustrated by reference to the Cashew Nut Shell Liquid (C.N.S.L.) plasticised laminate (see Chapter 8) punched at 160°C.

Using a translucent screen, illuminated from behind, the oscilloscope records were first traced onto the back of the photographic prints to facilitate measurement. The result for the first test-piece is shown in Figure 10.

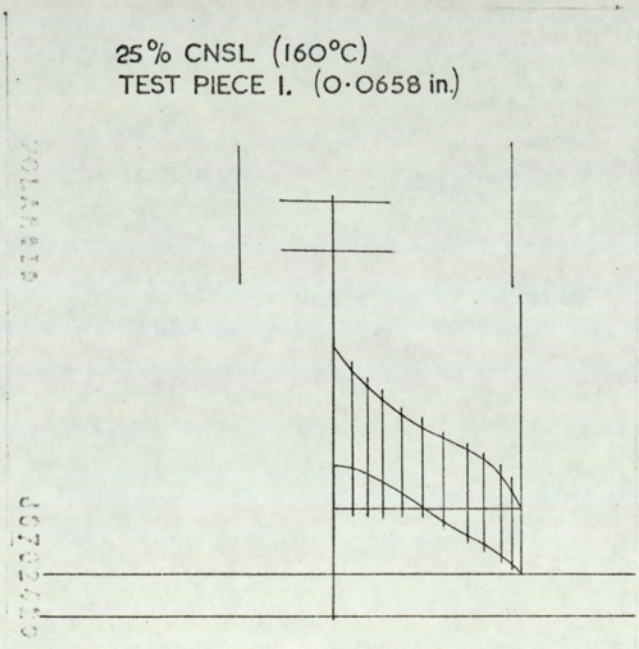


FIGURE 10. TRACING OF OSCILLOSCOPE RECORD.

Reference to the enlargement shown in Figure 11 will simplify the explanation.

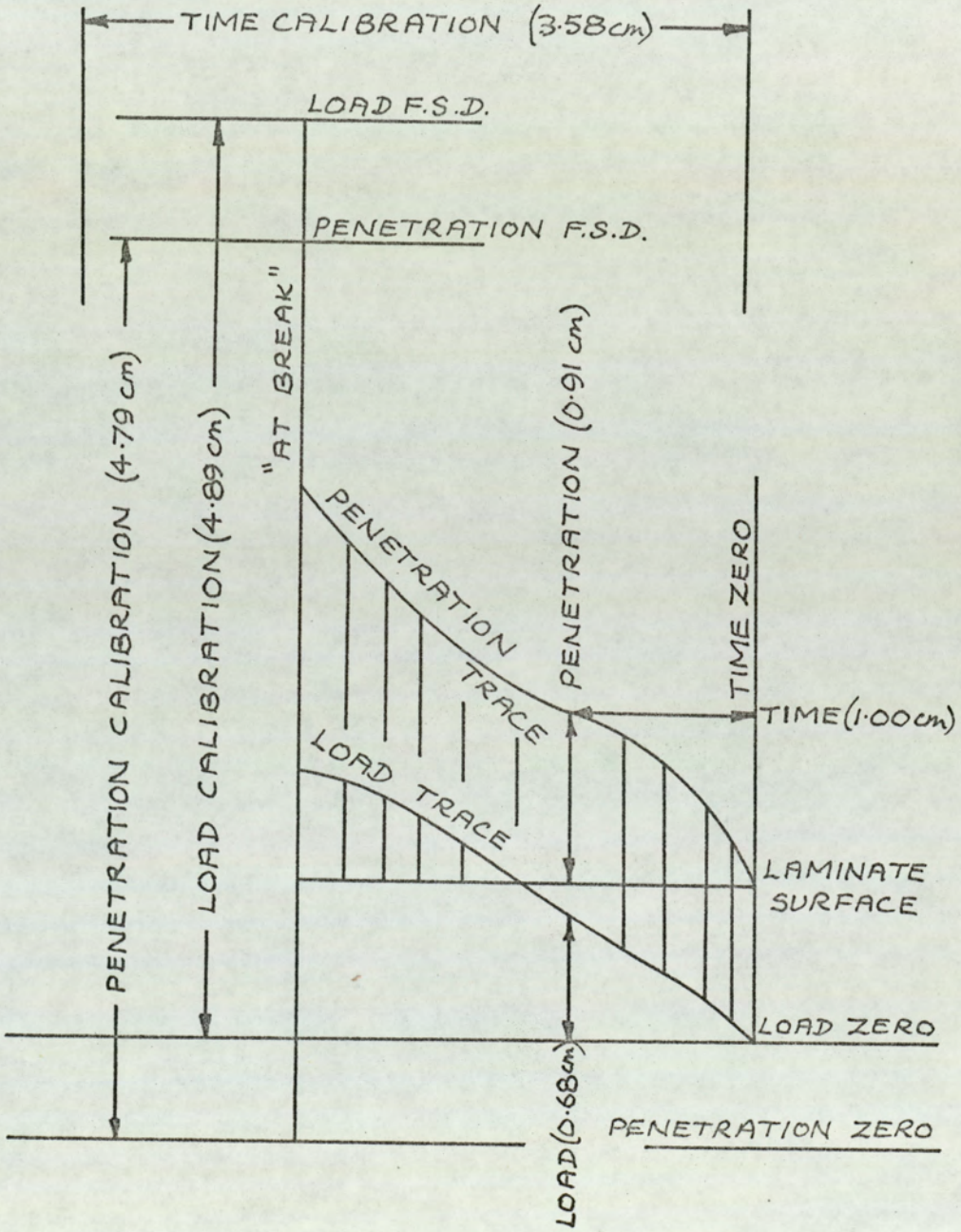


FIGURE 11. ENLARGEMENT OF TRACING OF OSCILLOSCOPE RECORD (NOT TO SCALE).

The lines corresponding to meter zero and F.S.D. for load and penetration calibration were traced first.

A vertical line (zero time) was constructed through the point from which the load trace left the load zero line. A horizontal line was constructed through the zero time point on the penetration trace. This latter line, in effect, represented the surface of the test-piece with reference to the penetration trace. The load and penetration traces were then drawn and a vertical line constructed 'at break' when the load trace fell rapidly away. This line was extended to intersect the calibration lines at F.S.D. and zero.

A series of vertical lines (i.e. each at one instant in time) were constructed to intersect the load and penetration traces and the 'laminate surface' line.

Finally the positions of the square wave peaks of the time calibration trace were drawn. Time, penetration and load measurements were then tabulated from the reconstructed trace as follows :

Time

The horizontal distance of each of the series of vertical lines from the zero time line was noted. For example, the fifth line was at a distance of 1.00 cm. The square wave peak to peak distance, equivalent to 8.00 ms was 3.58 cm.

Penetration

The vertical distance from the 'laminate surface' line to the penetration trace at each fixed instant of time was measured. For example, the fifth line gave 0.91 cm. The distance between the penetration zero line and its corresponding F.S.D. line gave 4.79 cm equivalent to 0.0270 in.

Load

The vertical distance from the zero load line to the load trace at each instant was measured, the fifth line giving 0.68 cm. The distance between the load zero line and its corresponding F.S.D. line gave 4.89 cm equivalent to 9940 lbf.

The values obtained by these measurements are set out in columns 1, 3 and 5 of Table 2.

TIME		STRAIN		STRESS	
Calibration factor $\frac{8.00}{3.58}$ ms/cm		Calibration factor $\frac{0.0270}{4.79}$ in/cm		Calibration factor $\frac{9940}{4.89}$ lbf/in^2	
cm	ms	cm	%	cm	lbf/in^2
0.12	0.27	0.22	1.9	0.13	850
0.26	0.58	0.42	3.6	0.25	1640
0.49	1.09	0.63	5.4	0.39	2560
0.71	1.59	0.78	6.7	0.51	3350
1.00	2.23	0.91	7.8	0.68	4460
1.29	2.88	1.06	9.1	0.88	5770
1.58	3.53	1.21	10.4	1.05	6890
1.81	4.04	1.41	12.1	1.21	7940
2.00	4.47	1.60	13.7	1.30	8530
2.21	4.94	1.80	15.4	1.39	9110
2.47	5.51	2.12	18.2	1.41	9250

TABLE 2. DATA FROM OSCILLOSCOPE RECORD

The values of time, strain and stress shown in Table 2 were obtained, using a slide rule, from the following general expressions where x, y and z are the respective distances, at any instant, measured from the photograph.

Time (ms) = x (cm) x calibration factor (ms/cm)

Strain (%) =

$$\frac{y(\text{cm}) \times \text{calibration factor (in/cm)}}{\text{laminate thickness (in)}} \times 100$$

Stress (lbf/in^2) =

$$\frac{z(\text{cm}) \times \text{calibration factor (lbf/cm)}}{\pi \times \text{punch diameter (in)} \times \text{laminate thickness (in)}}$$

(It should be emphasised that the terms stress and strain have been used rather loosely in this work. As can be seen above, stress was defined as load per unit area of sheared surface (i.e. peripheral length of punch contour x laminate thickness). Strain was defined as the percentage ratio of penetration to laminate thickness.)

Taking the fifth instant line as an example :

$$\text{Time} = 1.00 \times \frac{8.00}{3.58} = 2.23 \text{ ms}$$

$$\text{Strain} = \frac{0.91 \times \frac{0.0270}{4.79}}{0.0658} \times 100 = 7.8\%$$

$$\text{Stress} = \frac{0.68 \times \frac{9940}{4.89}}{\pi \times 1.502 \times 0.0658} = 4460 \text{ lbf/in}^2$$

Similar tables were produced in this way for the four remaining photographs.

The five individual thickness values were averaged to give the thickness of the laminate. Similarly the average time to break was calculated. The sum of the individual punching quality values provided the P.Q. value for the material. If required, the type of defects were noted, even if they occurred in one test-piece only.

Stress and strain values were plotted against time for all the test pieces on the same axes as shown in Figure 12 (p. 51).

'Average' stress/time and strain/time curves were then plotted. (In practice, lines were drawn through the results for each individual test-piece to assist in drawing the average lines but these have been omitted in Figure 12 for clarity.)

For each integer value of strain the corresponding time value was noted and then the corresponding stress value (e.g. 5.0 % strain occurred at 0.97 ms, hence at a stress of 2460 lbf/in^2).

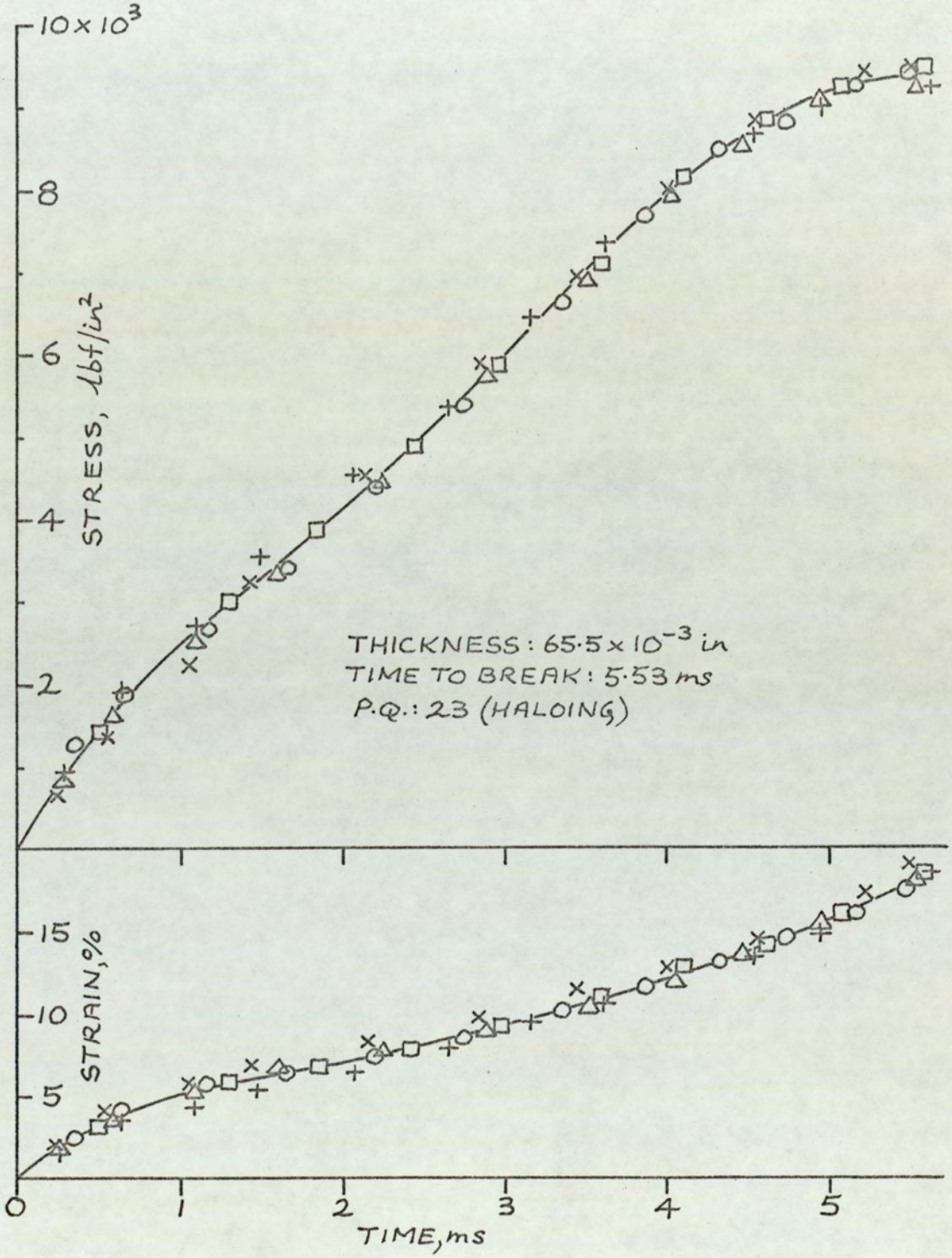


FIGURE 12. STRESS/TIME AND STRAIN/TIME CURVES.

Thus a table of time, strain and stress values was built up until the average time to break was reached when the corresponding values of stress and strain to break were recorded. (It was sometimes helpful to use non-integral values of strain where rapid changes in stress/time or slow changes in strain/time behaviour occurred). The resulting data for this example are shown in Table 3.

ms	%	lbf/in^2
0.12	1.0	400
0.26	2.0	820
0.43	3.0	1300
0.67	4.0	1840
0.97	5.0	2460
1.40	6.0	3180
1.92	7.0	4020
2.43	8.0	4920
2.87	9.0	5740
3.26	10.0	6540
3.60	11.0	7260
3.93	12.0	7840
4.26	13.0	8360
4.52	14.0	8740
4.79	15.0	9040
5.02	16.0	9240
5.25	17.0	9360
5.53	18.4	9380

TABLE 3. TIME/STRAIN/STRESS DATA

The stress/strain curve is shown in Figure 13.

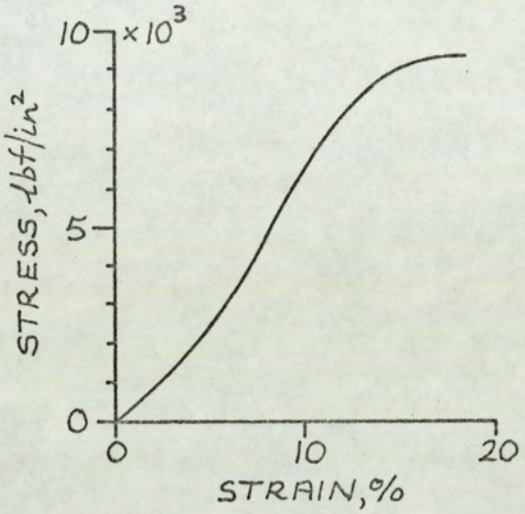


FIGURE 13. STRESS/STRAIN CURVE.

The C.N.S.L. plasticised laminate punched at 160°C was now characterised by values of time to break, stress and strain at break, P.Q. (together with visible defects) and a stress/strain curve.

-o-o-o-o-o-

CHAPTER 4.

THE EFFECT OF VARIABLES ARISING FROM THE TEST PROCEDURE.

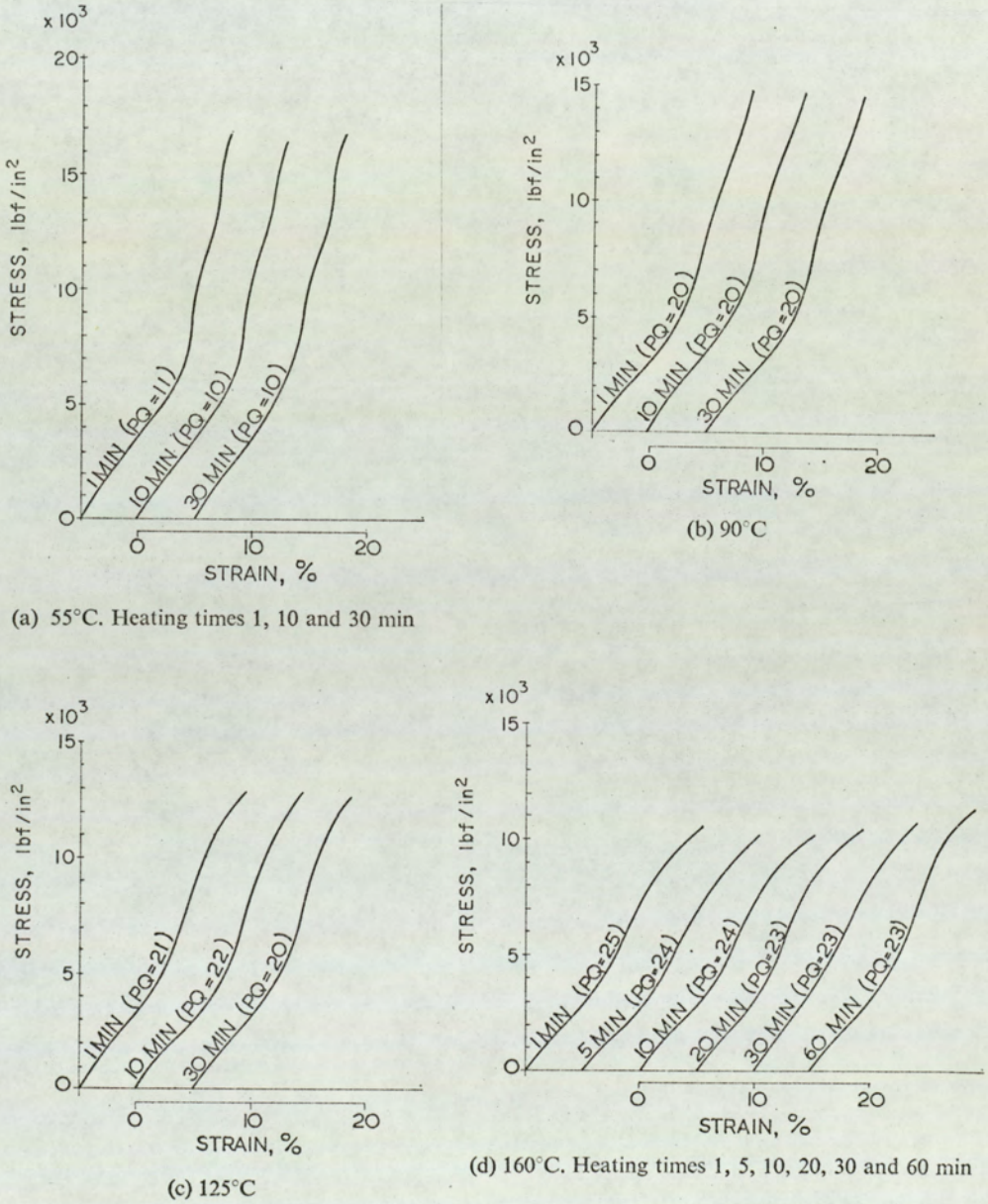
In Chapter 3 it was shown how a laminate could be characterised at a given temperature by reference to its behaviour during punching. It was seen in Section 3.3.1. that a preheating time of 10 min was used as a standard condition. The first part of the present chapter will show how this was determined. The general effect of punching temperature will then be described together with the effect of elapsed time between removal of the laminate from the heat source and the punching operation.

Two proprietary brands of material were used to explore the effect of these test variables on their punching characteristics. Their manufacturer recommended punching the first material at 80° - 100°C. For convenience this will be called the hot-punching grade. The second was a cold-punching material. Both were 1/16 in thick.

4.1. The effect of heating time.

To investigate this effect, the hot-punching material was used at 55°, 90°, 125° and 160°C. Initially, heating times of 1, 10 and 30 min were used but for the 160°C test additional times of 5, 20 and 60 min were used. Stress/strain curves with

corresponding P.Q. values for the various heating times are shown in Figure 14.



(a) 55°C. Heating times 1, 10 and 30 min

(b) 90°C

(c) 125°C

(d) 160°C. Heating times 1, 5, 10, 20, 30 and 60 min

FIGURE 14. STRESS/STRAIN CURVES SHOWING THE EFFECT OF HEATING TIME AT 55°, 90°, 125° and 160°C USING THE HOT-PUNCHING LAMINATE.

The results are summarised in Table 4.

HEATING TIME	EFFECT OF HEATING FOR PUNCHING AT			
	55°C	90°C	125°C	160°C
min				
1	Sufficient	Sufficient	Sufficient	Insufficient
5	-	-	-	Sufficient
10	Sufficient	Sufficient	Sufficient	Sufficient
20	-	-	-	Excessive
30	Sufficient	Sufficient	Sufficient	Excessive
60	-	-	-	Excessive

TABLE 4. SUMMARY OF HEATING TIME EXPERIMENTS

Significant differences were observed only at 160°C. Heating times of 5 and 10 min at this temperature gave similar results although yielding appeared to be slightly less at 5 min. Heating for 20, 30 and 60 min appeared to result in an increase in stress at break suggesting overcure.

To confirm that overcure had occurred, test-pieces were heated at 160°C for 10, 20, 30 and 60 min and allowed to cool at room temperature. Stress/strain curves for these test-pieces punched at 21°C were then compared with that of the same material which had not been preheated. Examination of Figure 15 (p.57) shows no significant difference between the results for 0 and 10 min, but after 20, 30 and 60 min an

increase in stress at break seemed to confirm that overcure had taken place.

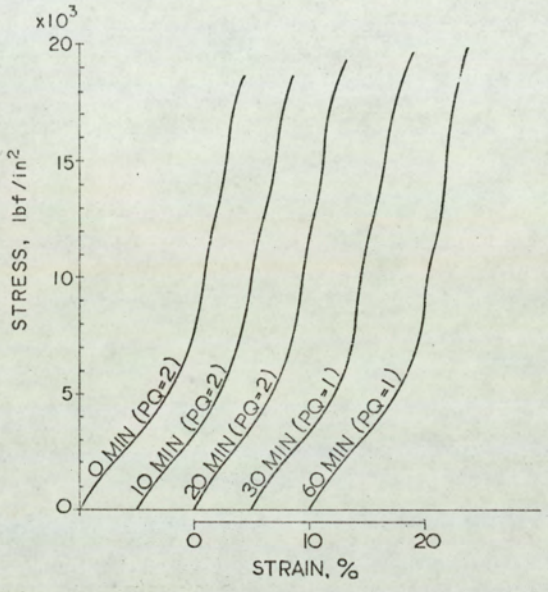


FIGURE 15. STRESS/STRAIN CURVES FOR HOT-PUNCHING LAMINATE AT 21°C AFTER PREHEATING AT 160°C FOR 0, 10, 20, 30 and 60 MIN.

These results suggested the use of a preheating time of 10 min.

Before examining the general effect of punching temperature with both materials it was necessary to establish that no significant overcure took place with the cold-punching grade after heating at 160°C for 10 min. Test-pieces of this material were, therefore, heated to 160°C for 10 min and allowed to cool at room temperature. The stress/strain curve for this material punched at 25°C was compared with that for

the unheated material punched at the same temperature. Reference to Figure 16 will show that there appeared to be no significant difference.

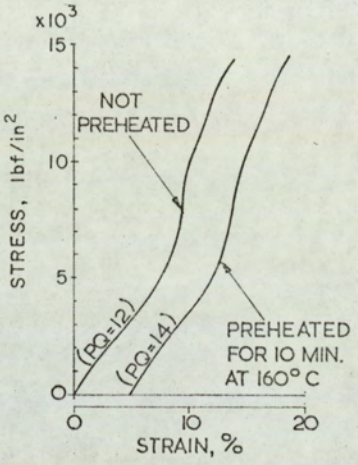


FIGURE 16. STRESS/STRAIN CURVES FOR COLD-PUNCHING LAMINATE AT 25°C COMPARING PREHEATED AND UNHEATED SAMPLES.

4.2. General effect of punching temperature.

Figures 17 and 18 (p. 59) show the stress/strain curves for the two materials punched at 25°, 55°, 90°, 125° and 160°C using heating times of 10 min.

Significant features in the stress/strain curves are summarised in Table 5 (p. 60).

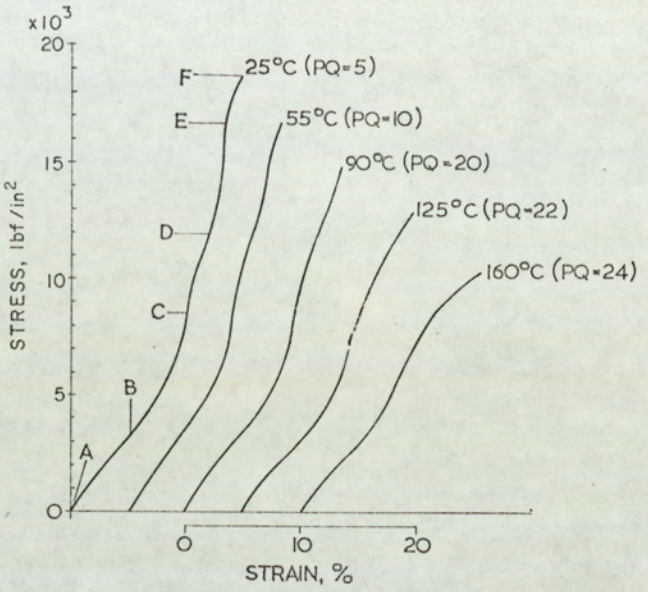


FIGURE 17. STRESS/STRAIN CURVES FOR HOT-PUNCHING LAMINATE AT 25°, 55°, 90°, 125° and 160°C (10 MIN HEATING TIME)

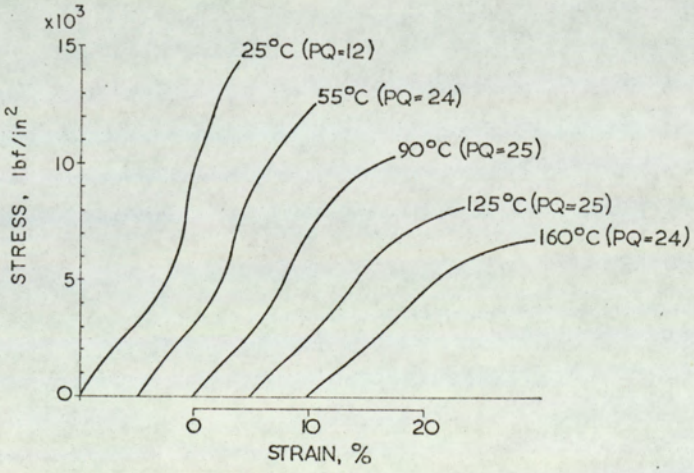


FIGURE 18. STRESS/STRAIN CURVES FOR COLD-PUNCHING LAMINATE AT 25°, 55°, 90°, 125° and 160°C (10 MIN HEATING TIME)

TEMP.	HOT-PUNCHING GRADE	COLD-PUNCHING GRADE
25°C	Primary (CD) and secondary (EF) yield regions present	Primary and secondary yield region present
55°C	Primary and secondary yield regions present	Secondary yield and hardening regions absent Primary yield extended
90°C	Secnndary yield region absent Hardening region (DE) present	Primary yield further extended
125°C	Hardening region absent Primary yield extended	Primary yield further extended
160°C	Primary yield further extended	Primary yield further extended

TABLE 5. SUMMARY OF SIGNIFICANT FEATURES IN STRESS/STRAIN CURVES FOR HOT- AND COLD-PUNCHING LAMINATES.

These features are clearly shown in the 25°C curve in Figure 17. After an initial increase in stress with increasing strain (AB) a region of hardening (BC) occurred. After primary yielding (CD) further hardening (DE) occurred until secondary yield (EF). It seemed that the shape of the stress/strain curve was indicative of the punching quality of the materials under given conditions. The secondary yield was present only when unsatisfactory P.Q. values (below 20) were obtained. With the hot-punching grade, satisfactory punching quality was found in the

presence of the hardening region without secondary yield.

Examination of the stress/time and strain/time curves for the hot-punching grade (see Figure 19) showed that punch movement was mainly responsible for the unusual shape of the stress/strain curves as discussed in Section 3.1.1.

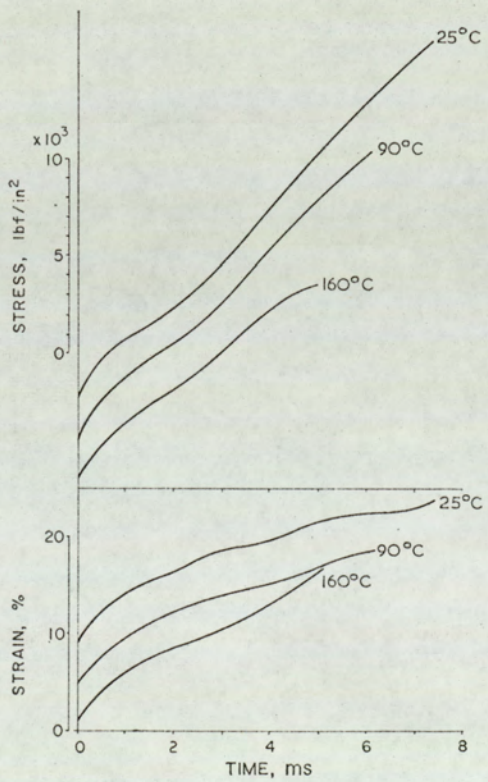


FIGURE 19. STRESS/TIME AND STRAIN/TIME CURVES FOR HOT-PUNCHING LAMINATE AT 25°, 90° and 160°C (10 MIN HEATING TIME).

The effect of temperature on stress and strain at break and time to break is shown in Figure 20.

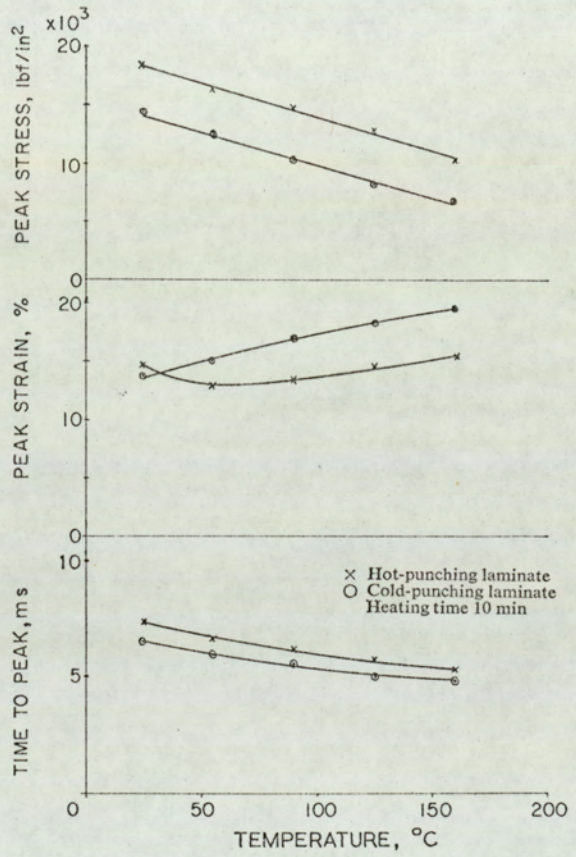


FIGURE 20. EFFECT OF TEMPERATURE ON STRESS AND STRAIN AT BREAK AND TIME TO BREAK USING THE HOT- AND COLD-PUNCHING LAMINATES.

Stress at break and time to break decreased with increasing temperature and strain at break showed a general increase (after an initial decrease with the hot-punching laminate).

4.3. Delay between heating and punching.

As discussed in Section 2.1.2., the transfer of the laminate from the heat source to the press should be as rapid as possible. In order to examine this experimentally, test-pieces of the hot-punching brand were heated to 90°C for 10 min and then permitted to cool at room temperature for 10, 30, 60, 100 and 200 s before punching. From Figure 21 it can be seen that after a delay of 10 s the shape of the stress/strain curve remained similar to that obtained with no delay and punching quality remained the same. Peak stress increased slightly.

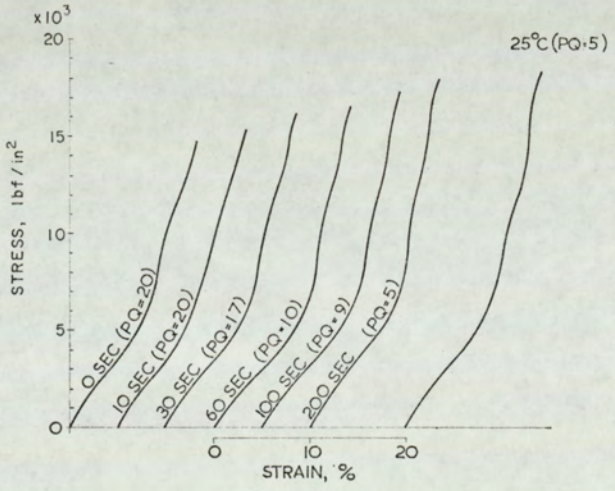


FIGURE 21. STRESS/STRAIN CURVES FOR HOT-PUNCHING LAMINATE AFTER COOLING FOR 0, 10, 30, 60, 100 and 200 S FROM 90°C (10 MIN HEATING TIME).

From 30 to 200 s delay, punching quality deteriorated and the stress/strain curves altered considerably.

After 200 s delay the material showed similar behaviour to that at 25°C.

4.4. General comments.

Although some of these results will be formally discussed in Chapter 9 it is now necessary to make the following two points :

1.) A preheating time of 10 min appeared to be satisfactory for the temperature range used. It was decided to use 10 min for all further work using the trigger and spring mechanism to minimise the delay (to 0.2 s) between heating and the punching operation.

2.) It seemed likely that punching quality was related to the shape of the stress/strain curves. This was kept in mind in examining the results of all later work.

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CHAPTER 5.

PUNCHING CHARACTERISTICS OF COMMERCIAL MATERIALS.

Before preparing any experimental laminates it was first necessary to obtain a background picture of how commercial materials behaved under typical production conditions[37].

5.1. The materials.

Sixteen commercial materials, all nominally of 1/16 in thickness were used for the work described in this chapter. Since the tool-set used was essentially similar to those encountered in production, although somewhat simpler, the mid-point of the recommended punching temperature range for each material was used. This value was rounded off to the nearest 5 deg C.

The materials were coded alphabetically in order of punching temperature and, for convenience, were divided into three classes. Materials having room temperature as their lowest recommended punching temperature were classified as cold-punching. Materials having their entire recommended temperature range above 100°C were classified as hot-punching. The remainder were classified as medium-punching.

Material A was found to punch unsatisfactorily at the mid-point of its recommended punching temperature range (40°C) and was retested at 55°C, at which satisfactory punching quality was achieved.

This temperature was still within the recommended range and the punching characteristics used for A were those from the 55°C test.

5.2. Test procedure.

As indicated in Section 4.4. a heating time of 10 min was used in all cases. Apart from having P.Q. values assigned to them, the test-pieces were carefully examined and the precise nature of the defects noted.

5.3. Stress/strain curves.

Stress/strain curves for the three classes of material are shown in Figure 22 (p. 67). Five materials exhibited a hardening region and eleven materials (including A at 55°C) showed primary yield only.

It is interesting to note that A at 40°C punched inadequately and that sudden yield was seen in the stress/strain curve. However, this sudden yield was not preceded by a hardening region as observed previously. This point will be raised again in Chapter 9.

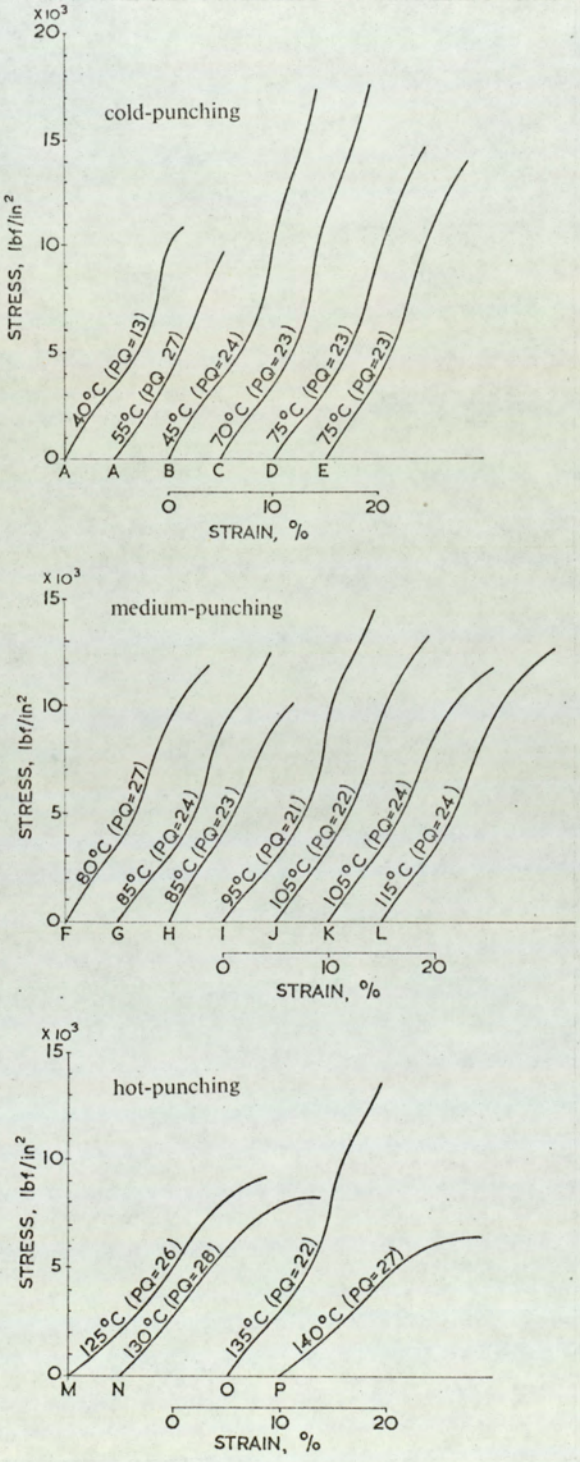


FIGURE 22. STRESS/STRAIN CURVES FOR THE COMMERCIAL SERIES AT THEIR RECOMMENDED PUNCHING TEMPERATURES.

5.4. Visible defects.

All materials (including A at 55°C) showed adequate punching quality.

Visible defects associated with both the pierced hole and the blanked disc are tabulated in Table 6 (p. 69).

Only material A, punched at 40°C, showed evidence of defects sufficiently severe to render the punching quality inadequate. In this case feathering was the main defect (see Figure 8, p. 41).

The minor defects associated with materials having good rather than excellent punching quality (i.e. P.Q. values between 20 and 25) were haloing, tensile cracking and lifting (Figure 8, p. 41). These defects were, at worst, only slight and did not always appear in all five test-pieces obtained from each material.

The cold-punching materials exhibited lifting as their main defect. At thetime, it seemed possible that the plasticisation techniques employed in the manufacture of cold-punching materials might have led to a reduction in strength between the plies. The medium punching materials showed tensile cracking as their principal defect with haloing as the next in importance. The origin of these defects will be returned to later.

PUNCHING			VISIBLE DEFECTS	
MAT-ERIAL	TEMP. °C	PQ	PIERCED HOLE	BLANKED DISK
A	40	13	Feathering and slight tensile cracking	Slight feathering
A	55	27	-	-
B	45	24	Very slight lifting	-
C	70	23	Slight lifting	-
D	75	23	Slight lifting	-
E	75	23	Very slight tensile cracking and very slight lifting	Very slight tensile cracking
F	80	27	-	-
G	85	24	Very slight tensile cracking	Slight haloing
H	85	23	Slight tensile cracking	Slight haloing and slight tensile cracking
I	95	21	Slight tensile cracking and slight lifting	Very slight tensile cracking
J	105	22	Very slight haloing and slight tensile cracking	Slight haloing and slight tensile cracking
K	105	24	Very slight haloing	Slight haloing and very slight tensile cracking
L	115	24	Very slight tensile cracking	Very slight haloing and very slight tensile cracking
M	125	26	-	-
N	130	28	-	-
O	135	22	Slight haloing and very slight lifting	Slight haloing
P	140	27	-	-

(As a rough guide PQ values of 10, 15, 20 and 25 may be regarded as bad, poor, good and excellent, respectively.)

TABLE 6. VISIBLE DEFECTS IN THE COMMERCIAL SERIES PUNCHED AT RECOMMENDED TEMPERATURES

5.5. Property values at break.

Figure 23 (p. 71) shows stress and strain at break, time to break and P.Q. plotted against the temperature at which the different materials were punched. Material A deviated in the stress/temperature and time/temperature plots and material O deviated in the stress/temperature and strain/temperature plots. In the strain/temperature plot, materialO, together with B which also deviated, fell on a line XX' of almost constant strain which was shared by all materials showing a hardening region. There seemed to be no clearly defined relationship between punching quality and temperature. If A, B and O were ignored however, then there seemed to be a tendency for P.Q. to improve with increasing temperature, especially if F was also ignored.

It was clear that, as temperature increased, the laminates tended to show similar trends to those displayed by the two materials in Chapter 4. Thus stress at break decreased and strain at break increased. Figure 24 (p. 72) appeared to confirm this and the 'grouping' of laminates in each class reflected the temperature dependence of stress and strain at break although materials H and A deviated.

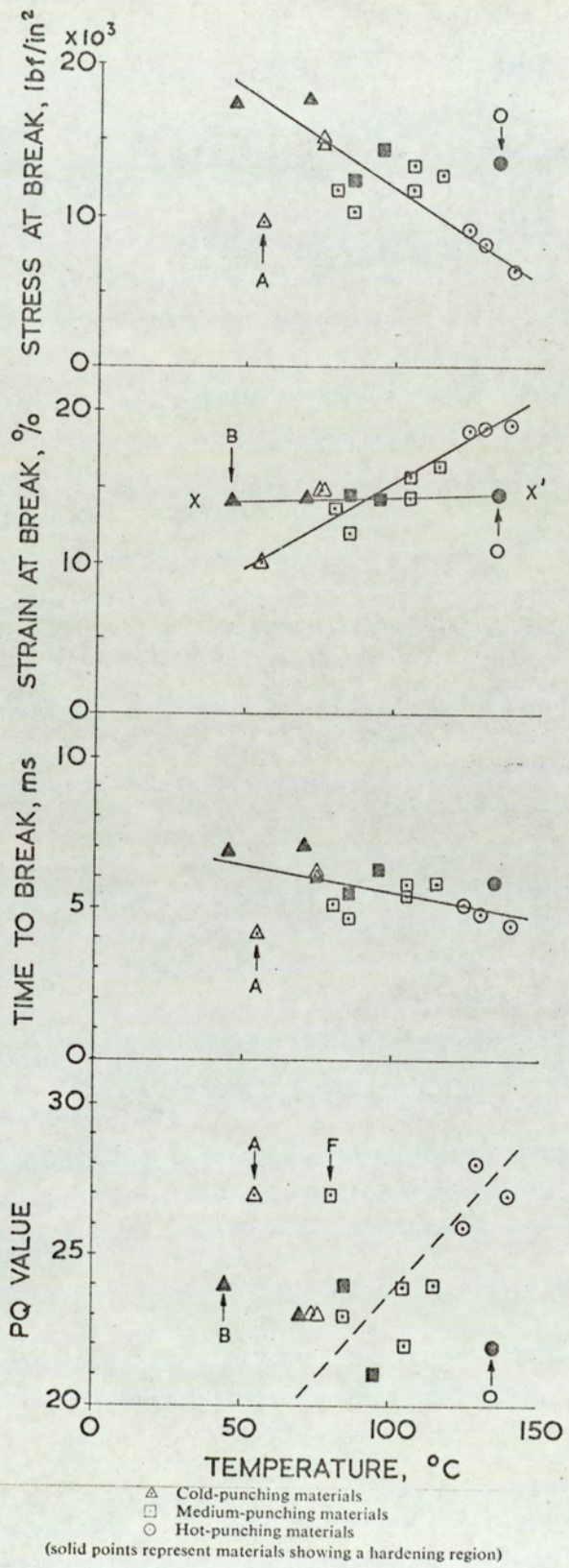
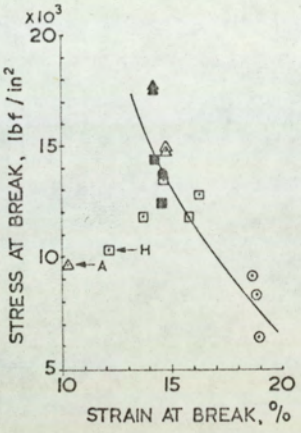


FIGURE 23. STRESS AND STRAIN AT BREAK, TIME TO BREAK AND P.Q. VALUES FOR INDIVIDUAL MATERIALS PLOTTED AGAINST THEIR RESPECTIVE PUNCHING TEMPERATURES.



△ Cold-punching materials
⊡ Medium-punching materials
⊙ Hot-punching materials
(solid points represent materials showing a hardening region)

FIGURE 24. RELATIONSHIP BETWEEN STRESS AND STRAIN AT BREAK FOR THE COMMERCIAL SERIES PUNCHED AT THE RECOMMENDED TEMPERATURES.

Time to break decreased with increasing temperature together with the possibility of an improvement in punching quality.

5.6. General comments.

The results seemed to suggest the expected variations in properties with temperature, implying that the materials tested were essentially similar although scatter was rather pronounced.

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CHAPTER 6.

THE EFFECT OF PROCESSING VARIABLES.

Before any investigations into the effect of resin composition it was clearly essential to assess the effect of manufacturing variables on punching characteristics using a given resin/paper system[38].

The effects of drying time, resin content and drying temperature were therefore examined using a bleached kraft paper. Impregnated and dried bleached kraft paper was then used to determine the effect of pressing conditions.

The effect of two different types of paper was examined by comparing the temperature dependence of punching characteristics of the bleached kraft based laminate with that of a cotton linter based laminate. Finally, the two papers, without resin, were consolidated under heat and pressure to attempt to gain some indication of their individual contributions to the properties of their finished laminates.

A commercial ammonia catalysed cresol/formaldehyde resin, dissolved to 50% solids in industrial methylated spirits, was used throughout the investigation. The bleached kraft paper had a thickness of 13×10^{-3} in and the cotton linter paper 12×10^{-3} in.

6.1. Preparation of the experimental materials.

6.1.1. General method.

The bleached kraft paper was impregnated in a laboratory scale continuous impregnator which is illustrated in Figure 25.

FIGURE 25. THE LABORATORY SCALE IMPREGNATOR.

Apart from the resin content experiments, the paper was impregnated twice and thus the resin content was maintained between 45.9 - 48.8% for all the laminates described in this chapter. The air temperature was controlled at 95° - 100°C to flash

off most of the solvent. The residence time in the oven of any point on the paper was 1 3/4 min.

The impregnated paper was then dried in a forced draught hot-air oven at 85°C (except for the drying temperature experiments) for the required length of time. Although this temperature was lower than that normally used in commercial practice, the need for precise control of the state of the dried paper outweighed the disadvantage of the extra time involved.

The dried paper was then cut into sheets and seven plies, unidirectionally stacked, were pressed between matt finish stainless steel plates in a 100 ton hydraulic press equipped with steam heated/water cooled platens. Five sheets of 5×10^{-3} in thick unbleached kraft paper were used as a pad between each plate and press platen. The standard pressing conditions used were 60 min at 150°C and 1000 lbf/in^2 followed by cooling under pressure for 10 min. (Appendix 3 gives further details of all the materials used and prepared in this thesis.)

6.1.2. Drying time experiment.

Batches of the impregnated bleached kraft paper were dried for 10, 20, 40, 60, 80 and 100 min at 85°C.

Volatile and resin contents were determined for each batch by heating 2 in squares of the dried, impregnated paper at 150°C for 5 min in a hot-air oven. (Appendix 2 gives details of the control methods used for laminate preparation.)

A sensitive version of the flash test was also used in which four 2 in squares of dried impregnated paper were pressed for 5 min at 150°C and 1000 lbf/in^2 (see Appendix 2). The weight of the flash was expressed as a percentage of the weight of the original four squares.

The density of the finished laminate was obtained from the thickness and weight of the 1½ in diameter circular blanks from the punching test.

Volatile content, flash values, density and thickness of the finished laminate have been plotted against drying time in Figure 26 (p. 77). From this, and the punching characteristics of the materials (see Section 6.3.1.) it was concluded that drying was essentially complete after 60 min and further drying to 100 min made little difference.

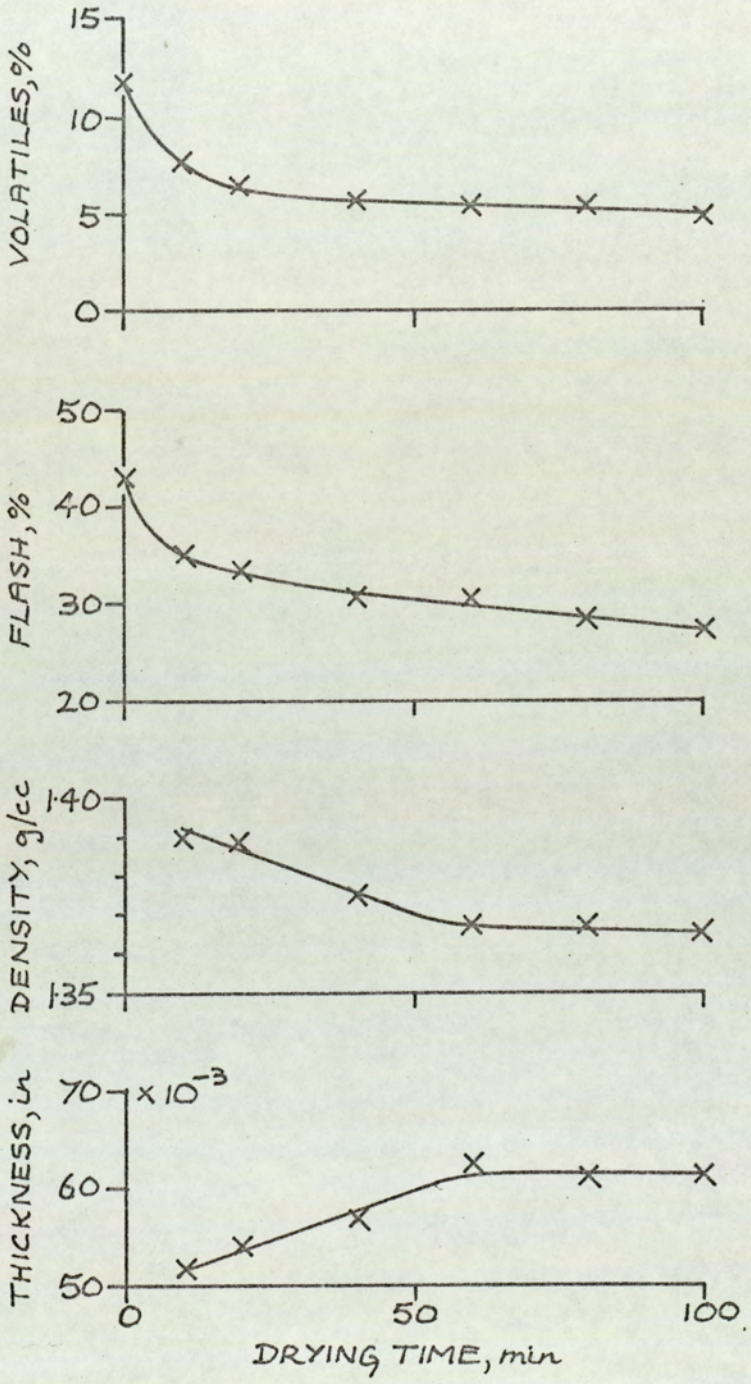

FIGURE 26. VOLATILE CONTENT, FLASH VALUE, DENSITY AND THICKNESS PLOTTED AGAINST DRYING TIME.

6.1.3. Resin content experiment.

Resin contents of 38.0, 48.1 and 51.9% were achieved by single, double and triple impregnations of the bleached kraft paper. The impregnated paper was then dried for 60 min at 85°C and pressed under the standard conditions. Density and thickness have been plotted against resin content in Figure 27.

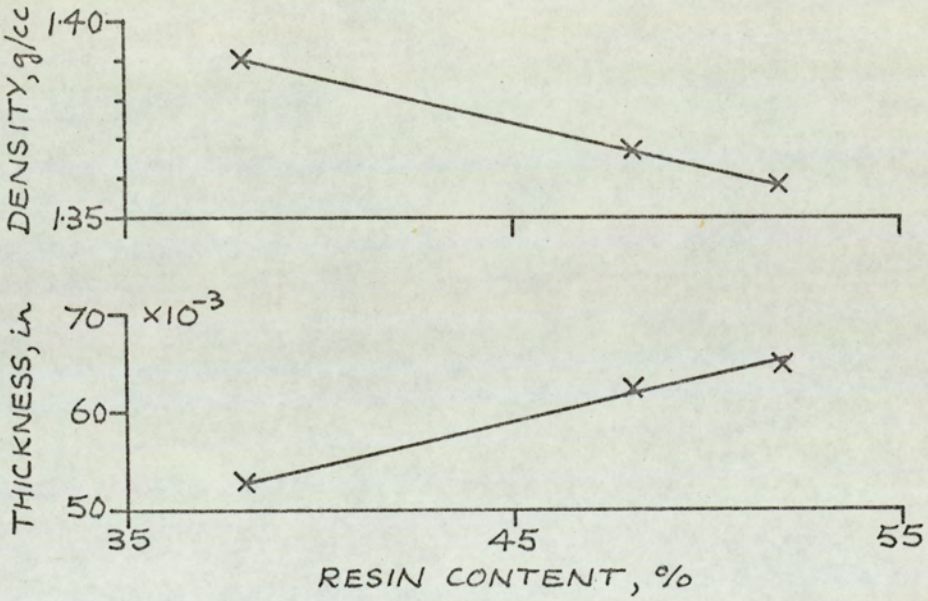

FIGURE 27. DENSITY AND THICKNESS PLOTTED AGAINST RESIN CONTENT.

The 38.0% paper was also used to prepare an eight ply laminate to examine the effect of laminate thickness.

6.1.4. Drying temperature experiment.

Doubly impregnated bleached kraft paper was dried at 70, 85 and 100°C and the drying time controlled so that a volatile content of 4.9 - 5.3% was achieved (4.8 - 5.4% being the values obtained after drying for 100 and 60 min respectively in section 6.1.2.). In this way it was hoped to provide better control than the use of a fixed drying time since, to some extent, ageing of the resin and different properties of the two papers used would be compensated for. Pressing conditions were standard.

6.1.5. Pressing experiments.

Doubly impregnated bleached kraft paper was dried at 85°C until the volatile content was between 4.9 - 5.3%. Pressing temperature, pressure and time were then varied independently to give the following values on either side of the standard conditions.

Temperature, °C	135	150	165
Pressure, lbf/in^2	750	1000	1250
Time, min	30	60	90

6.1.6. Comparision between bleached kraft and cottpn linter laminates.

The general method described in Section 6.1.1. was used. Both impregnated papers were dried at 85°C until the volatile content was 4.9 - 5.3%. Pressing conditions were standard.

6.1.7. Paper boards consolidated without resin.

In both cases eleven plies of paper were pressed for 60 min at 150°C and 1000 lbf/in^2 with 10 min cooling under pressure. This procedure gave boards 1/16 in thick.

6.2. Procedure for determining punching characteristics.

A heating time of 10 min was used in all cases.

The materials for investigating the impregnating and pressing variables were punched at 55°C.

The comparison between the bleached kraft and cotton linter laminates was made by punching these materials at 25°, 55°, 90°, 125° and 160°C. The nature of the visible defects was noted.

The consolidated papers were punched at 25°, 90° and 160°C.

6.3. Punching characteristics of the experimental materials.

6.3.1. Drying time experiment (Figure 28 p.81 and Table 7 p. 82).

Figure 28 shows an initial decrease in punching quality which levelled off after 60 min. The 10 and 20 min stress/strain curves showed no secondary yield and punching quality was good in these cases only. Table 7 shows that stress at break remained constant whereas strain tended to decrease very slightly.

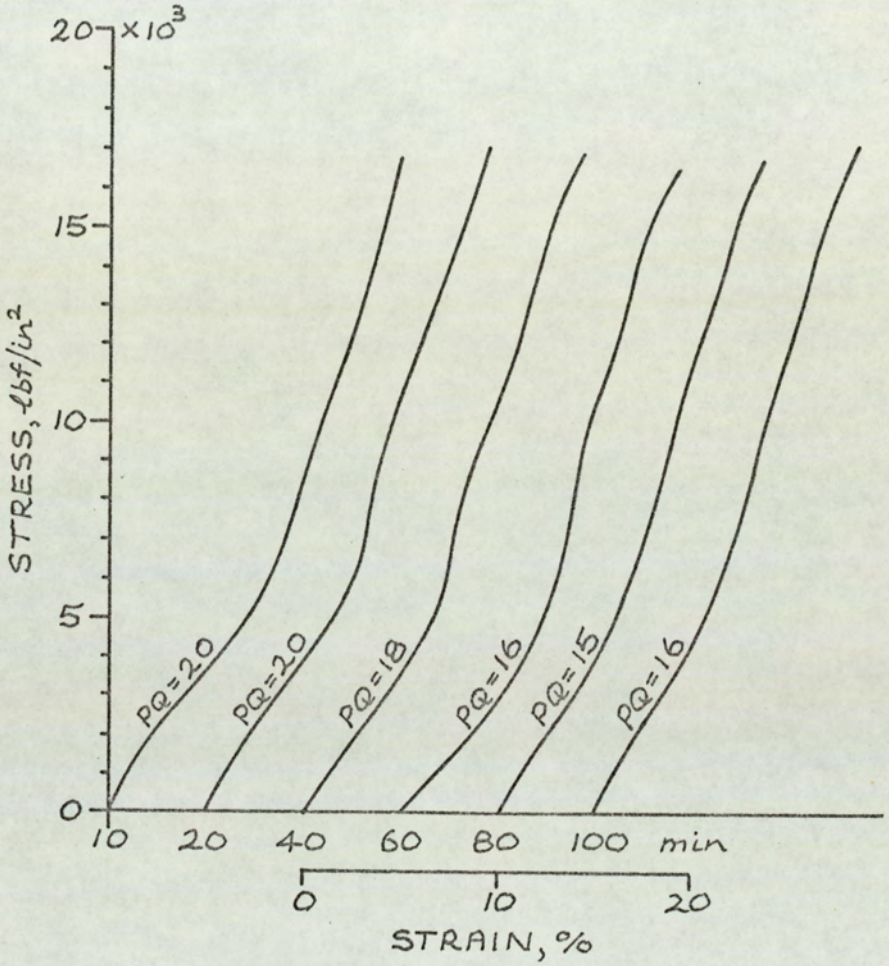

FIGURE 28. STRESS/STRAIN CURVES FOR DRYING TIME EXPERIMENT.

Time to break appeared to increase slightly initially and levelled off after 60 min.

The levelling of density and thickness, together with punching quality and time to break indicated that this represented the time after which drying was essentially complete, although flash and volatiles continued to decrease slowly up to 100 min.

EXPERIMENTAL VARIABLE	DENSITY (g/c.c.)	PROPERTIES AT BREAK		
		TIME (m sec)	STRAIN (%)	STRESS (lbf/in^2)
Drying Time (min).				
10	1.390	6.56	15.0	16800
20	1.389	6.83	14.6	17040
40	1.375	6.75	14.5	16840
60	1.367	6.98	14.6	16540
80	1.367	6.86	13.8	16700
100	1.365	6.93	13.8	17080
Resin Content (%)				
38.0	1.390	6.53	15.8	16840
48.1	1.367	6.98	14.6	16540
51.9	1.358	7.21	13.4	16980
38.0(8 ply)	1.387	7.23	15.5	17060
Drying Temperature (°C)				
70	1.370	6.89	14.1	16500
85	1.367	6.98	14.6	16540
100	1.371	6.72	13.5	16620
Laminating Temperature (°C) (Time, 60 min., Pressure 1000 lbf/in^2)				
135	1.371	6.47	13.5	15700
150	1.367	6.98	14.6	16540
165	1.363	7.09	15.1	17200
Laminating Pressure (lbf/in^2) (Time, 60 min., Temperature 150°C)				
750	1.361	6.66	14.8	15280
1000	1.367	6.98	14.6	16540
1250	1.365	6.77	14.8	16180
Laminating Time (Min) (Pressure 1000 lbf/in^2, Temperature 150°C)				
30	1.372	6.61	13.4	16180
60	1.367	6.98	14.6	16540
90	1.368	6.82	14.1	16720

TABLE 7. SUMMARY OF THE EFFECT OF MANUFACTURING VARIABLES.

The trends in density and thickness with increasing drying time up to 60 min were in parallel to those due to increasing resin content (see Figure 27 p. 78). These trends and the increasing flash values at lower drying times indicated an increasing loss of resin during pressing as the drying time was reduced below 60 min. This was confirmed by the parallel trends in punching characteristics with the resin content experiment (see Section 6.3.2.).

For drying times between 60 and 100 min it appeared that any resin loss in pressing was sufficiently constant to give similar properties to the laminates. However, there did seem to be a continued very slight decrease in strain at break with increasing drying time above 60 min, possibly related to the corresponding slight decrease in volatiles and flash values.

6.3.2. Resin content experiment (Figure 29 p. 84 and Table 7 p. 82).

Increasing resin content was accompanied by a marked decrease in punching quality. The stress/strain curve for the 38.0% material showed no secondary yield and punching quality was good. Stress at break remained constant but strain decreased and time increased with increasing resin content. Density decreased and thickness increased also.

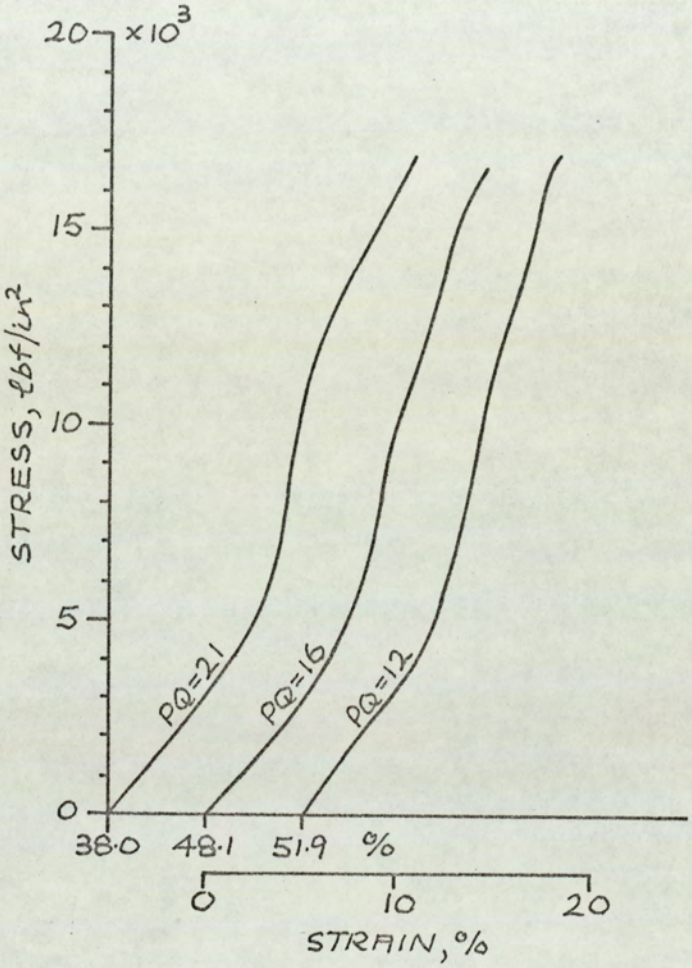

FIGURE 29. STRESS/STRAIN CURVES FOR RESIN CONTENT EXPERIMENT

Bearing in mind the work of Cox and Pepper[39], the decreasing density with increasing resin content suggested that the laminates in this range of resin content were free from voids, the density decreasing because of the increasing proportion of resin (of lower density than the paper fibres).

A comparison between the stress/strain curves

for the seven and eight ply laminates (at 38.0% resin content) is shown in Figure 30.

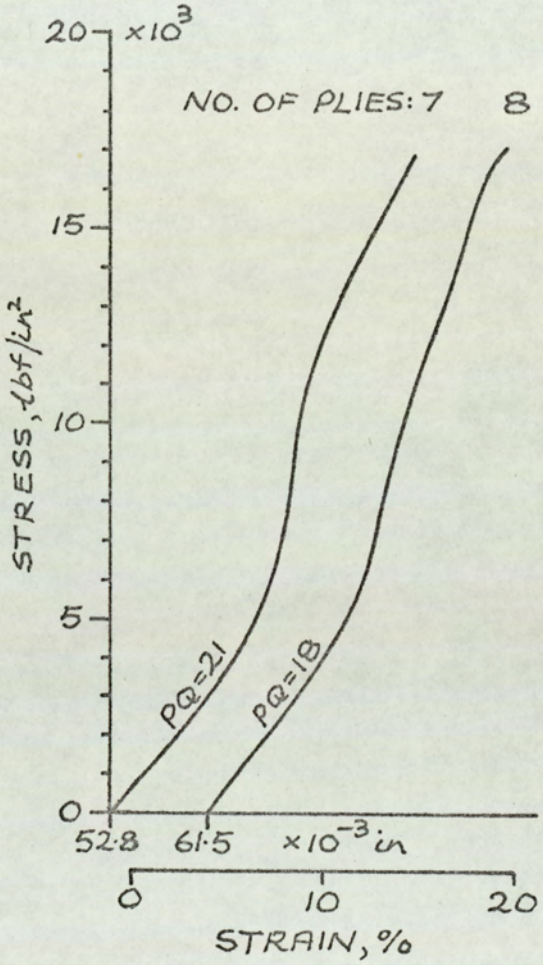

FIGURE 30. STRESS/STRAIN CURVES FOR SEVEN AND EIGHT PLY LAMINATES (38.0% RESIN CONTENT).

There was no significant difference between stress and strain at break but the thicker laminate showed increased time to break with a reduction in P.Q. (with the corresponding appearance of secondary yield in the stress/strain curve). The punching quality, however,

was still significantly better than that for the 48.1% laminate although the thicknesses were very similar (62.5×10^{-3} in for the 48.1% laminate compared with 61.5×10^{-3} in).

6.3.3. Drying temperature experiment (Figure 31 and Table 7 p. 82).

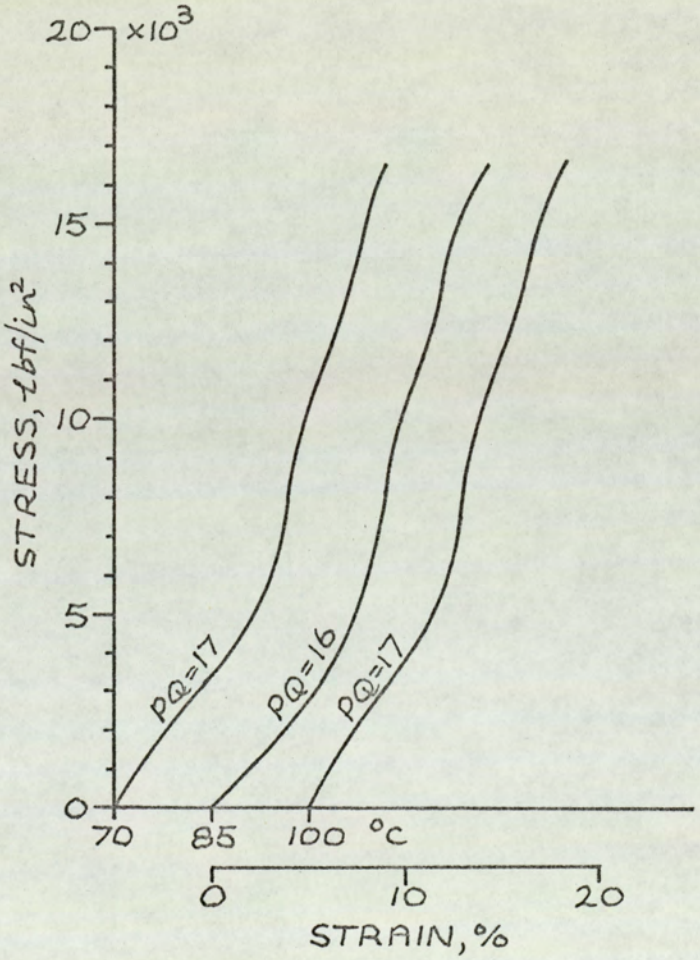

FIGURE 31. STRESS/STRAIN CURVES FOR DRYING TEMPERATURE EXPERIMENT.

Drying temperature appeared to have no significant effect over the range employed, although for the 100°C

material strain at break and time to break seemed slightly low.

6.3.4. Laminating temperature experiment (Figure 32 and Table 7 p. 82).

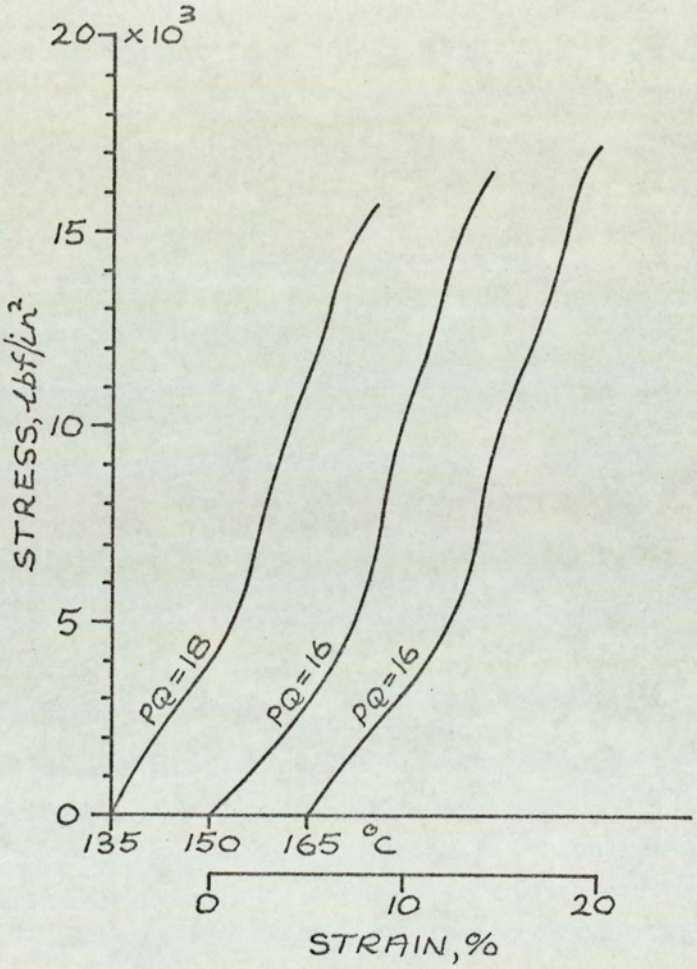

FIGURE 32. STRESS/STRAIN CURVES FOR LAMINATING TEMPERATURE EXPERIMENT.

Punching quality for the laminate pressed at 135°C was significantly better than those of the materials made at 150° and 165°C. The increase in stress at break with increasing laminating temperature

was accompanied by an increase in strain and time to break and a decrease in density.

These trends suggested that a less advanced state of cure had a beneficial effect on punching quality.

6.3.5. Laminating pressure experiment (Figure 33 and Table 7 p. 82).

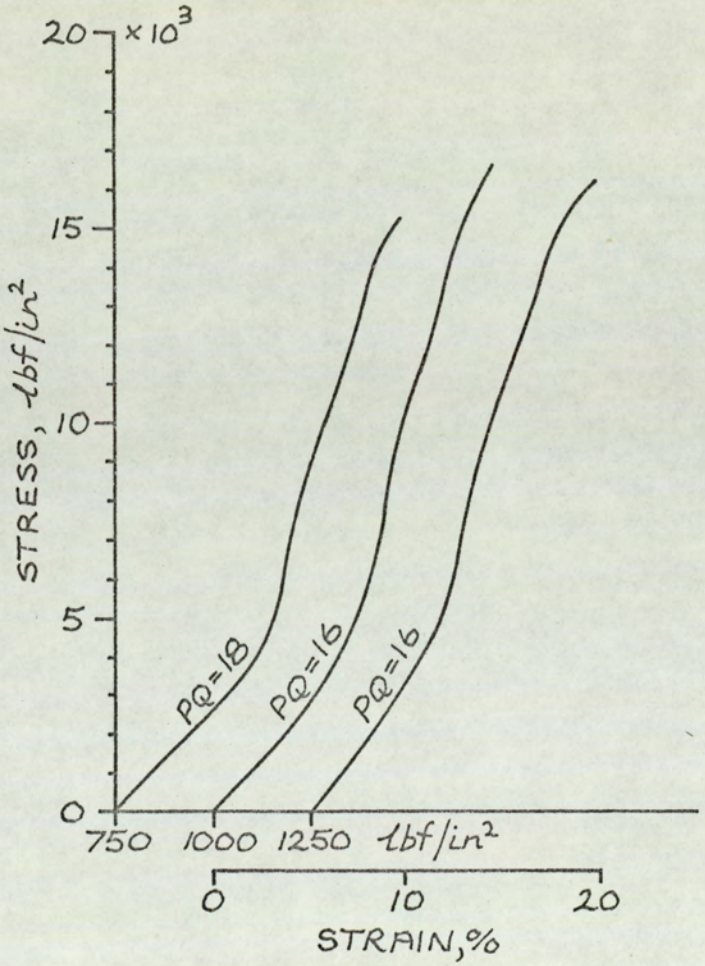

FIGURE 33. STRESS/STRAIN CURVES FOR LAMINATING PRESSURE EXPERIMENT.

Punching quality was significantly better for the laminate pressed at 750 lbf/in^2 and stress at break was

significantly lower than the other materials. Time to break was possibly slightly reduced although strain did not appear to be affected. The density appeared to be rather low.

The low density suggested the possibility of voids resulting in improved P.Q. and reduction in stress (and possibly time).

6.3.6. Laminating time experiment (Figure 34 and Table 7 p. 82).

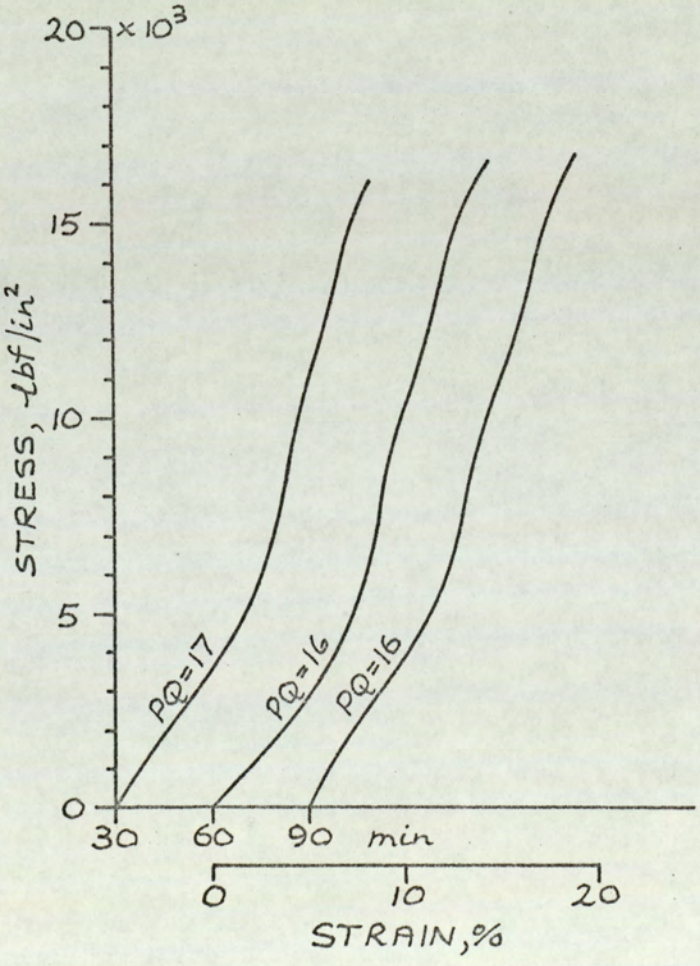

FIGURE 34. STRESS/STRAIN CURVES FOR LAMINATING TIME EXPERIMENT.

There appeared to be little effect due to laminating time (i.e. curing time) though stress, strain and time to break were possibly significantly lower at 30 min. With this in mind the P.Q. value of 17 could have indicated a significant improvement.

6.3.7. Comparison of bleached kraft and cotton linter laminates.

The stress/strain curves for the bleached kraft laminate are shown in Figure 35 and for the cotton linter laminate in Figure 36 (p. 91).

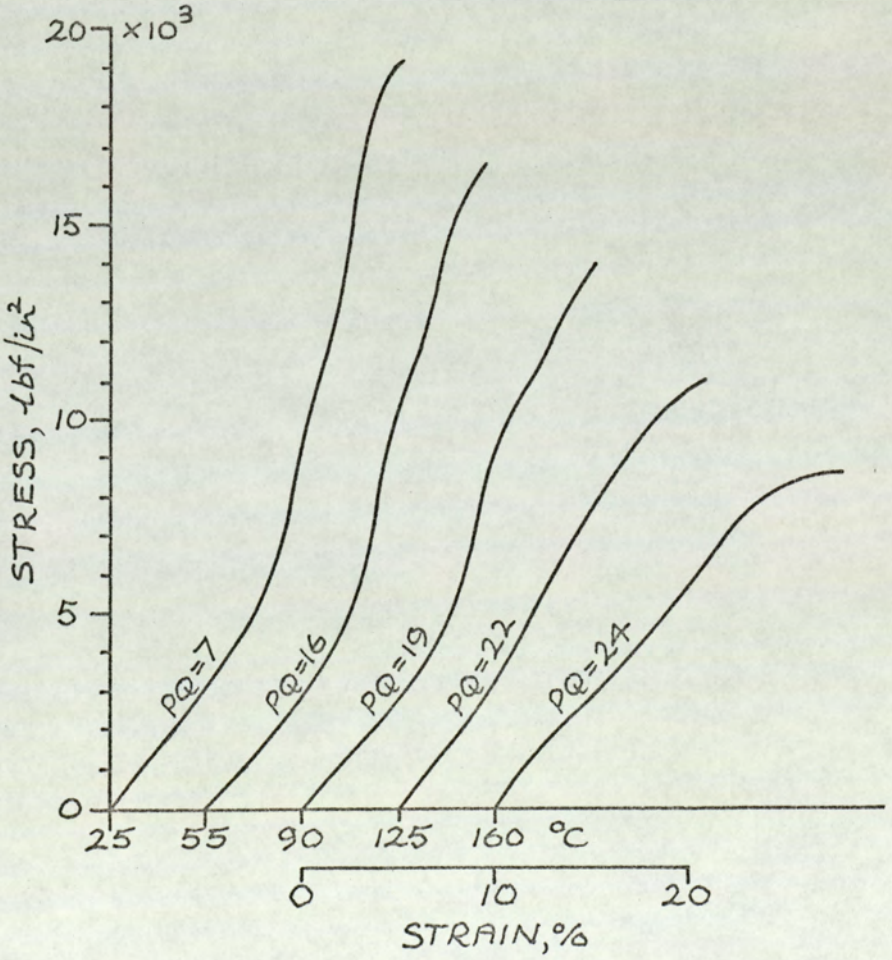

FIGURE 35. EFFECT OF TEMPERATURE ON BLEACHED KRAFT LAMINATE.

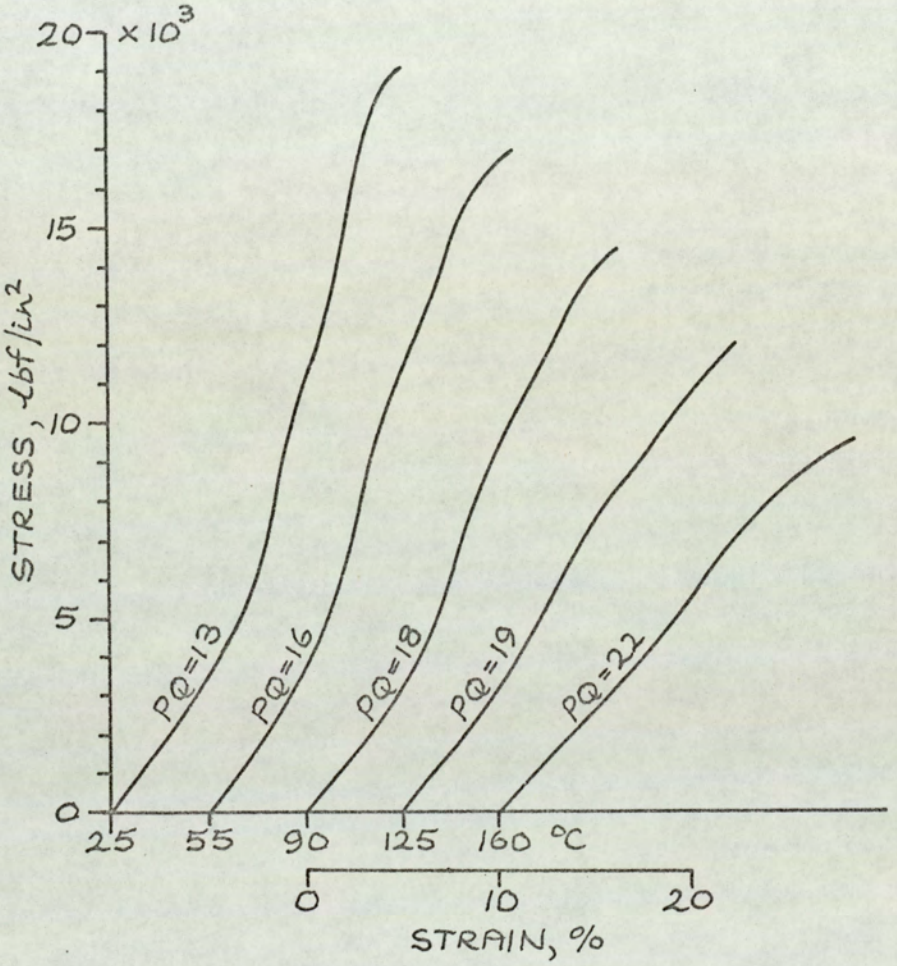

FIGURE 36. EFFECT OF TEMPERATURE ON COTTON LINTER LAMINATE.

The punching characteristics for both laminates are plotted against punching temperature in Figure 37 (p. 92) and the visible defects are tabulated in Table 8 (p. 93).

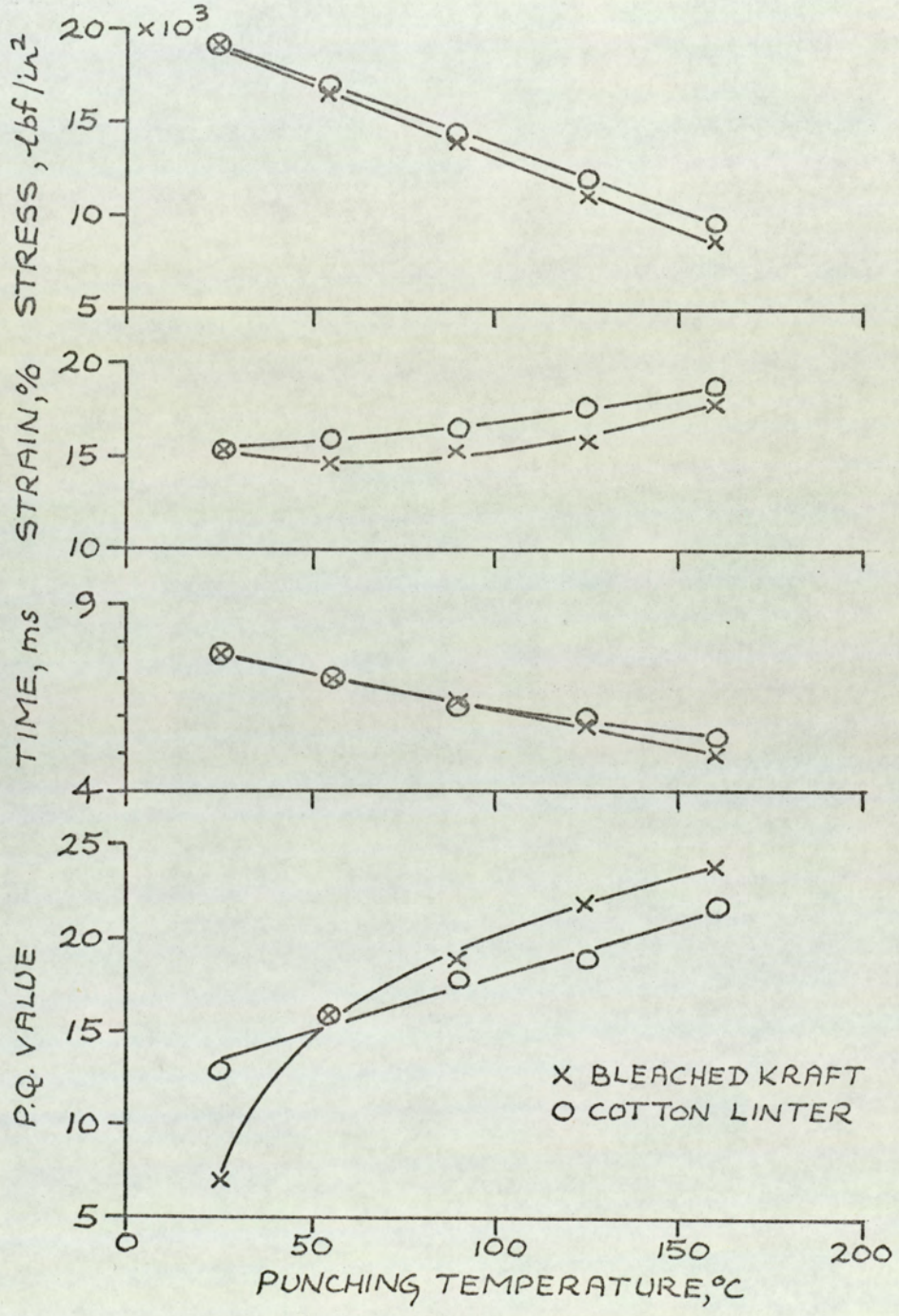

FIGURE 37. STRESS AND STRAIN AT BREAK, TIME TO BREAK and P.Q. VALUES FOR BLEACHED KRAFT AND COTTON LINTER LAMINATES PLOTTED AGAINST TEMPERATURE.

TYPE OF LAMINATE	PUNCHING TEMPERATURE (°C)	VISIBLE DEFECTS	PQ VALUE
Bleached kraft	25	Lifting, Haloing and Feathering	7
Bleached kraft	55	Haloing and slight Feathering	16
Bleached kraft	90	Haloing	19
Bleached kraft	125	Slight haloing	22
Bleached kraft	160	Very slight haloing	24
Cotton linter	25	Lifting, haloing and severe tensile cracking	13
Cotton Linter	55	Haloing and tensile cracking	16
Cotton Linter	90	Haloing and tensile cracking	18
Cotton Linter	125	Haloing and tensile cracking	19
Cotton Linter	160	Very slight haloing and tensile cracking	22

TABLE 8. COMPARISON OF VISUAL DEFECTS FOR THE BLEACHED KRAFT AND COTTON LINTER LAMINATES.

Both materials showed the expected decrease in stress and time to break and increase in strain to break with increasing temperature, although the bleached kraft laminate showed an initial decrease in the strain/temperature curve. The cotton linter material became increasingly stronger and took increasinglylonger to punch than the bleached kraft as the temperature increased. From 55°C upwards the

cotton linter laminate showed between 1 - 2% greater breaking strain than the bleached kraft.

The bleached kraft material, which was considerably inferior in punching quality at 25°C showed more rapid initial improvement than the cotton linter paper as the temperature was increased until it became better. The inferior P.Q. of the cotton linter laminate at higher temperature was due to tensile cracking arising from the radial tensile stress operating in the top surface of the test-pieces around the edge of the punch. For the cotton linter material, the presence of tensile cracking was presumably the penalty paid for the increased stress and strain at break.

6.3.8. Paper consolidated without resin.

The stress/strain curves for bleached kraft paper are shown in Figure 38 (p. 95) and for cotton linter paper in Figure 39 (p. 96).

On examination, the sheared surfaces of both materials punched at 25°C showed slight evidence of 'drawing-down' (Figure 8, p. 41) into the clearance between punch and die. Considerable drawing-down was seen at 90°C with less at 160°C.

The marked yield in the stress/strain curves was probably due to the drawing-down. Increased drawing-

down and yield were observed at 90°C. The corresponding reduction at 160°C suggested embrittlement of the paper by the preheating period at that temperature.

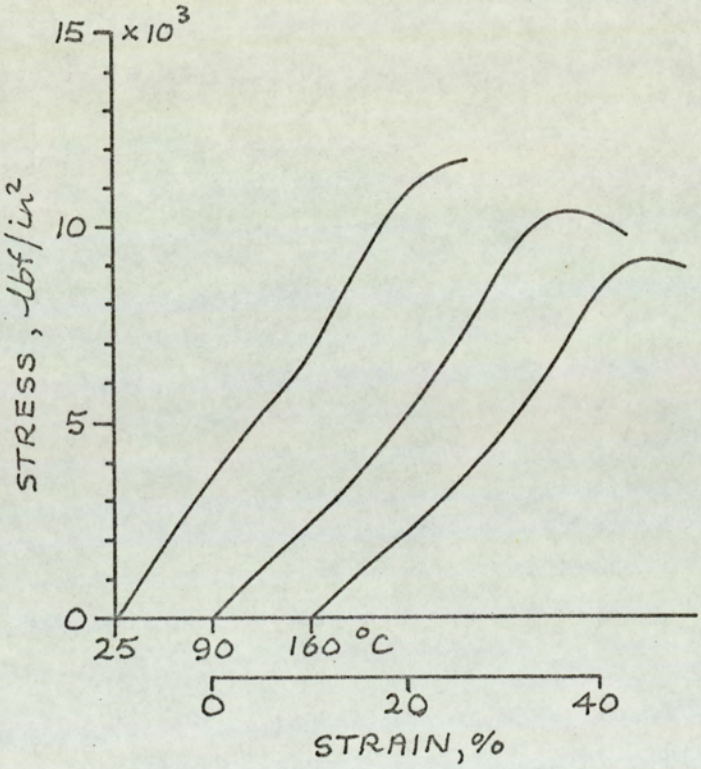

FIGURE 38. STRESS/STRAIN CURVES FOR CONSOLIDATED BLEACHED KRAFT PAPER PUNCHED AT 25°, 90° and 160°C.

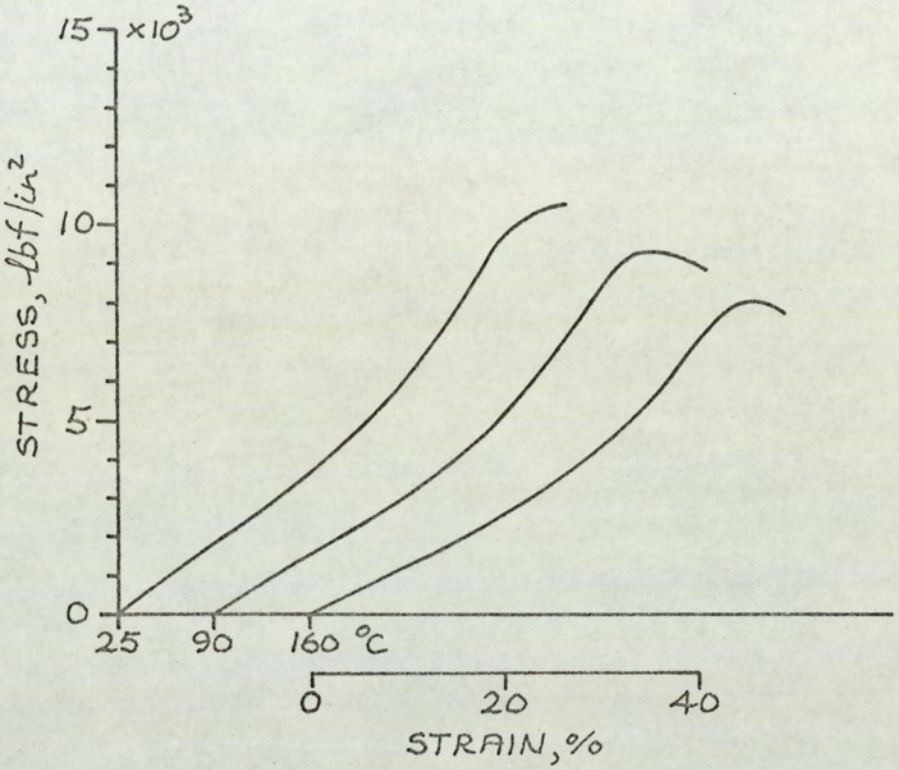

FIGURE 39. STRESS/STRAIN CURVES FOR CONSOLIDATED COTTON LINTER PAPER PUNCHED AT 25°, 90° and 160°C.

6.4. General comments.

These comments summarise the findings of this chapter and serve to emphasise the points which had to be kept in mind during later work when direct comparisons were made between different resins.

Processing variables, on the whole, showed the effects that might have been expected although the punching characteristics of the laminates were somewhat surprisingly insensitive to these variables.

The effect of drying time of the impregnated paper was important. If this was insufficient, resin loss by flow occurred during pressing. Reduced resin content in itself had a beneficial effect on punching quality but the reduced thickness of the finished laminate had an independent beneficial effect.

The effect of varying the paper drying temperature between 70° - 100°C had little, if any, effect.

A reduction in the state of cure of the resin resulted in significantly improved punching quality. This was effected by either reducing the cure temperature or the cure time, although in the latter case the effect was small.

A reduction in laminating pressure resulted in significantly improved punching quality possibly due to the presence of a small proportion of voids.

The comparison between the bleached kraft and cotton linter laminates indicated the important influence of the type of base-paper on punching characteristics.

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CHAPTER 7.

THE EFFECT OF THE BASE-PAPER.

The experimental data presented in Chapter 6 suggested that the choice of paper influenced punching characteristics, especially punching quality.

In the light of these results it was felt that the commercial series of materials (Chapter 5) should be re-examined in an attempt to classify them according to paper type[40]. The manufacturers were approached and provided the information regarding the general types of paper used. Of the sixteen materials, seven were based on unbleached kraft material, five on bleached kraft, three on cotton linter and one on alpha cellulose.

The re-examination of these results suggested the value of punching all the materials at the same temperature, which for convenience was fixed at 55°C.

Pepper and Barwell[41] have described a method of assessment of brittleness based on the comparison between the normal ultimate tensile stress of a phenolic laminate and the ultimate tensile stress of a test-piece with a hole in its centre. The resulting 'stress concentration factor' was used to assess the brittleness of the material. A similar approach was adopted in the present work to help interpret the results from punching the series of materials at the same temperature.

Having cnnfirmed that different papers exhibited varying effects on the punching characteristics of their laminates it was necessary to decide which paper was the most suitable for emphasising resin effects. Four laminates were therefore obtained which had been prepared from papers of the same types encountered in the commercial series. These laminates were provided by BXL Plastics Materials Group and had been prepared under similar conditions using an ammonia catalysed cresol/formaldehyde resin. The papers were impregnated and dried at 150°C to a volatile content between 3.0 - 3.7%. Resin content ranged between 45.6 - 47.2% and the laminates were nominally 1/16 in thick (see Appendix 3).

7.1. Test procedures.

7.1.1. Measurement of punching characteristics at 55°C.

A punching temperature of 55°C was selected since this could readily be achieved using the heating equipment associated with the tensile testing machine. Room temperature was not used because of the difficulty of ascribing accurate P.Q. values when punching quality was very bad.

A heating time of 10 min was used and P.Q. values, type of defects and features in the stress/strain curves were noted.

7.1.2. Tensile testing.

For each material, ten rectangular test-pieces

measuring 4.0 in x 0.75 in were cut in the lengthwise and crosswise directions, parallel to the edges of the boards. A circular saw was used for this purpose. The long edges of each test-piece were carefully sandpapered.

'Notched' test-pieces were prepared by drilling a 0.25 in diameter hole in the centre of five test-pieces from each direction.

The tensile testing machine was provided with a hot-air box enclosing the clamps. The temperature was controlled at 55°C and the test-pieces were preheated in the box for 10 min before testing. The crosshead speed was fixed at 10 in/min.

Five 'notched' and five 'unnotched' test-pieces were used for each direction for each material. The average thickness and average tensile strength were determined for each set. The average ultimate tensile stress (U.T.S.) was then calculated for each set, taking the reduced cross-sectional area into account for the notched test-pieces.

7.1.3. Measurement of punching characteristics for the laminates based on different papers.

Each of the laminates was punched at 20°, 55°, 90°, 125° and 160°C (10 min heating time). P.Q. values and type of defects were noted together with features of the stress/strain curves.

7.2. Punching characteristics at recommended temperatures.

The punching characteristics obtained at recommended punching temperatures (Chapter 5) have been replotted in Figure 40 (p. 102) but, in this case, classified according to paper type (cf. Figure 23 p. 71). Lines showing the observed trends have only been plotted for the unbleached and bleached kraft materials.

Clear separation between the two paper types was observed in their temperature dependence. Stress and time decreased and strain at break increased with increasing temperature in both cases. Punching quality appeared to increase for the bleached kraft materials but there was uncertainty with the unbleached kraft materials. Logically it might have been expected that no trends should have been seen in punching quality since all the materials were punched at the recommended temperatures. The bleached kraft materials, on the whole, appeared to punch better than the unbleached.

Two of the cotton linter materials appeared to behave in a similar fashion to the unbleached kraft but the remaining one seemed to be exceptional. It was not possible to associate the alpha cellulose laminate with either class.

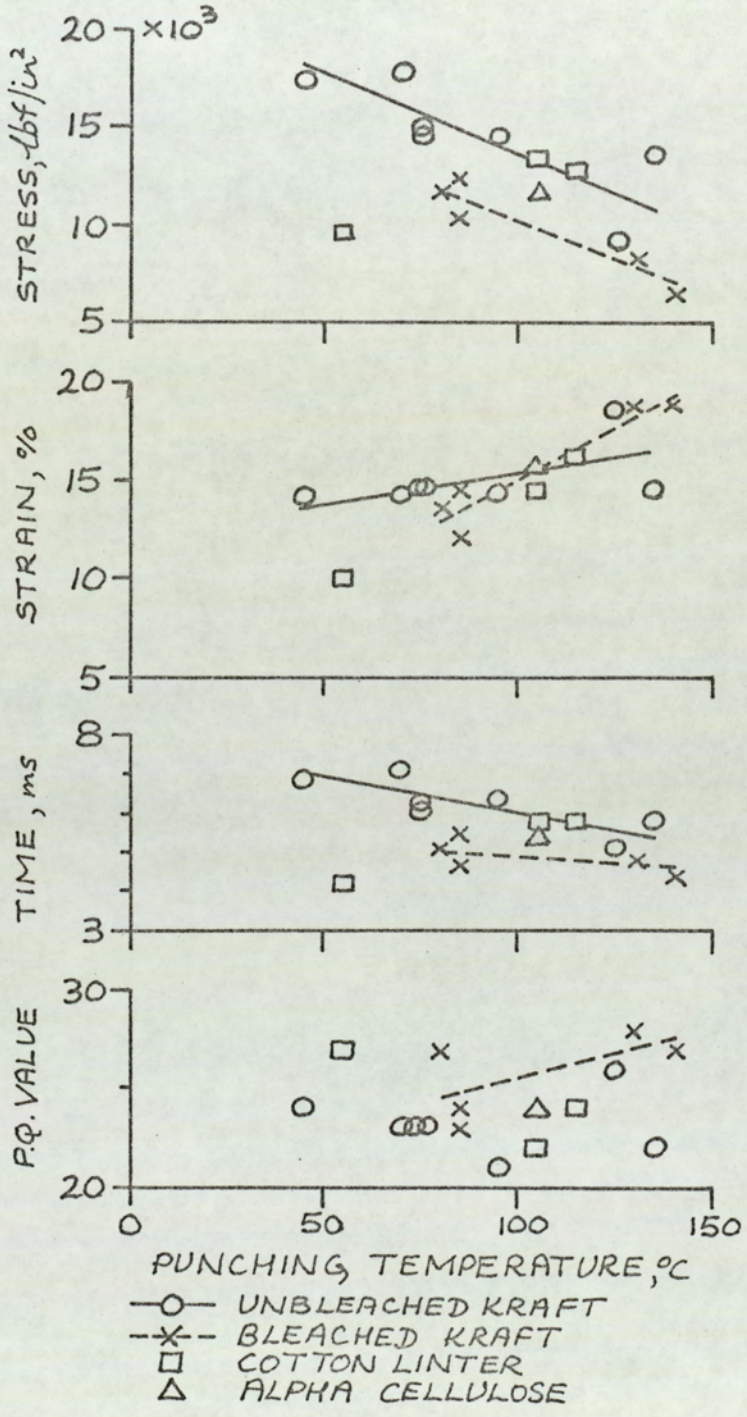

FIGURE 40. STRESS AND STRAIN AT BREAK, TIME TO BREAK AND P.Q. VALUES FOR COMMERCIAL SERIES PLOTTED AGAINST PUNCHING TEMPERATURE (RECOMMENDED) AND CLASSIFIED ACCORDING TO PAPER TYPE.

7.3. Punching characteristics at 55°C.

It was hoped to isolate the property or properties associated with punching quality by plotting the punching characteristics at a fixed temperature against the temperature at which the materials should have been punched (i.e. recommended punching temperature). This has been done in Figure 41 (p. 104).

Separation between unbleached kraft and bleached kraft materials was again clear. Stress and time to break for the unbleached kraft materials appeared to be constant although the bleached kraft materials did tend to show a very slight increase in stress and decrease in time. Punching quality fell with increasing recommended temperature, especially with the bleached kraft materials. The interesting point was that strain at break decreased for both classes.

On the whole, the two cotton linter materials still appeared to be more closely associated with the unbleached kraft materials, the third remaining exceptional. The alpha cellulose material appeared to behave as the bleached kraft materials except in strain at break.

The visible defects shown by each group of materials have been tabulated in Table 9 (p. 105). The most significant point emerging seemed to be that only unbleached kraft materials showed lifting and

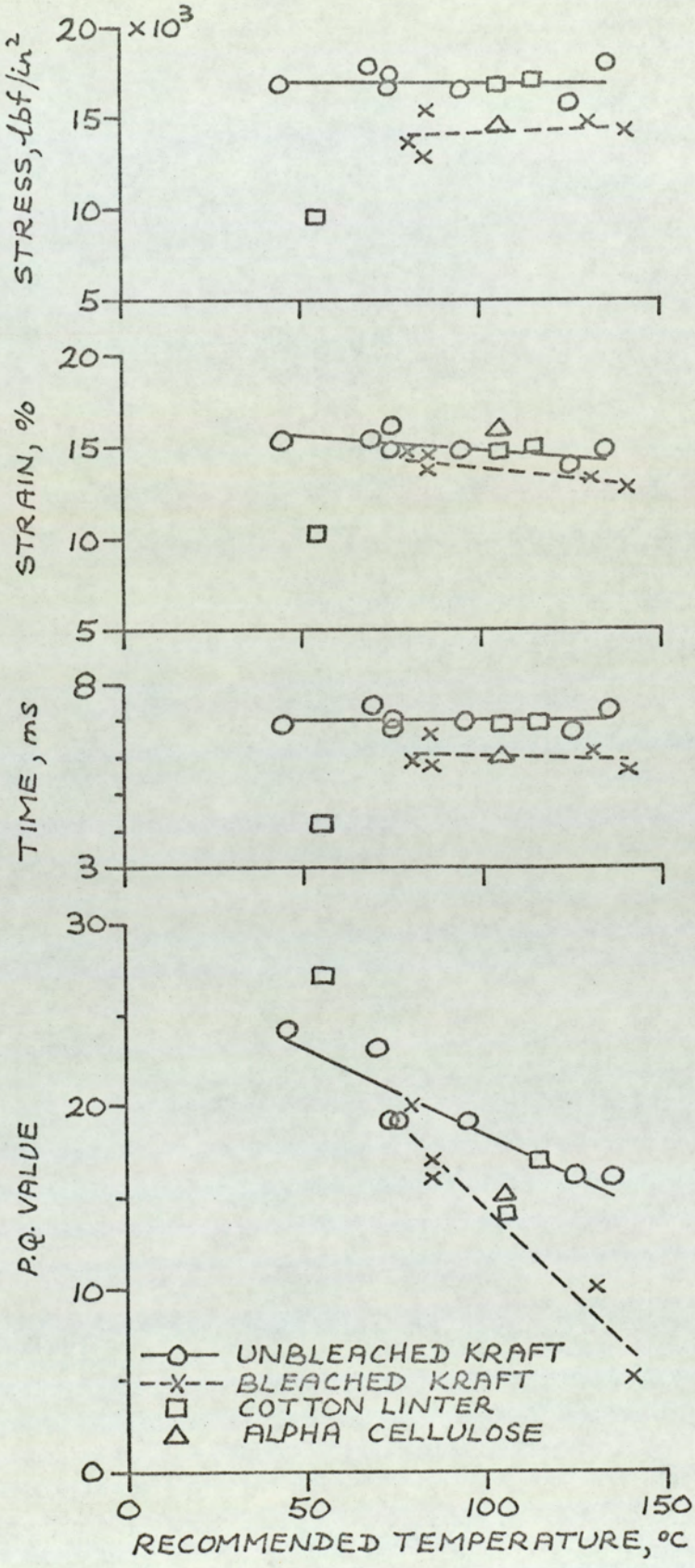

FIGURE 41. STRESS AND STRAIN AT BREAK, TIME TO BREAK AND P.Q.VALUES FOR COMMERCIAL SERIES PUNCHED AT 55°C PLOTTED AGAINST RECOMMENDED PUNCHING TEMPERATURE AND CLASSIFIED ACCORDING TO PAPER-TYPE.

that no unbleached kraft material showed feathering.

PAPER	MATERIAL	PQ	VISIBLE DEFECTS *	STRESS/STRAIN FEATURES **
COTTON LINTER	A	27	-	1y
	J	14	FHT	1y H 2y
	L	17	HT	1y H 2y
ALPHA CELLULOSE	K	15	HT	1y H 2y
BLEACHED KRAFT	F	20	HT	1y H
	G	16	HT	1y H 2y
	H	17	FHT	1y H 2y
	N	10	FHT	1y H 2y
	P	5	FHT	linear
UNBLEACHED KRAFT	B	24	L	1y
	C	23	L	1y
	D	19	L	1y H 2y
	E	19	LT	1y H 2y
	I	19	LT	1y H 2y
	M	16	HT	1y H 2y
	O	16	LH	1y H 2y

* F = Feathering
L = Lifting
H = Haloing
T = Tensile cracking

** 1y = primary yield
H = hardening region
2y = secondary yield

(The anomalous behaviour of material P will be discussed in Section 9.1.)

TABLE 9. SUMMARY OF PUNCHING QUALITY DATA FOR THE COMMERCIAL LAMINATES PUNCHED AT 55°C

7.4. Ultimate tensile stress at 55°C.

The decrease in strain at break at 55°C at apparent constant stress at break as punching quality deteriorated suggested a corresponding increase in 'brittleness' (i.e. a decrease in work of fracture). This led to the adoption of the tensile testing procedure based on the work of Pepper and Barwell[41].

Ultimate tensile stress (U.T.S.) has been plotted against punching quality for unnotched and notched test-pieces in both stronger and weaker directions (see Figure 42 p. 107). The resulting trends have been replotted on the same axes at the bottom of the figure for easy comparison.

It was clear that increasing P.Q. values were accompanied by a general increase in U.T.S. There was clear separation between the unbleached kraft and bleached kraft laminates. The unbleached kraft materials, on the whole, punched better and showed higher U.T.S. values than bleached kraft.

The value of U.T.S. on the 'stronger (unnotched)' line divided by the value of U.T.S. on the 'weaker (unnotched)' line at any point on the P.Q. axis represented the tensile anisotropy at that point. The extreme values of tensile anistropy for both paper types have been indicated at the appropriate points on Figure 42.

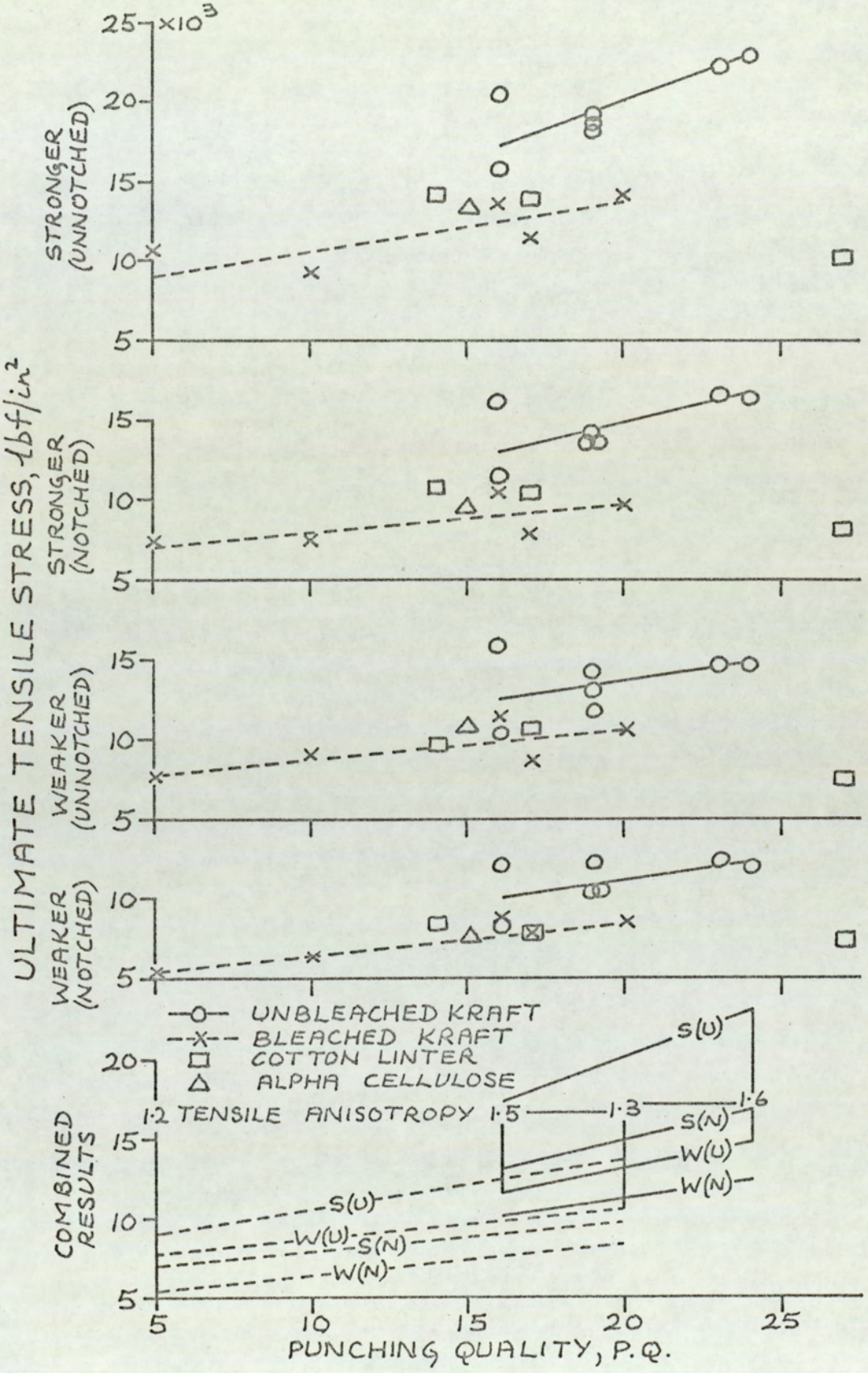

FIGURE 42. ULTIMATE TENSILE STRESS VALUES AT 55°C PLOTTED ACAINST PUNCHING QUALITY at 55°C FOR THE COMMERCIAL SERIES.

It was clear that the tensile anistropy range for the unbleached kraft laminates was higher than for the bleached kraft and that tensile anisotropy increased with increasing punching quality for both groups. It was interesting to note that the U.T.S./P.Q. line for notched bleached kraft test-pieces in the stronger direction was lower nn the U.T.S. axis than the unnotched line in the weaker direction.

On the whole, both cotton linter and alpha cellulose materials were more closely associated with the bleached kraft properties. The third cotton linter material proved to be exceptional once again.

Values of Pepper and Barwell's experimental stress concentration factor were calculated individually for each material in each direction. This was done by simply dividing U.T.S. (unnotched) by U.T.S. (notched) in each case. P.Q. values have been plotted against stress concentration factor in Figure 43 (p. 109). There appeared to be a significant decrease in P.Q. value with increasing stress concentration factor in the weaker direction. The unbleached kraft laminates were closely grouped but the bleached kraft exhibited a wide range of stress concentration factors. There appeared to be no significant trend in the stronger direction.

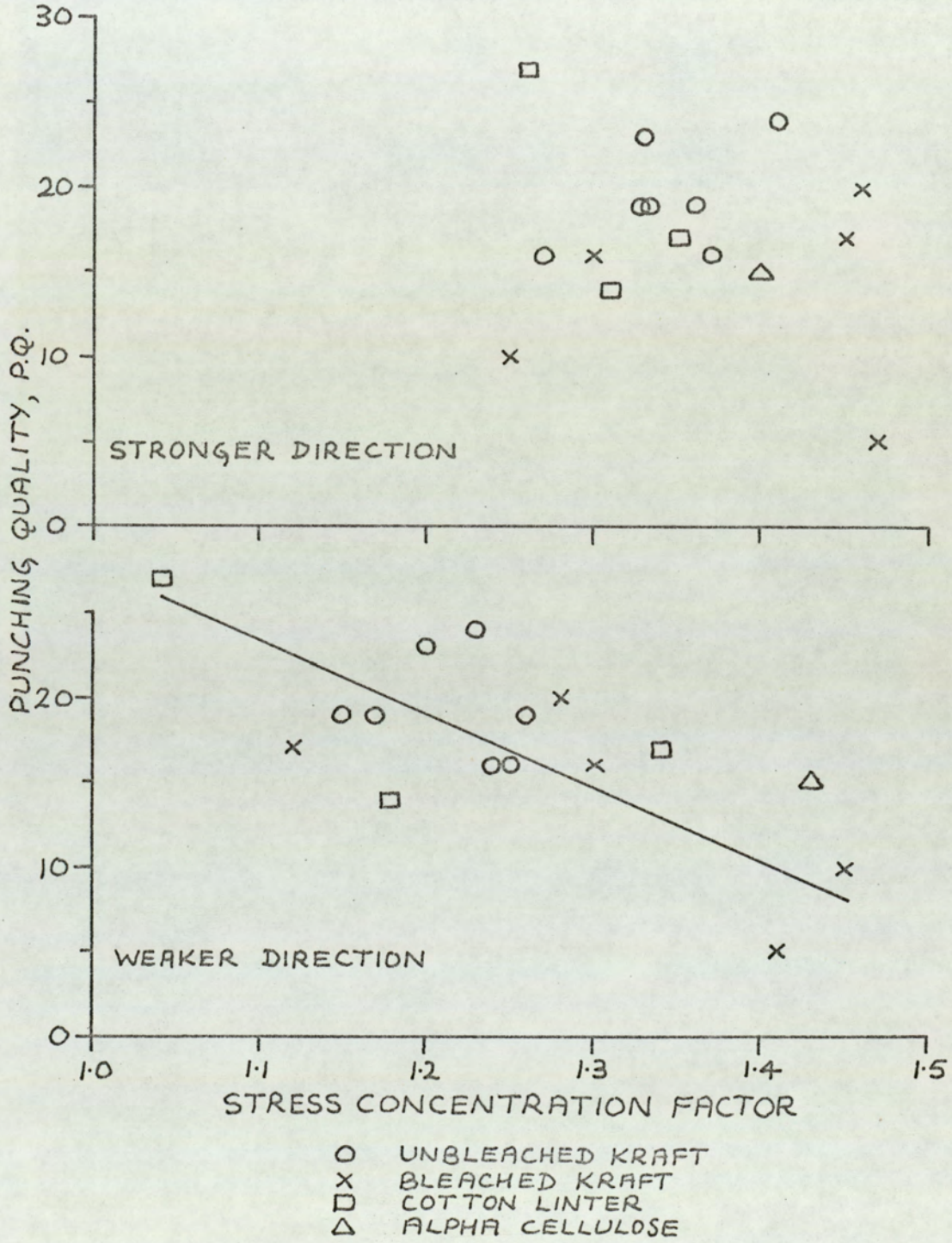

FIGURE 43. PUNCHING QUALITY PLOTTED AGAINST STRESS CONCENTRATION FACTORS FOR THE COMMERCIAL SERIES.

The fractured edges of the unnotched tensile test-pieces in the weaker direction were cleaner and straighter than in the stronger direction for all materials. The edges for the stronger direction were uneven and cracks were present which tended to turn towards the weaker direction (e.g. as in Figure 44).

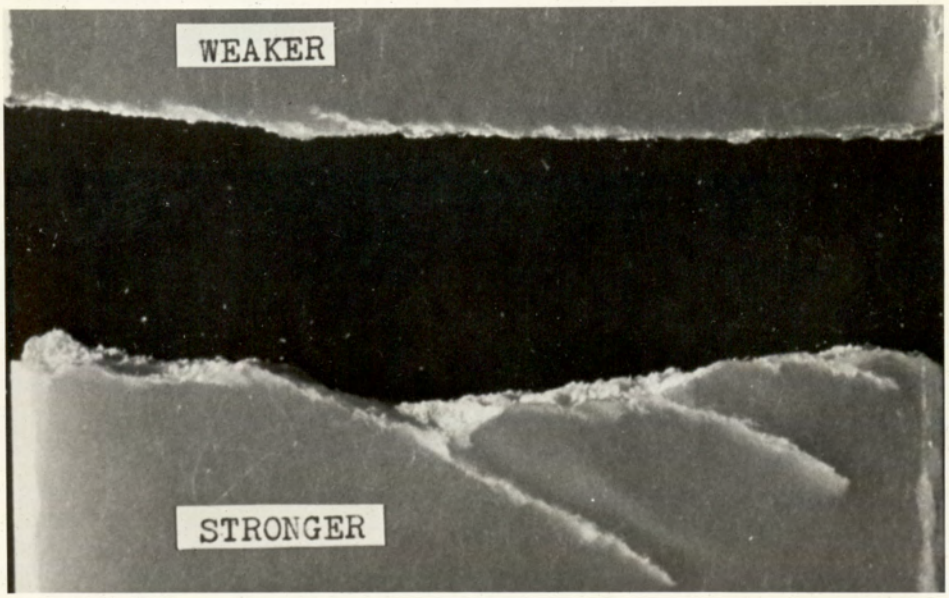

FIGURE 44. EXAMPLE OF FRACTURED EDGES OF TENSILE TEST-PIECES IN THE WEAKER AND STRONGER DIRECTIONS.

7.5. Punching characteristics of the laminates based on different papers.

Figures 45a to 45d (pp. 112-115) show the punching characteristics for these materials plotted against punching temperature and Table 10 (p. 116) shows the type of defects observed.

The alpha cellulose and cotton linter based laminates tended to show higher stress and strain at break and time to break than the unbleached kraft and bleached kraft materials. Although they punched better at low temperatures they showed a peak in punching quality (as did unbleached kraft) with a subsequent decrease.

The bleached kraft materials provided the widest range of P.Q. values and showed increasing punching quality over the whole temperature range. It was quite clear, therefore, that this paper was the most suitable for investigating resin effects.

The peak in the P.Q./temperature curve for all materials except bleached kraft was possibly related to the sharp increase in strain at higher temperatures. This suggested that 'yield' defects such as haloing and tensile cracking could arise from high values of strain at break. The bleached kraft material, which showed relatively low values of stress and strain at break, was presumably able to reach its 'at break' condition before serious damage had occurred.

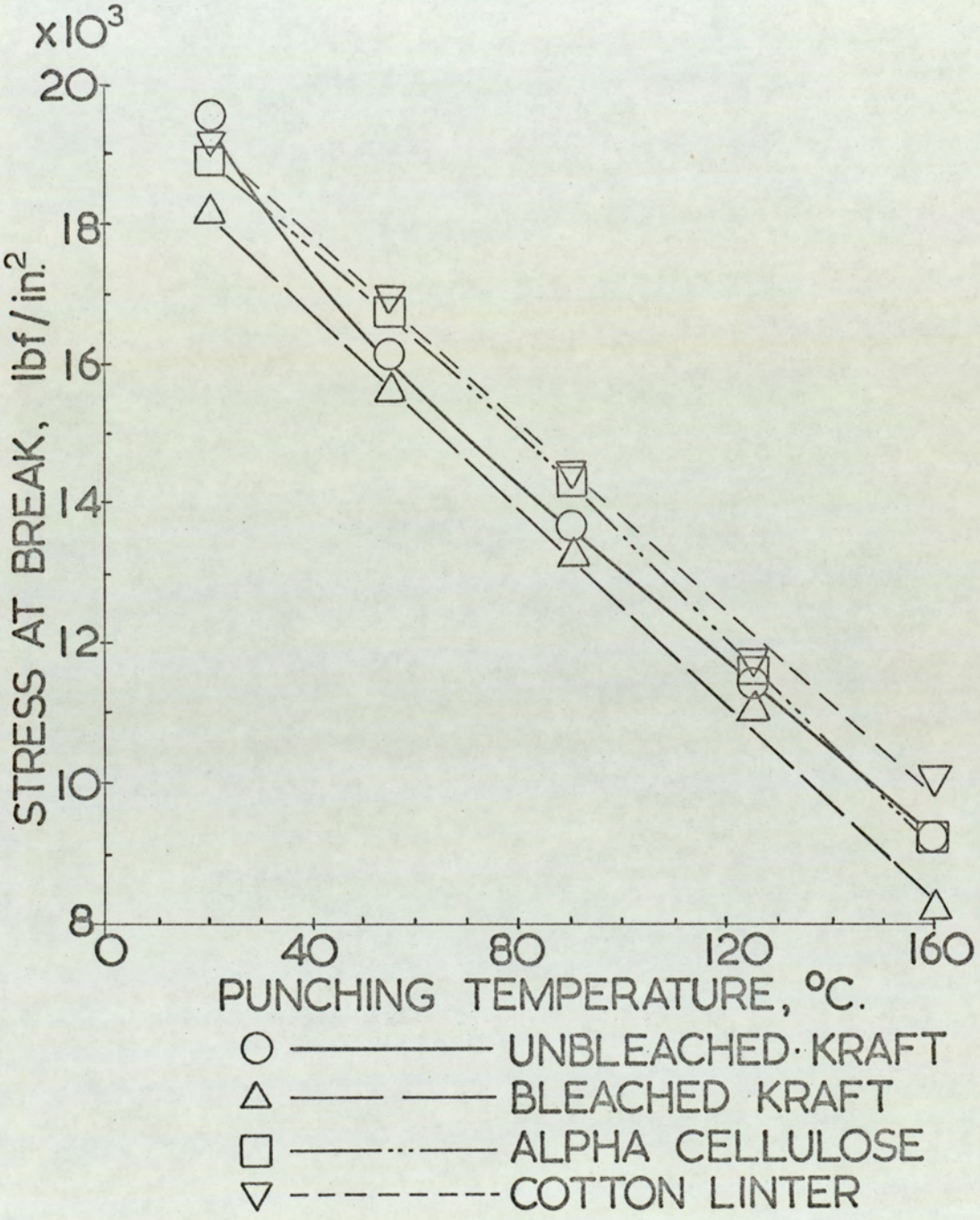

FIGURE 45a. STRESS AT BREAK AGAINST PUNCHING TEMPERATURE.

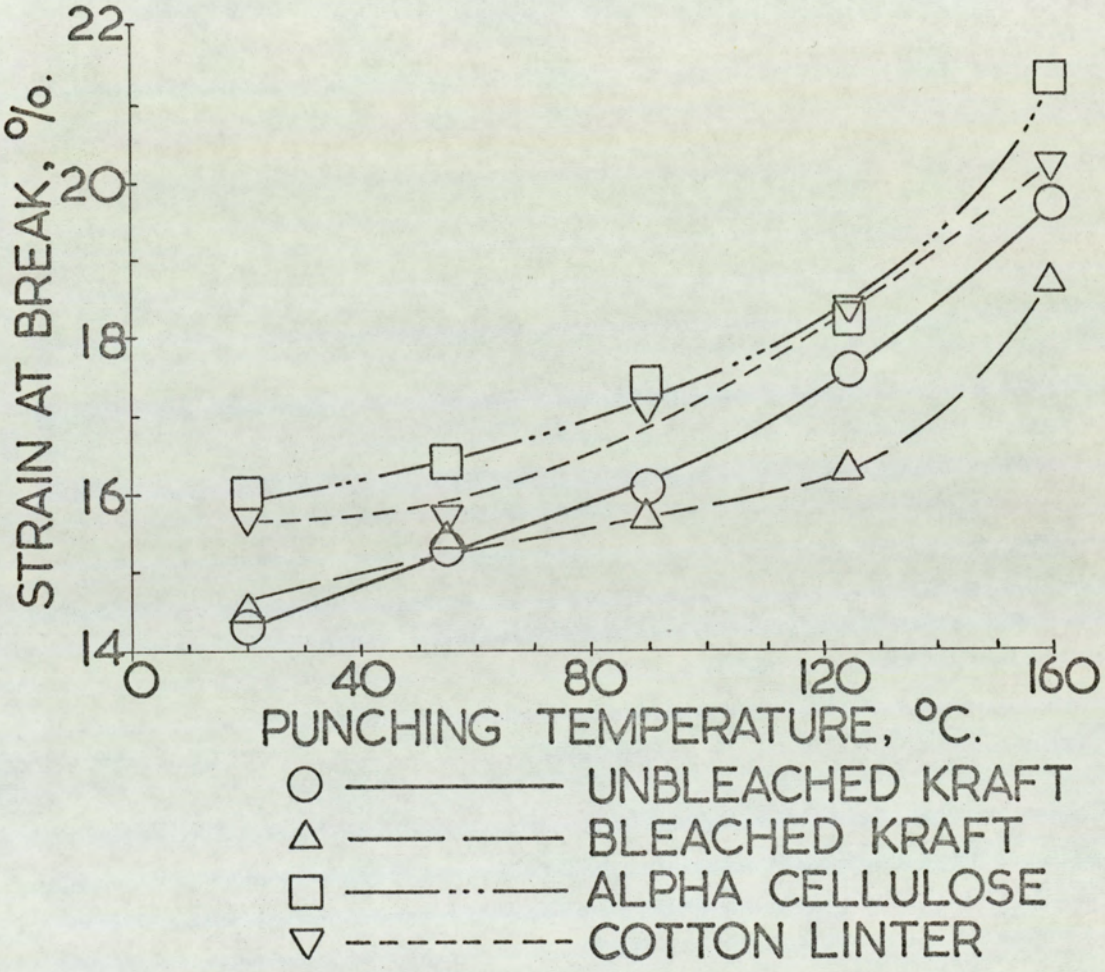

FIGURE 45b. STRAIN AT BREAK AGAINST PUNCHING TEMPERATURE.

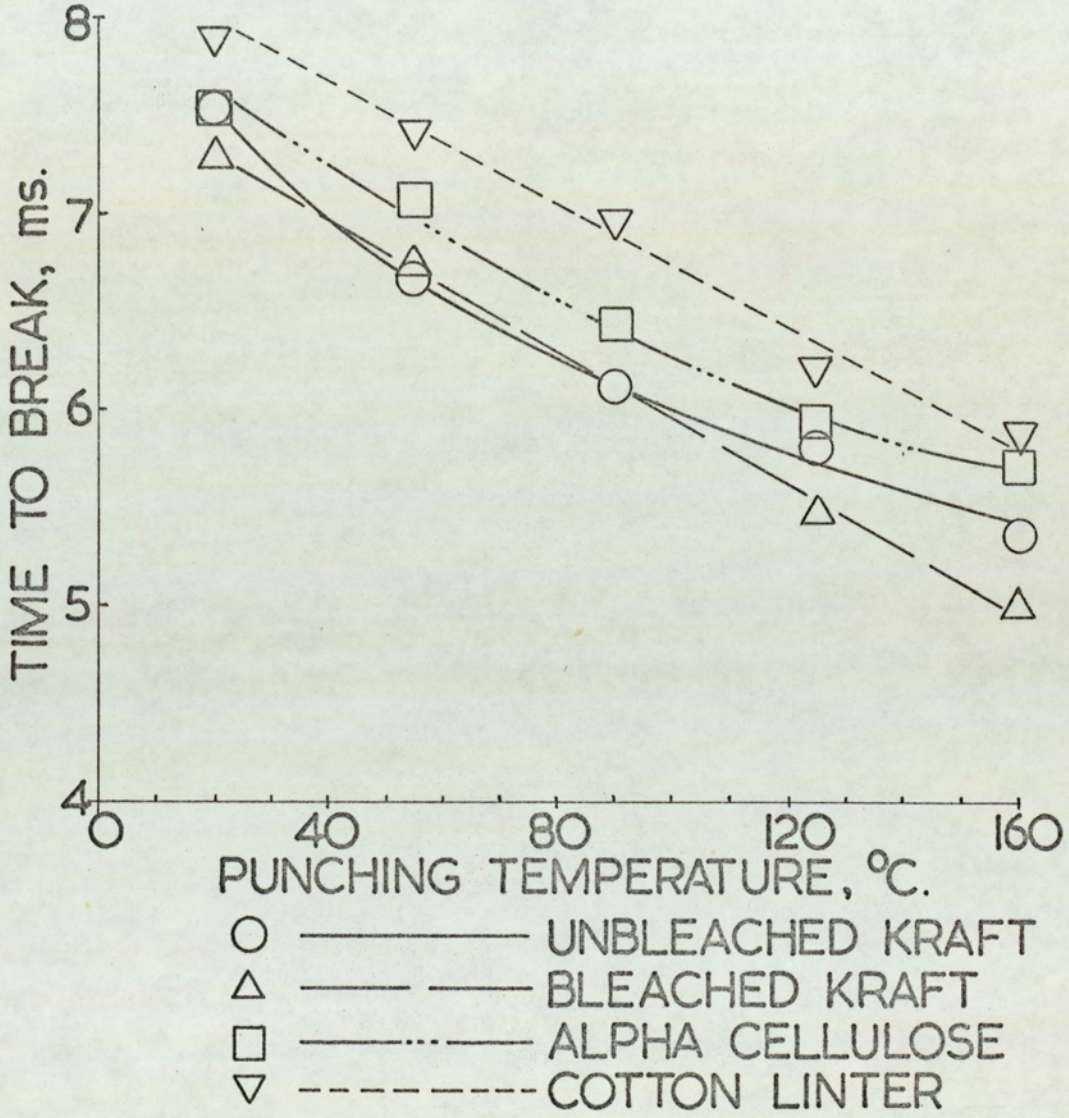

FIGURE 45c. TIME TO BREAK AGAINST PUNCHING TEMPERATURE.

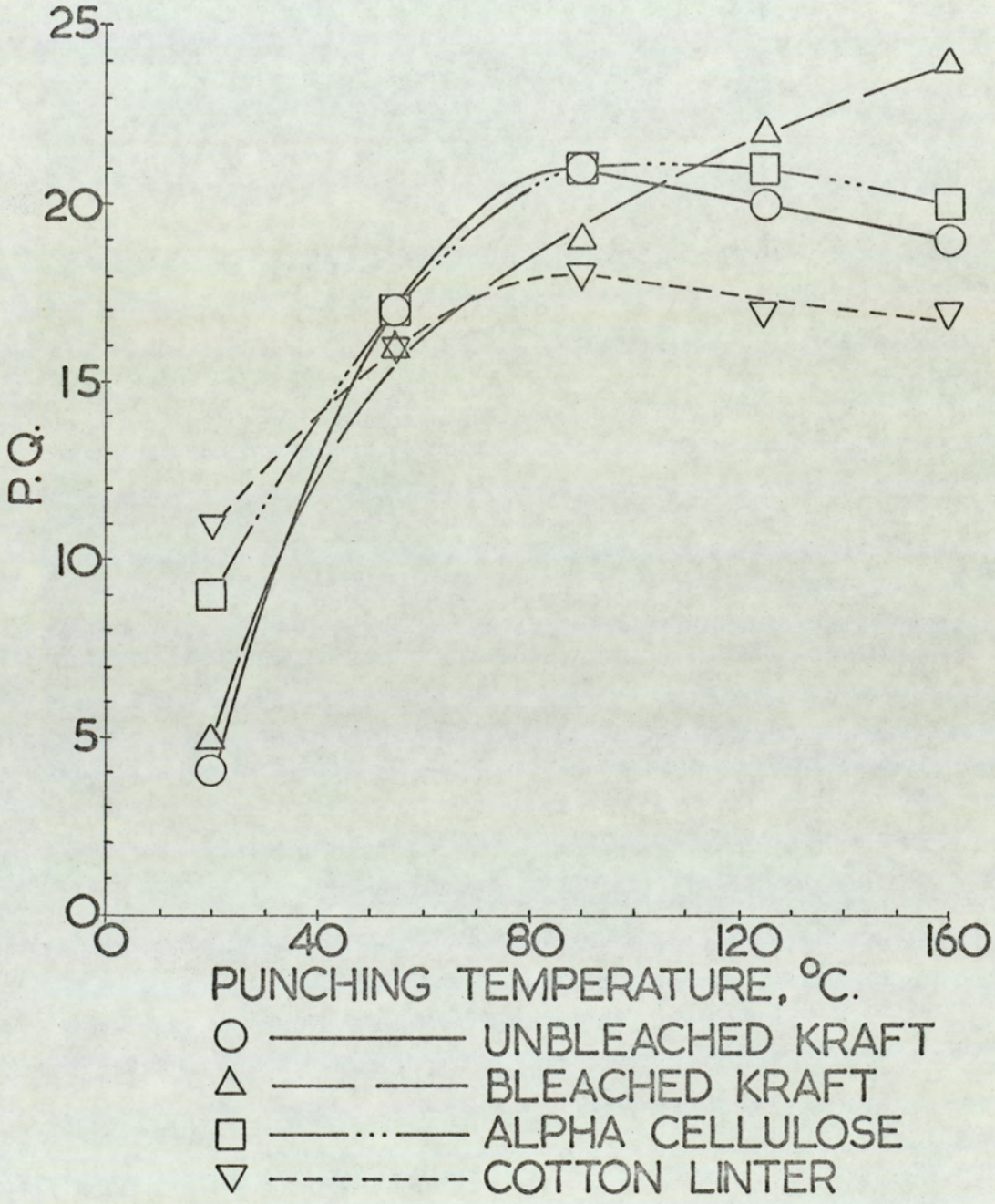

FIGURE 45d. PUNCHING QUALITY AGAINST PUNCHING TEMPERATURE.

PAPER	PUNCHING TEMP, °C	PQ	VISIBLE DEFECTS *	STRESS/STRAIN FEATURES **
UNBLEACHED KRAFT	20°C	4	ELH	1y H 2y
	55°C	17	LH	1y H 2y
	90°C	21	LHT	1y
	125°C	20	LHT	1y
	160°C	19	LHT	1y H 2y
BLEACHED KRAFT	20°C	5	ELH	1y H 2y
	55°C	16	LH	1y H 2y
	90°C	19	LHT	1y H 2y
	125°C	22	HT	1y
	160°C	24	HT	1y
ALPHA CELLULOSE	20°C	9	LH	1y H 2y
	55°C	17	LH	1y H 2y
	90°C	21	LH	1y
	125°C	21	HT	1y
	160°C	20	HT	1y
COTTON LINTER	20°C	11	ELHT	1y H 2y
	55°C	16	HT	1y H 2y
	90°C	18	HT	1y H 2y
	125°C	17	HT	1y H 2y
	160°C	17	HT	1y H 2y

* E = Cracks to edge
F = Feathering
L = Lifting
H = Haloing
T = Tensile cracking
D = Drawing down

** 1y = primary yield
H = hardening region
2y = secondary yield

TABLE 10. SUMMARY OF PUNCHING QUALITY DATA FOR THE LAMINATES BASED ON DIFFERENT PAPERS

7.6. General comments.

There were five main points arising from the 55°C tests :

1) strain at break and punching quality decreased as the recommended punching temperature (at which the materials should have been punched) increased,

2) punching quality showed an increase with increasing ultimate tensile stress,

3) punching quality increased as tensile anisotropy increased,

4) punching quality decreased as the stress concentration factor increased in the weaker direction, and

5) unbleached kraft and bleached kraft materials showed a clear division in properties, unbleached kraft being generally stronger and better punching at 55°C.

From the work with the four prepared laminates it was decided to investigate the effect of resin composition using bleached kraft based laminates.

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CHAPTER 8.

THE EFFECT OF RESIN COMPOSITION.

Having obtained a background picture of the way in which the commercial materials behaved and of the possible pitfalls in the impregnating and pressing stages of laminate manufacture, work now began on the effect of resin composition using bleached kraft based materials[42].

In the time available it was only possible to make and test four laminates. It was necessary both to lay down the technique by which further work could proceed and at the same time to select the resins to give as much information as possible.

In view of the normally accepted concept of phenolic resins as a three dimensional crosslinked structure three resins were prepared which, it was hoped, would demonstrate the effect of crosslink frequency. The first two resins were simple phenol/formaldehyde compositions having P/F ratios of 1/1.45 and 1/1.15. The third resin was made from phenol/formaldehyde (P/F : 1/1.15) and p-cresol/formaldehyde (p-Cr/F : 1/1) mixed (before reaction) to give a ratio p-cresol/phenol of 3/1.

It has been shown in Section 2.2.1. that most commercial methods of plasticisation of resins for punching involve the use of unsaturated hydrocarbon

chains. The final resin was, therefore, a phenol/formaldehyde composition (P/F : 1/1.45) incorporating Cashew Nut Shell Liquid (25% w/w based on phenol). This material was used in order to minimise the likelihood of plasticiser migration.

8.1. Preparation of laminates.

The phenol and p-cresol were general purpose laboratory grade materials and the formaldehyde was in solution as formalin (35.8% w/w). Since electrical properties were not to be investigated crude Cashew Nut Shell Liquid (C.N.S.L.)was used.

All four resins were catalysed with barium hydroxide (4g $Ba(OH)_2.8H_2O$ per g mole of phenol or p-cresol) and were neutralised with 10% sulphuric acid before vacuum distillation.

The resins were prepared in a glass reflux apparatus (see Figure 46 p.120) provided with a tap to enable the distillate return to be sampled as required. The reactants were refluxed until the formaldehyde concentration in the distillate had fallen below 0.5% w/w. The analytical technique was based on the sulphite method described by Walker[43] and is described in more detail in Appendix 2. After reflux the resins were cooled. In the case of the plasticised resin the C.N.S.L. was added at this point and the temperature held at 80°C for 15 min before cooling.

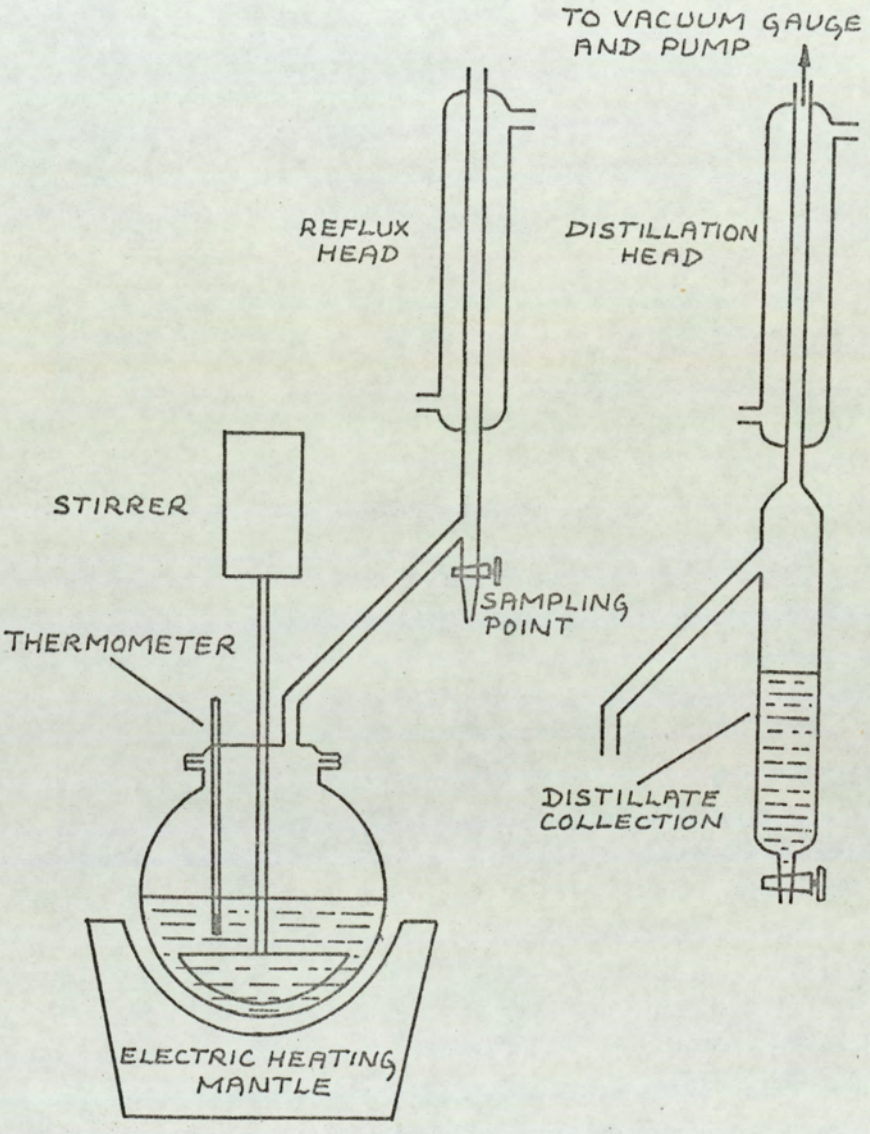

FIGURE 46. RESIN STILL.

After neutralisation, vacuum distillation was carried out at less than 25mm Hg until the resin temperature began to rise. For the P/F : 1/1.15 resin and the p-cresol resin the temperature was allowed to

rise to 80°C. For the remaining two resins distillation was stopped at 30°C since, from the behaviour of the bubbles formed during distillation, the viscosity appeared to have begun to increase. It was thought preferable to impregnate the paper with lightly condensed resins to minimise differences at the impregnation stage. This practice was expected to result in good impregnation of the fibres and thus to minimise the masking of resin properties by the fibres.

The resins were dissolved in industrial methylated spirits to give a solids content of 50% as determined by a technique very similar to the British Standard method[44] (see Appendix 2).

The bleached kraft paper was impregnated once with the 50% solids solution. The resin content of the paper was then built up with successive impregnations using the same solution diluted to 25% solids. The impregnation was otherwise carried out as has previously been described (see Section 6.1.).

The impregnated paper was dried in a forced draught hot-air oven controlled at 103°C. The higher temperature, compared with that previously used (see Section 6.1.1.) was necessary to advance the lightly condensed resins satisfactorily although

the p-cresol resin required yet a further drying period at 123°C.* The original intention was to dry all the papers to a flash test value of 10 - 15%. In practice the range was 8.9 - 14.8%. Since different resins were being used on the same paper it seemed sensible to control the drying stage by using a function of the resin flow characteristics rather than drying to a fixed volatile content. Resin content for the four materials ranged between 46.0 - 48.5%. A pack of seven or eight plies (to give a nominal laminate thickness of 1/16 in) of the dried impregnated paper were then pressed between stainless steel plates at 150°C and 1000 lbf/in^2 for 10 min followed by 10 min cooling under pressure.

Further details of the preparation of these laminates are given in Appendix 3.

8.2. Measurement of punching characteristics.

Each of the laminates was punched at 20°, 55°, 90°, 125° and 160°C (10 min heating time). P.Q. values and visible defects have been tabulated in Table 11 (p. 123). Features noted in the stress/strain curves have also been included in this table.

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* It was noted that this practice could have resulted in some loss of lower molecular weight material from the lightly condensed resins.

RESIN	PUNCHING	PQ	VISIBLE DEFECTS *	STRESS/STRAIN FEATURES **
P/F:1/1.45	20°C	5	EFLHT	1y H 2y
	55°C	15	FLHT	1y H 2y
	90°C	18	HT	1y H 2y
	125°C	19	H	1y H 2y
	160°C	21	HT	1y
P/F:1/1.15	20°C	12	FLHT	1y H 2y
	55°C	16	FH	1y H 2y
	90°C	19	H	1y H 2y
	125°C	21	H	1y
	160°C	23	H	1y
p-Cr/P:3/1 (p-Cr/F:1/1) (P/F:1/1.15)	20°C	12	FLH	1y H 2y
	55°C	17	H	1y H 2y
	90°C	19	H	1y H 2y
	125°C	22	H	1y
	160°C	22	HD	1y
P/F:1/1.45 + 25% C.N.S.L. (based on P)	20°C	16	FLH	1y H 2y
	55°C	19	H	1y H 2y
	90°C	22	H	1y
	125°C	22	H	1y
	160°C	23	H	1y

* E = Cracks to edge
F = Feathering
L = Lifting
H = Haloing
T = Tensile cracking
D = Drawing down

** 1y = primary yield
H = hardening region
2y = secondary yield

TABLE 11. SUMMARY OF PUNCHING QUALITY DATA FOR THE LAMINATES MADE FROM DIFFERENT RESINS

8.3. Punching characteristics.

Punching characteristics are plotted against punching temperature for the four materials in Figures 47a to 47d (pp. 124-127).

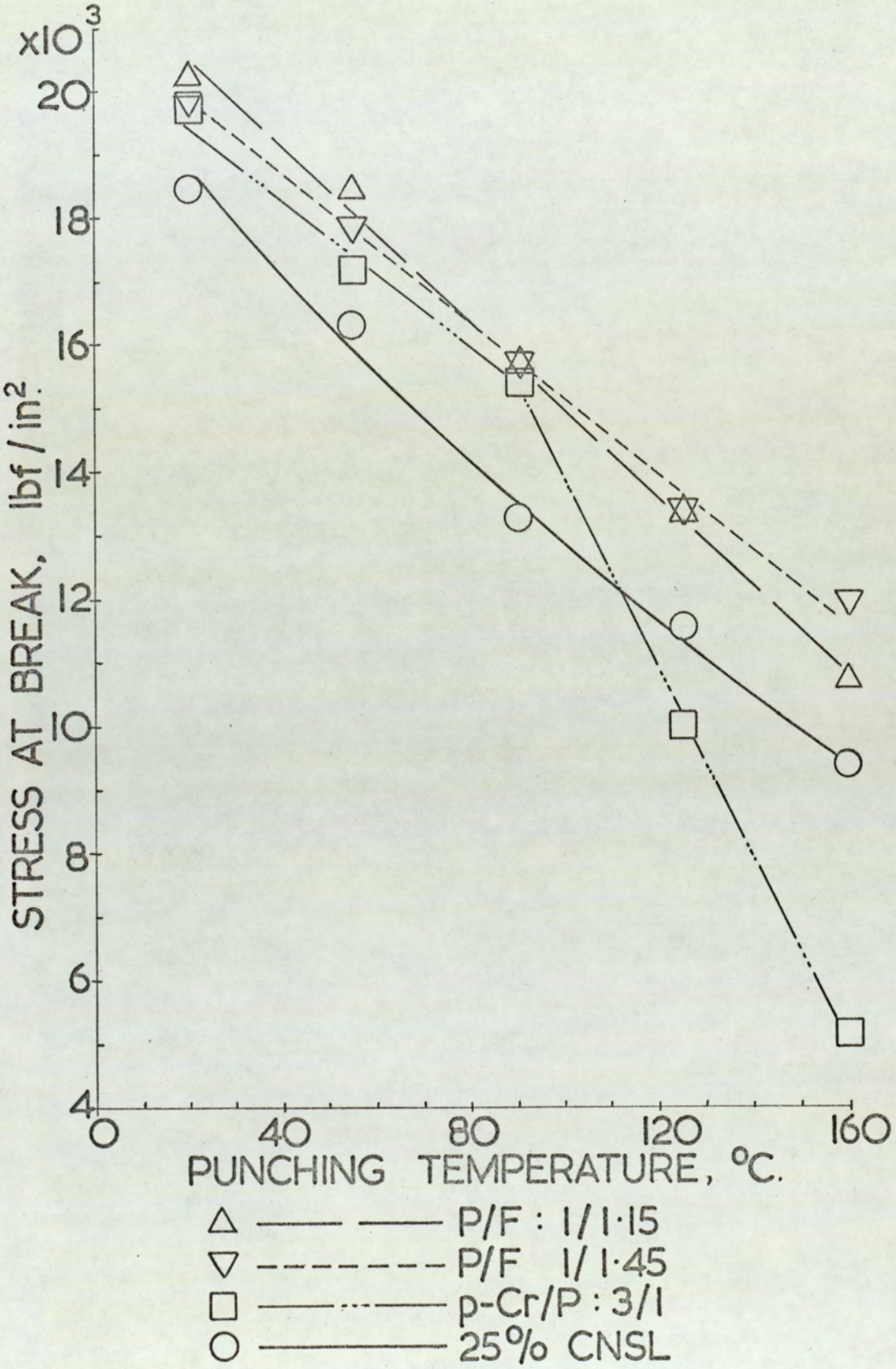


FIGURE 47a. STRESS AT BREAK AGAINST PUNCHING TEMPERATURE.

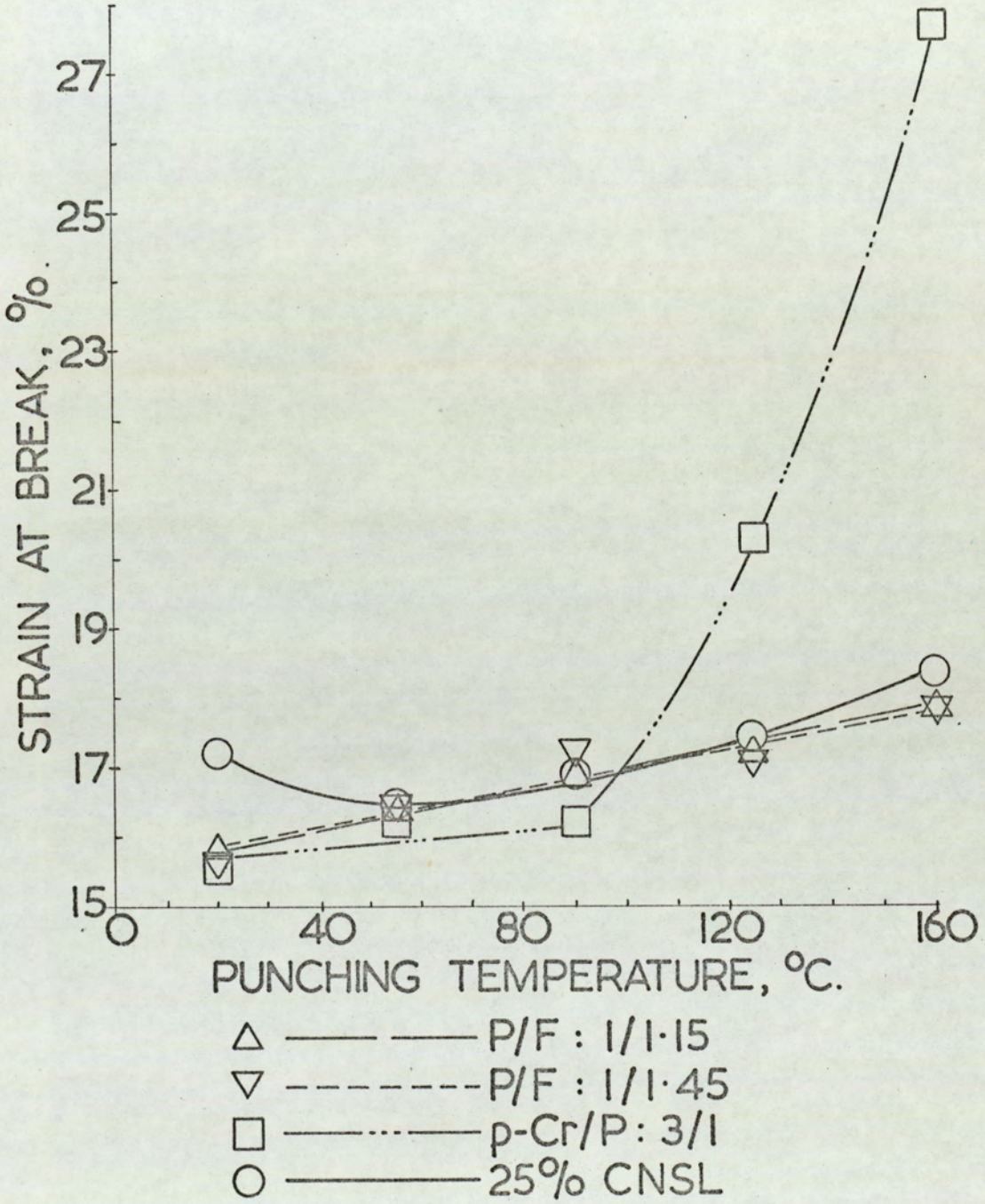


FIGURE 47b. STRAIN AT BREAK AGAINST PUNCHING TEMPERATURE.

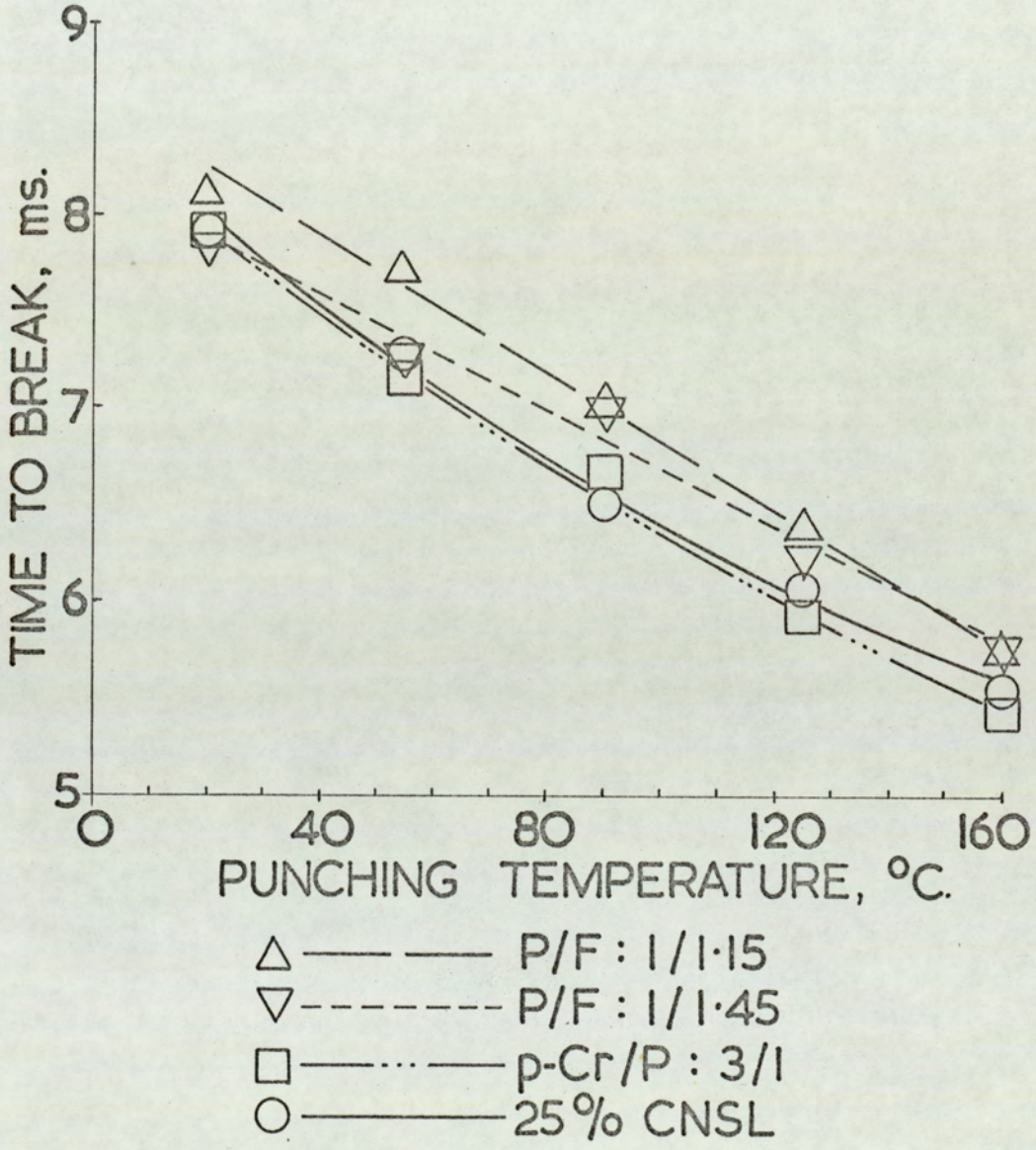


FIGURE 47c. TIME TO BREAK AGAINST PUNCHING TEMPERATURE.

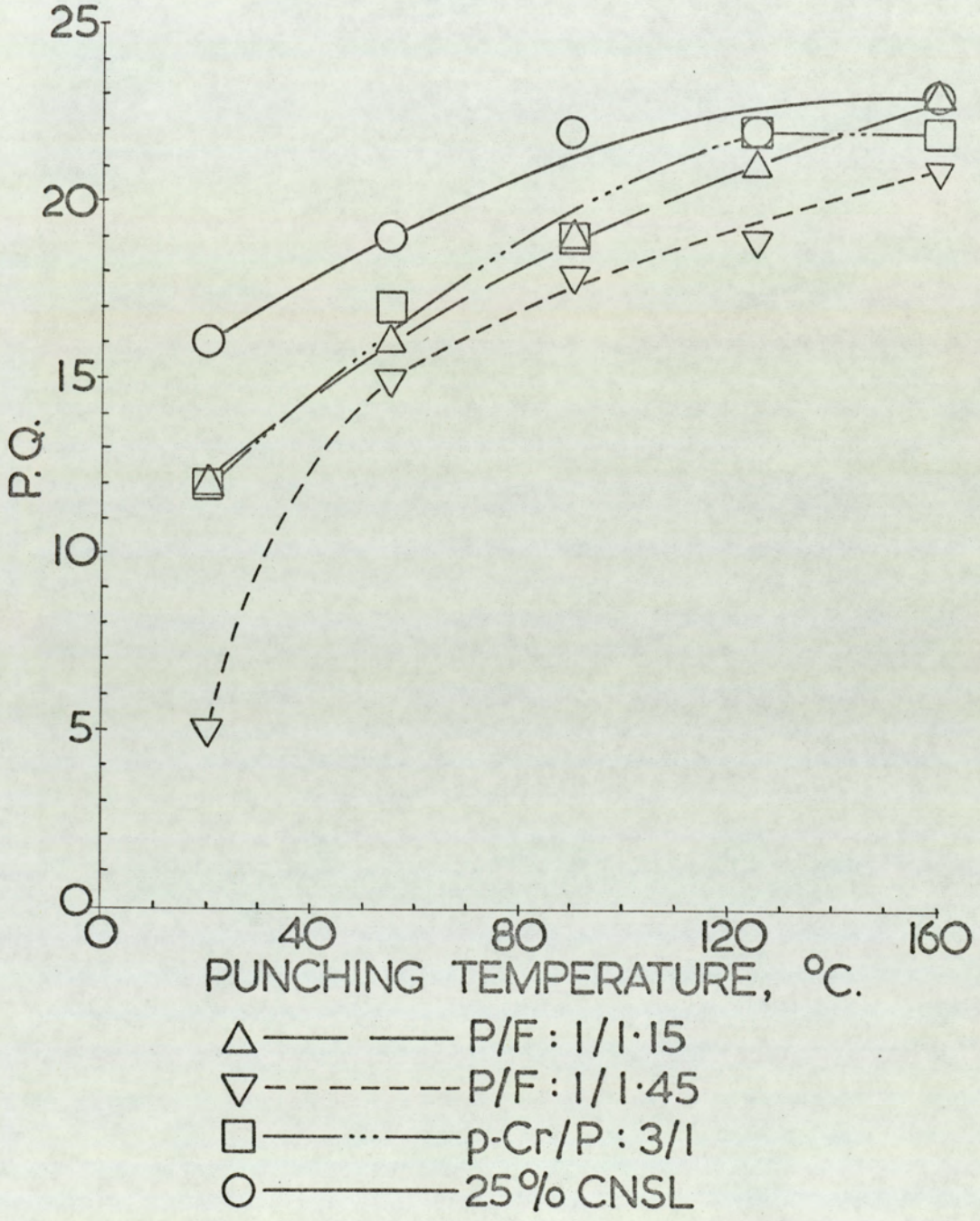


FIGURE 47d. PUNCHING QUALITY AGAINST PUNCHING TEMPERATURE.

Stress at break.

The simple phenol/formaldehyde resins showed very similar trends. P/F : 1/1.15 showed slightly greater temperature dependence than 1/1.45 since it was stronger at lower temperatures and weaker at higher temperatures. The p-cresol resin was similar to the simple resins until 90°C from which temperature stress at break rapidly decreased. The C.N.S.L. plasticised laminate was clearly weaker than the rest (except for the p-cresol laminate at higher temperatures) and its temperature dependence seemed to decrease slightly as the punching temperature increased.

Strain at break.

The simple resins seemed to behave almost identically. The p-cresol resin showed comparatively low strain at break up to 90°C, when it rapidly increased. The C.N.S.L. plasticised laminate showed an initial decrease whereafter it behaved like the simple resins between 55°-125°C, finally showing slightly increased strain at break at 160°C.

Time to break.

Again the 1/1.15 material appeared to be more sensitive to temperature than the 1/1.45. The p-cresol and C.N.S.L. laminates showed very similar behaviour and gave shorter times than the simple resins.

P.Q.

The 1/1.45 material showed inferior punching quality over the whole temperature range, whereas the 1/1.15 behaved similarly to the p-cresol material. C.N.S.L. had a markedly beneficial effect on punching quality especially at low temperatures.

-o-o-o-o-o-

CHAPTER 9.

DISCUSSION.

9.1. Interpretation of the shape of the stress/strain curves.

Several workers have postulated mechanisms to explain the fracture processes involved in punching laminates.

Frerichmann[3] arrested the punch travel at various penetrations and examined the cut edges. He found that a paper-based thermosetting laminate exhibited mainly elastic behaviour up to a penetration of 14% of the sheet thickness. Microcracks then appeared within the material which were followed by macrocracks. Sudden brittle fracture occurred after 28% penetration and peak force occurred at 50%.

Hojo[35] arrived at similar conclusions using a similar technique but found that peak force was reached at between 15 and 25% penetration depending on conditions.

Nakano[27] tentatively postulated a similar mechanism by reference to the shape of his punching force/penetration curves. Initially surface irregularities in the material were smoothed by the punch. A relaxation stage was reached after about 7% penetration when small cracks were formed in the

surface of the material. Further relaxation occurred later with crack growth which was complete after maximum punching pressure had been reached at about 25% penetration.

In the light of the discussion above, the following hypothetical mechanism is suggested to explain the shape of the stress/strain curves in general terms. Reference to Figure 48 (taken from Figures 17 (p. 59) and 19 (p. 61)) will help the explanation.

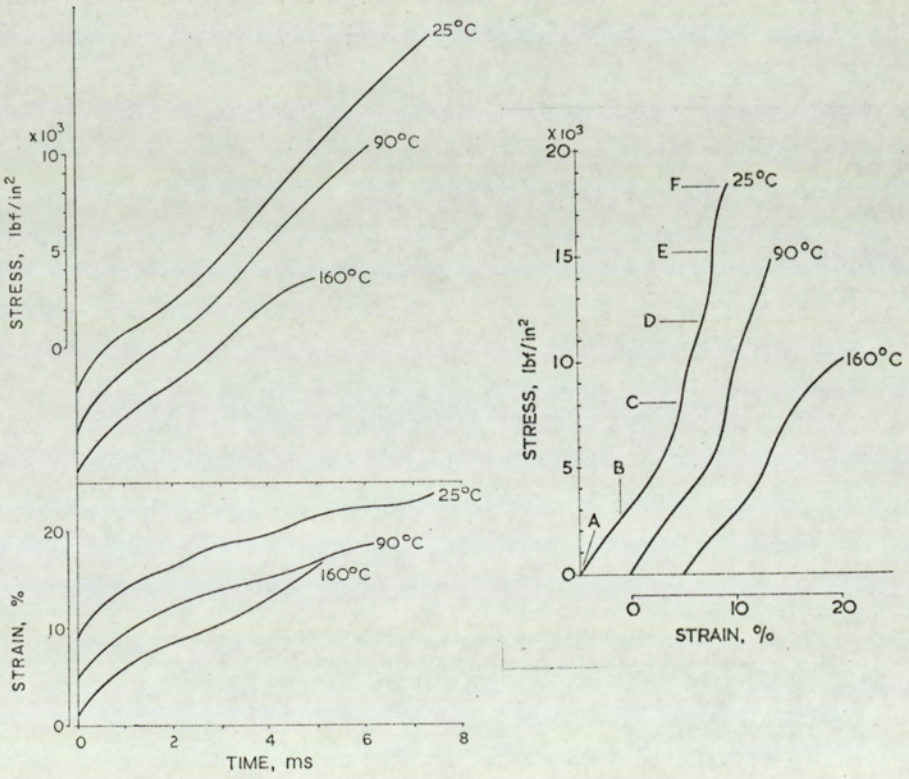


FIGURE 48. STRESS/TIME AND STRAIN/TIME CURVES WITH THEIR DERIVED STRESS/STRAIN CURVES FOR HOT-PUNCHING LAMINATE AT 25°, 90° and 160°C.

During the stage AB considerable reduction in punch velocity occurs. Because of this it might be unwise to place too close an interpretation on the shape of this part of the curve although smoothing of surface irregularities and 'bedding-down' of the test-piece would occur here. Along BC, shear stress builds up in the test-piece until, at C, the formation of microcracks begins within the material. CD represents the yield due to the formation of microcracks. If the applied stress necessary to propagate the microcracks exceeds the applied stress which produced them then the slope of the curve would increase as seen in the region DE. The curved region EF is only present when conditions are such that punching quality is inadequate and is associated with catastrophic failure resulting in severe damage to the test-piece. In the 90°C curve secondary yield (EF) is absent and punching quality is satisfactory. It is suggested that the crack propagation stage in this case proceeds smoothly until the fracture process is complete. At 160°C the reduction in applied stress necessary for crack propagation appears to be reduced to an order similar to that for the crack initiation step. Owing to softening, and hence toughening, of the material, cracks are discouraged from propagating out of the sheared zone.

Examination of all the results obtained in this

work will show that all the stress/strain curves obtained under conditions leading to unsatisfactory punching quality (i.e. P.Q. less than 20) were of the same general shape as that for the 25°C curve in Figure 48 (p. 131) with the exception of two. No material punching satisfactorily (P.Q. equal to or greater than 20) showed secondary yield.

The two exceptions referred to above are shown in Figure 49.

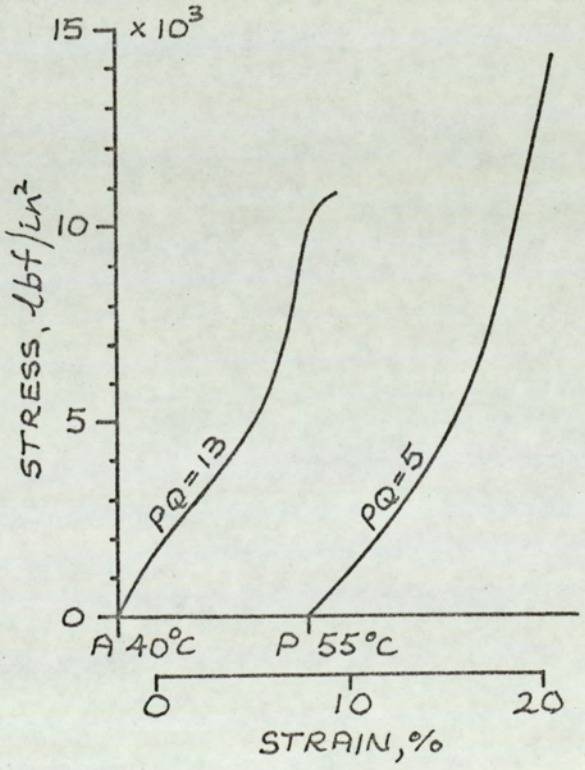


FIGURE 49. STRESS/STRAIN CURVES FOR MATERIAL A AT 40°C AND MATERIAL P AT 55°C.

Both these materials were members of the commercial series (A at 40°C and P at 55°C). In the case of A at 40°C sudden yield was seen in the stress/strain curve but not preceded by a hardening region. It was assumed that in this case crack initiation and unrestricted propagation (the resin not being toughened by elevated temperature) occurred virtually simultaneously. This implied a close relationship between filler and resin since otherwise the resin/filler interfaces would be expected to hinder the propagation stage. This was consistent with the fact that A was a material with good electrical properties and low water absorption.

In the case of P at 55°C the 'bedding-down' stage was followed by a region of linear behaviour. At present, no explanation can be offered for this.

Taking the results as a whole there seems to be conclusive evidence that the presence of secondary yield is almost always associated with unsatisfactory punching quality. This suggests the possible use of the general technique as a pass/fail test for punching quality (see Section 2.3.), although it would clearly require simplification since the present test, with calculations, can take 10 hours for one material at one temperature.

The fact that improved punch penetration measurements have probably been achieved is suggested

by the observation that the range of 'strain at break' values observed was 10.2 - 21.3% (excluding the p-cresol material at higher temperatures). This is significantly lower than those obtained by other workers referred to in this Section which suggests that the extra strain which they observed was probably due to mechanical deflections between their reference point and the punch face. This also suggests why other workers have not observed the connection between shape of the stress/strain curve and punching quality, although Nakano[27] appeared to have been in a position to do so.

9.2. The effect of base-paper.

Although the effect of paper variables was not a primary objective of this work it became necessary to examine this briefly with a view to selecting the most suitable paper for the comparison of different resins.

The comparison between the bleached kraft and cotton linter laminates (Chapter 6) provided the first experimental evidence of the differences in punching characteristics that can arise as a result of different base-papers.

The greater stress, strain and time to break of the cotton linter material over the bleached kraft material at higher temperatures suggested that the cotton linter fibres tended to act as better crack stoppers than the bleached kraft fibres. The low

punching quality of the bleached kraft laminate at 25°C and the relatively greater improvement with increasing temperature indicated that the bleached kraft fibres exerted less control upon the crack propagation stage. The temperature dependence of the resin itself appeared to be more significant in this case.

The results using the papers consolidated with no resin (Figures 38 p. 95 and 39 p. 96) suggested that the paper fibres themselves might have been capable of supporting a significant proportion of the stress at break of their laminates. Obviously the environment of a fibre in the consolidated board was different from that in a laminate, since in the board the fibre was merely supported by secondary chemical forces and entanglement with its neighbours whereas in the laminate it was embedded in a resin matrix. It might be supposed that the independent strength of the paper would be even greater in a resin matrix where, with proper support, the fibres would be able to exhibit a greater proportion of their full mechanical strength.

Initially it was accepted that the scatter observed in the trends obtained with the commercial series (Chapter 5) could not be resolved. However, the results from the two materials discussed above in this section suggested classifying them according to paper type. Reference to Figure 40 (p. 102) shows that this

was justified. In order to simplify the picture and to attempt to isolate the property or properties associated with punching quality the materials were all punched at 55°C (Figure 41 p. 104).

For convenience, the five main points arising from the 55°C tests (Section 7.6.) are repeated below :

1) strain at break and punching quality decreased as the recommended punching temperature increased,

2) punching quality increased with increasing U.T.S.,

3) punching quality increased with increasing tensile anisotropy,

4) punching quality decreased with increasing stress concentration factor in the weaker direction, and

5) unbleached kraft and bleached kraft materials showed a clear division in properties, unbleached kraft being generally stronger and better punching at 55°C.

The first two points may be explained on the basis of resin content variations. Table 7 (p. 82) showed that, for the materials described in Section 6.1.3., increasing resin content gave a reduction in strain at break since the 48.1% material gave 14.6% strain at break whereas the 8 ply 38.0% material (of comparable thickness) gave 15.5%. Stress at break was virtually unaltered but punching quality improved at the lower resin content (16 at 48.1% and 18 at 38.0%).

Pepper and Barwell[41] described the effect of resin content on the tensile properties of a phenolic

laminate made from high-density kraft paper pressed at 2000 lbf/in^2. Tensile strength was shown to increase with resin content as resin replaced voids in the paper. When the voids were filled, tensile strength decreased with further addition of resin as the proportion of the stronger component, the paper fibres, was reduced.

The commercial laminates were assumed to be void free and hence to be in the region in which tensile strength was decreasing with increasing resin content. As punching quality would have also decreased with increasing resin content then it was concluded that, in this region, as U.T.S. increased then so did punching quality.

Thus, within each paper type, the trends in punching characteristics at 55°C and the trends in the U.T.S./P.Q. curves were consistent with changes in resin content.

If this interpretation was correct, then the increase in tensile anisotropy with increasing punching quality might have been no more than a further manifestation of decreasing resin content. Anisotropy arising from orientation of paper fibres in the finished laminate would tend to be reduced by increased resin content. Thus as resin content decreased (and punching quality increased) then there would be a tendency for increasing anisotropy.

The fact that cracks in the stronger unnotched tensile test-pieces appeared to turn towards the weaker direction suggested the importance of the weaker direction in the crack propagation process. This was consistent with the decrease in punching quality with increasing stress concentration factor or brittleness in the weaker direction.

The gross differences between the unbleached kraft and bleached kraft laminates were thought to be due to the better crack stopping properties of the longer, stronger unbleached kraft fibres and comparatively poor resin/fibre interaction leading to the increased strength and improved punching quality of these materials.

Only the unbleached kraft materials showed lifting, which implied a reduction of interlaminar strength. This was consistent with the more coherent and less soft, fluffy appearance of unbleached kraft paper. There would, presumably, have been less involvement of unbleached kraft fibres with those of an adjacent ply. The absence of feathering could have been associated with superior crack stopping properties or with the difficulty in observing visual defects because of the opaque nature of most of the unbleached kraft materials.

There was little to be noted about the cotton linter or alpha cellulose materials because of

insufficient data. One of the cotton linter materials (Material A at 55°C) had exceptional, and desirable, properties which might have been associated with the resin system used or with resin/paper interaction.

To summarise, the results suggested that, at 55°C, the punching characteristics of the commercial laminates examined primarily depended upon the paper used. Without direct evidence, there were indications that resin content was a secondary factor. Comparison of tensile properties in the weaker and stronger directions of the laminates suggested that fibre orientation might play some part in determining punching quality.

The work with the four laminates simply showed that bleached kraft paper was the most suitable for subsequent work with different resin systems. This was in agreement with the results already shown in Figure 37 (p. 92) in which punching characteristics were compared for the bleached kraft and cotton linter laminates. It was interesting to note that, once again, the unbleached kraft material was the worst offender in respect of lifting since this occurred over the whole temperature range. On the same basis, least lifting occurred with the cotton linter material. Feathering did not occur with any of the four materials.

9.3. The effect of resin composition.

9.3.1. The fine structure of cured phenolic resins.

Before considering the experimental results from the present work it is appropriate to consider, very briefly, the structure of a cured phenolic resin. As Carswell[45] said, "It is obviously impossible to give any definite formula for a cross-linked phenoplast .....". He did however suggest that the structure shown in Figure 50 (taken from his book) was probably typical though oversimplified.

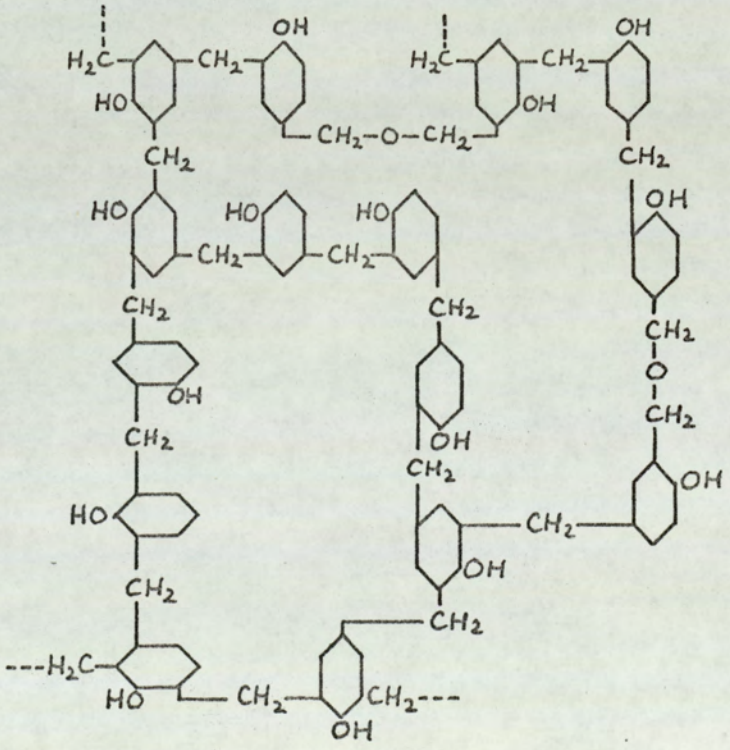


FIGURE 50. SIMPLIFIED REPRESENTATION OF CURED PHENOLIC RESIN STRUCTURE (AFTER CARSWELL[45]).

Megson[46] examined steric effects and rigidity by reference to some resin intermediates and went on to consider the structure of cross-linked resins. He suggested that if two Novolak chains were brought together then the inter-chain distances between active centres would be very variable because of the complex highly kinked nature of the chains. He pointed out that both distances and angles between phenolic nuclei must be correct for cross-linking. He concluded that a completely cross-linked structure (phenol/ methylene : 2/3) is most unlikely. Hence, a cured resite would possess a structure containing a considerable number of voids.

Working along similar lines, Pritchett[47] also concluded that cross-linking must be difficult. By building models of phenolic resins he found that component nuclei would not rotate around the methylene bridge. He suggested that, during the hardening process, the resin molecule was firstly a simple slow-growing chain, and other chains subsequently condensed on to it to form branches. This process continued until separate molecules entangled to form a gel. As the hardening continued further growth and entanglement took place and the resin molecules became immobilised and, therefore, insoluble and infusible. He suggested that this mechanism could account for the properties of the hardening resins, even if cross-linking was completely absent.

Megson[46] suggested that Pritchett's theory was not incompatible with his own and that it seemed probable that in a normal hardened resin, there may be light cross-linking as well as molecular entanglement present at the same time. As will be seen in the next section it is particularly relevant to note that, in the present context, he suggested that in special cases (e.g. p-cresol resins) molecular entanglement alone may be sufficient to explain the observed properties. He pointed out that further evidence was needed.

Again, in the present context, Megson's interest in phenol-dimethylene chains[46] might well be relevant. He suggested that the molecules would not be rigid although his point that cross-linking might be much more complete suggests that using such a system in cold-punching applications may not have the advantages anticipated at first glance.

The fine physical structure of resins is not discussed in this thesis but it might be helpful to consider this in future work.

9.3.2. An examination of the experimental results.

The P/F : 1/1.45 resin showed inferior punching quality to the 1/1.15 resin. The lower temperature sensitivity in stress and time was presumably due to a higher cross-link density giving a structure containing elements less capable of rotational freedom.

There was, however, little evidence that the temperature dependence of strain at break was less for the 1/1.45 material.

Up to 90°C the p-cresol resin showed similar behaviour to the simple resins in stress at break although it was slightly weaker and showed less strain at break. 90°C seemed to correspond to a glass transition point and at 160°C the stress/strain curve was very similar to that for a consolidated bleached kraft paper board. These curves are compared in Figure 51.

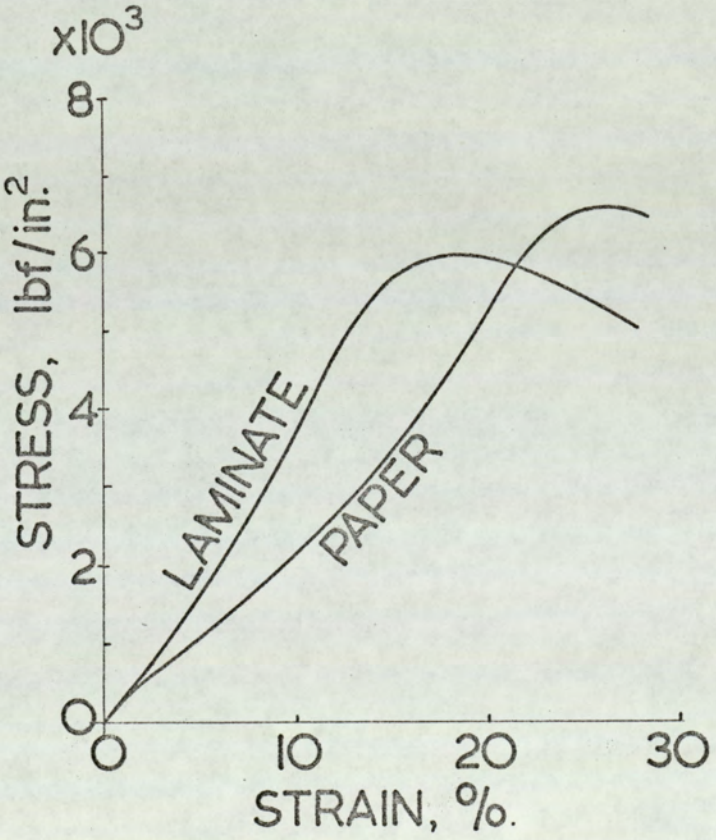


FIGURE 51. STRESS/STRAIN CURVES FOR CONSOLIDATED BLEACHED KRAFT PAPER AND P-CRESOL/PHENOL LAMINATE PUNCHED AT 160°C.

The paper curve was taken from the results shown in Figure 38 (p. 95) but corrected to the same number of plies as used in the laminate. The resin seemed only to produce peak stress at a lower strain value and appeared to contribute no strength to the system. This suggested the tree-like structure put forward by Pritchett[47], in this case the branches being so sparse that insufficient entanglement led to a loss of rigidity above 90°C. At this temperature it appears that the 'molecules' possessed sufficient energy to overcome the barriers to movement relative to one another.

Sprung[48] found that when various phenols and paraformaldehyde were reacted in the presence of triethanolamine, phenol reacted about three times as fast as p-cresol. He also found that phenol provided a much faster rate of condensation than p-cresol. Admittedly reaction conditions in the present work were not the same, but Müller and Müller[49] compared the reactivities of several phenols under alkaline conditions by measuring the points at which their resins gelled. This usually occurred when about two-thirds of the resin was in the infusible state. Relative reaction velocities for phenol and p-cresol were 1.0 : 0.6 respectively. Thus if phenol showed higher rates of reaction and condensation it might be expected that the fine

structure of the phenol/p-cresol resin would comprise 'trunks' consisting mainly of phenol groups surrounded by 'branches' consisting mainly of p-cresol groups.

Jones[50] studied the melt viscosity of a series of phenol/formaldehyde Novolaks over a temperature range of 100° - 250°C. It was shown that the energy of activation for viscous flow fell rapidly as the temperature increased and tended to steady values at higher temperatures. The steady values were almost linearly related to molecular weight. The rapid fall in energy of activation as temperature increased was attributed to the breakdown of association, mainly consisting of hydrogen bonds. It was believed that, at high temperatures, flow took place by the movement of single molecules, but at low temperatures the large energies of activation suggested that flow took place by associated dimers, trimers etc. breaking away from the general association field that surrounded them. It is also perhaps significant that precautions were taken to remove as much water and phenol as possible since these both appreciably altered the viscosity of resins containing them (1% water having been found to decrease the viscosity of a Novolak by five times!).

Bearing Jones' work in mind it is interesting to note that, despite the apparent lack of cross-links the punching quality of the p-cresol material was virtually identical with the 1/1.15 resin up to 90°C.

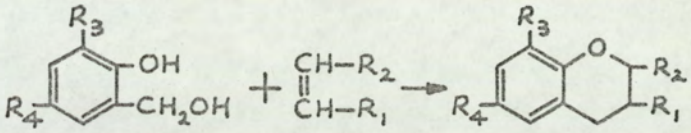
This raised the question as to whether the brittleness below 90°C was due to the greater opportunity for hydrogen bonding in the comparatively open structure. This might also help to provide an explanation for the higher strength of the 1/1.15 resin compared with 1/1.45 at lower temperatures. Little significance could be attached to the punching quality of the p-cresol laminate above 90°C because of its apparent 'thermoplastic' characteristics.

The effect of C.N.S.L. in reducing the overall stress at break and increasing strain at break at low and high temperatures raised some interesting points. If it could be assumed that, by 160°C, the effect of secondary forces was slight, then the properties at this temperature were mainly indicative of the primary structure. The somewhat low stress and possibly the higher strain at break at 160°C compared with the simple resins, therefore, suggested a lower cross-link density. This was consistent with the presence of the linear hydrocarbon chains in the meta position of the phenolic components of C.N.S.L.[51]. These substituents would be likely to hinder addition at the ortho and para positions. This, however, was not the complete explanation for the superior punching quality of the C.N.S.L. laminate since the apparent lack of cross-links in the p-cresol resin did not have the same effect.

As has already been mentioned in Section 2.2.2. Freeman and Traynor[22,23] plasticised phenolic resins by introducing substituents into the phenol molecule which, they suggested, prevented the close approach of polar centres by steric hindrance with consequent reduction in hydrogen bonding. Sprengling and Traynor[24] incorporated nitrile rubber into phenolic resins resulting in improvement of their cold-punching properties. They also suggested a reduction in hydrogen bonding resulting from the presence of a flexible chain 'diluent' and by the elimination of phenolic hydroxyl groups by chemical reaction between phenolic ortho-methylol groups and carbon-carbon double bonds in the nitrile rubber.

The side chains in C.N.S.L. provided both a potential chain diluent and carbon-carbon double bonds and it, therefore, seemed likely that similar arguments were applicable.

The reactions of ortho-methylol phenol and unsaturated compounds have been widely discussed in the literature[52,53,54,55,56]. In the present context it is sufficient to say that there is much evidence to support the formation of chromane compounds in the following way :



This possibility suggests a mechanism whereby reaction with unsaturated compounds could lead to a reduction in hydrogen bonding by elimination of some phenolic hydroxyl groups in the cross-linked structure.

Admittedly, the above arguments are somewhat speculative but they suggest the following factors which may be important in determining good cold-punching properties in a phenolic laminate :-

a) the resin structure should not contain too many cross-links since there should be sufficient scope for segmental motion,

b) the length of phenolic chain segments should not be too great since this may provide increased opportunities for hydrogen bonding, and

c) the presence of unsaturated hydrocarbon chains may be effective in decreasing hydrogen bonding in the cross-linked structure.

9.4. Some speculations together with recommendations for future work.

Further financial support has been given for an extension of this work and it is now appropriate to

consider the possibilities for future activities. There are two broad areas which should be investigated, namely the fracture mechanism and resin structure.

9.4.1. Fracture mechanism.

Although the broad hypothetical process outlined in Section 9.1. clearly served its purpose for the present work it would be advantageous to examine this in somewhat greater detail.

Hojo[57] analysed the punching process in some depth. Although he proposed two sophisticated techniques for improvement of punching quality these were based on somewhat impracticable machining techniques with no particular reference to the structure of the material. As may be seen from Hojo's paper, an analysis of the punching process is an exceedingly complicated business. In addition to this, the material itself is highly complicated and any analysis attempted would have to account for the resin matrix, the paper fibres (with consequent laminar and anisotropic effects) and interaction between the two. An attempt at analysing the process with reference to a 'model' of the material would therefore present a formidable task with no guarantee of practical advantage. It seems certain that the most effective approach will therefore be to extend the semi-empirical approach used so far to a greater depth in certain areas.

It is now appropriate to further classify the types of defect observed (Figure 8 p. 41) into three divisions.

(a) Crack propagation defects.

Crack propagation defects include feathering and cracks to the edge of the test-piece. These presumably arise from unrestricted propagation of cracks due to the brittleness of the material and are likely to be partly responsible for secondary yield. It seems likely that the presence or absence of such cracks could be associated with some measurement of the brittleness or 'ductility' of the material.

Keeling[58] suggested measuring the crack arrest temperature using a modified notched Izod impact test and determining breaking energy of laminates at different temperatures. He observed that the change from brittle to ductile behaviour was accompanied by a visible change in the angle at which the fracture propagated across the laminate. He supported this with data from a free torsional vibration technique which he used to obtain information about thermal transitions occurring within the laminate and within the component resin and paper. These transitions were partly substantiated by differential thermal analysis. By using the ASTM punching test[29] at room temperature he concluded that materials

having relatively high damping at room temperature and secondary transitions below 0°C punch well. This all seemed to indicate that toughening of the resin by segmental motion hindered the propagation of cracks, which is reasonable enough.

Keeling's crack arrest temperature data was scattered, presumably due to anisotropic effects or limitations of the technique but the principle would seem worth pursuing. A technique based on the tensile testing procedure (Chapter 7) at different temperatures should be considered as a possibility.

Gordon[59] suggested that overcure or undercure of the resin will have an important effect on crack propagation energy depending on the adhesion of the resin to the fibres. Photomicrographs of failed tensile test-pieces, considered together with staining techniques, indicated that if the resin is undercured the fibres pull out of the resin rather than break. If the resin is overcured the fibres will break straight across the line of fracture leading to brittle behaviour. A satisfactory degree of cure should result in the resin cracking first and, before the fibres fail, a certain amount of permanent set obtained by the fibres slipping relative to the resin or realigning themselves relative to the stress. Such a technique could well prove to be a most useful adjunct to mechanical testing for brittleness and of great value in investigating resin/paper

interaction which has scarcely been touched upon in the present work.

(b) Yield defects.

These include haloing and tensile cracking which, under unsatisfactory punching conditions, can be detected by the presence of secondary yield in the stress/strain curves.

Tensile cracking, as its name implies, was assumed to have originated from the radial tensile stress operating in the top surface of the test-piece around the edge of the punch. Haloing was assumed to have originated in a similar way except that stress relief occurred by ply separation within the material close to the sheared edge.

Although Learmonth and Watson[37] suggested that these defects arose because of lack of flexibility it seemed clear, from their later work[42], that they could also arise from too much flexibility as manifested by a sharp increase in strain at break at higher temperatures (see Section 7.5.). Although the growth of such defects must be a crack propagation process the damage is more confined to the area immediately surrounding the sheared zone. This implies a more controlled process and it would be interesting to identify the source of this control, or rather, lack of control with the propagation defects. Nevertheless, feathering defects often appear

to have begun as tensile cracks (see Figure 8 p. 41). It might well prove that there is little essential difference between crack propagation and yield defects.

Mechanical testing based on cross-breaking strength tests might be interesting since this mode of deformation is related to the bending of the test-piece in the region of the sheared zone (Figure 1 p. 15). Interpretation could be difficult however.

Convential microscopic examination of tensile cracks from punched test-pieces might be of value although the use of the scanning electron microscope would probably lead to easier interpretation.

Haloing would be difficult to pursue and a sectioning technique such as that used by Hojo[35] is the only likely method. It could be that haloing is a delamination defect of the interlaminar shear variety arising from bending.

(c) Delamination defects.

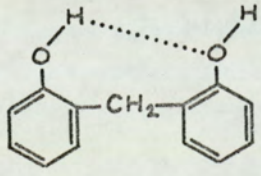
It seems clear that lifting arises from the withdrawal of the punch when interlaminar bond strength is poor. At present this is little understood since the withdrawal stage has not been investigated, but this would be a comparatively simple matter using the instrumented power press.

Drawing-down seems to be a phenomenon not observed in a proper laminate and unless it occurs unexpectedly could well be left.

9.4.2. Resin composition and structure.

The three factors proposed which may influence punching properties (Section 9.3.2.) need verification and further development. The use of the instrumented power press is clearly capable of providing further valuable information but the introduction of supporting techniques would now give great advantages. It seems clear that the first question to be answered is whether hydrogen bonding is, in part, responsible for the brittleness of these materials at low temperatures.

Sprengling[60] carried out solution studies of the acidity of some phenolic resin intermediates by a titration technique. His results led him to believe that phenolic resins linked essentially by ortho-methylene bridges would be relatively rigid since the tendency to hydrogen bonding would hold adjacent phenolic nuclei in fixed positions relative to one another thus:



Further, the formation of intramolecular hydrogen bonds precludes, in corresponding degree, the formation of hydrogen bonds between adjacent molecules thus impairing intermolecular cohesion. He noted here

that Novolaks are generally brittle solids.

Cairns and Eglinton[61] examined the infra red absorption spectra of substituted Novolaks. They found that, in carbon tetrachloride solution, these molecules assumed well-defined, intramolecularly hydrogen bonded conformations both as monomers and, in certain cases, as intermolecularly bonded dimers.

This brings to mind the work of Jones[50] discussed in Section 9.3.2. and suggests that brittleness could arise from intramolecular hydrogen bonding with consequent zones of intermolecular weakness. Such zones could certainly give rise to stress concentrations.

It is interesting to note that Richards and Thompson[62], discussing infra red data, suggested that one factor in the curing of phenolic resins might be a change from intra- to inter-molecular association giving rise to higher melting points and greater hardness.

Infra red techniques could very usefully be applied to the present problem although a reflectance technique might be necessary because of the nature of the materials and a means of heating the sample would be required. Apart from hydrogen bonding in the resin itself, comparison of data from the laminate and from the component resin and paper could conceivably give information about the resin/paper interface (although

the surface layer of the laminate might need to be removed). By applying the method to a C.N.S.L. plasticised laminate it might be possible to decide whether the phenolic hydroxyl group had reacted.

Having obtained a picture of the influence, or otherwise, of hydrogen bonding on the brittle behaviour of laminates further work on other features of the resin structure may then be carried out on a more rational basis. At this stage it is difficult to predict which course this should take. However, the work of Doroshenko, Korshak and Sergeev[26] suggests that the incorporation of polymethylene linkages of known length would be a valuable exercise, possibly using their method of preparation. In this way the effect of saturated hydrocarbon chains could be examined. From the paper cited it seems clear that there is an effect on impact and flexural strengths and probably hardness. It seems likely that this is due to the separation of polar centres although this is pure conjecture. It would then be of interest to incorporate pendant saturated hydrocarbon chains which would not act as cross-links. Freeman and Traynor[22,23] used 3-n-pentadecylphenol although it is difficult to draw any conclusions from the results given. This compound would provide an interesting comparison with C.N.S.L. and would presumably hinder cross-linking to a similar extent.

Interesting possibilities are also raised by Hermann's suggestion[63] of reacting olefin, vinyl and butadiene polymers with phenols in the presence of catalysts such as $ZnCl_2$ and BF_3 and using the products to prepare resins.

More information is needed before any further work can be suggested but if the above recommendations are successful then the point should have been reached when some reasonably confident conclusions can be reached about the resin fine structure with regard to brittleness. This should then help to decide which phenolic starting materials, readily capable of synthesis, may be used in manufacturing paper-based phenolic laminates which are easily punched (see Section 1.1.).

9.5. Critical appraisal of the work.

The time spent on this work was apportioned as follows :-

Time spent	Activities.
6 months	Initial literature survey (first paper), initial planning, current literature searching.
3 months	Development of apparatus.
5 months	Development of test technique, effect of test variables (second paper).
2 months	Punching characteristics of commercial materials (third paper).

5 months	Impregnating and pressing variables (fourth paper).
2 months	Commercial materials classified according to paper type (fifth paper).
6 months	Selection of best paper to show resin effects, effect of resin composition (sixth paper).
2 months	Visits, meetings, conferences, leave.

This left five months for the preparation and submission of the thesis and preparation of review papers.

As can be seen from this breakdown, 20 months were spent in obtaining and analysing experimental results and preparing them for publication. Because it was necessary to ensure a secure basis to enable direct comparison of resin effects to be made with confidence only five months were spent on the resin work (one month having been spent in testing the four laminates based on different papers). At its face value this appears to have been a somewhat inefficient exercise since the effect of resin structure was the primary objective. Nevertheless the background work was essential and some useful information has come out of it. Admittedly some of the conclusions were not new to the industry but nevertheless provided some confidence in the instrumented power press.

The comparatively short time spent on the resin work has raised some interesting questions already. Now that much of the necessary technique has been developed and established the next three years could well go a long way to answering them.

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CHAPTER 10.

CONCLUSIONS.

During the punching process, paper-based phenolic laminates may be characterised by stress and strain at break, time to break and the shape of the stress/strain curve which may be related to an independent visual assessment of punching quality. It appears that the punching process is controlled by the relative magnitudes of the applied stress required to initiate and propagate cracks in the laminate and that the crack propagation stage largely controls the quality of the punched article. It seems possible to predict, from the shape of the stress/strain curve, whether the crack propagation stage is likely to result in satisfactory punching quality or not. It is suggested that this technique could be used as a basis for a pass/fail test of punching quality. It is certainly a valuable tool for examining the factors involved in determining punching quality and has been used as such with some success.

On the whole, punching characteristics are surprisingly insensitive to impregnating, drying and pressing variables (over the range studied) provided that constant resin content and laminate thickness are maintained.

The effect of the type of base-paper used in

making a laminate is important probably because of the way in which the paper fibres control the propagation of cracks. The results of examining a series of commercial materials (of various recommended punching temperatures) at a fixed temperature suggest that, under these conditions, punching characteristics are primarily dependent upon paper-type. Without direct evidence, there are indications that resin content is a secondary factor and that fibre orientation may take some part in determining punching quality. These conclusions seem to suggest that the different manufacturers tend to use similar resins.

By examining laminates based on the four types of paper encountered in the commercial series (but otherwise similar), bleached kraft paper appears to be the most suitable for demonstrating effects due to the resin.

Resin composition has an important effect on punching quality. It appears that cross-link density (or branch frequency) and segmental length, hence chain rigidity, are obvious factors. The presence of unsaturated hydrocarbon chains is effective in improving punching quality. It seems that part of the explanation might be that hydrogen bonding is, to some extent, responsible for brittle behaviour but it should be possible to test the truth of this by further work.

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ACKNOWLEDGEMENTS.

Many people, both University Staff and from industry, have contributed to this project in providing advice, materials and background information not obtainable from the literature. It is not possible to mention all these by name but the author is especially grateful to the following people and organisations who must be mentioned :

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BXL Plastics Materials Group, who gave the four laminates based on different papers (Chapter 7),

BP Chemicals Limited, who gave the sample of Cashew Nut Shell Liquid (Chapter 8),

the manufacturers who gave the laminates comprising the commercial series (Chapters 5 and 7),

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Mr. John Ludlow, who made the heating block, the spring and trigger mechanism and the combined compression pad/stripper plate (Chapter 3),

the following people, who provided much background information relating to the manufacture and punching of industrial laminates :

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Mr. Dennis Vaughan (Tufnol Limited),

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and Mrs. M.S.Watson, who typed this thesis and whose patience and encouragement over the last three years is greatly appreciated.

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APPENDIX 1.

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APPENDIX 2.

CONTROL METHODS FOR RESIN PREPARATION, PAPER IMPREGNATION AND DRYING.

Method 1. Determination of formaldehyde content of distillate return.

This method depends on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulphite.

$$HCHO(aq) + Na_2SO_3 + H_2O \longrightarrow NaOH + CH_2(NaSO_3)OH.$$

50 ml of a molar solution of sodium sulphite, together with three drops of thymolphthalein indicator solution were neutralised with normal sulphuric acid to a colourless end-point. This was added to 2.0 ml of the distillate return, which had been measured with a pipette, diluted with 10 ml of distilled water and neutralised to thymolphthalein. The mixture was titrated slowly with the standard acid to a colourless end-point.

1 ml of normal acid is equivalent to 0.0300 g of formaldehyde,

therefore, the formaldehyde content of the distillate return = $\frac{\text{Acid titre} \times 0.0300 \times 100}{2.0}$

= Acid titre x 1.5% w/v (for normal acid).

Method 2. Determination of solids content of resin solution.

25.0g of acid-washed silver sand (44-85 mesh) was placed in a circular aluminium dish (6 cm diameter x 1 cm depth) together with a clean steel rod (1/16 in diameter x 3 in length). These were placed in a forced circulation hot-air oven at 135°C for 60 min and then weighed (to the nearest mg) after cooling in a desiccator. 1.0 g of resin solution was weighed onto the sand from a polythene dropper bottle. The weight of the bottle (to the nearest mg), before and after, was used to minimise evaporation effects. The resin was then dispersed on the sand by stirring 7 ml of acetone into the mixture with the steel rod. The dish was placed on top of the oven for 15 min to evaporate most of the solvent and then placed inside the oven (still at 135°C) for 120 min. The dish was placed in a desiccator to cool and then weighed (to the nearest mg). The determination was carried out in duplicate and the arithmetic mean of the results used.

weight of dish + sand + rod = W_1,

weight of resin solution = W_2 and

weight of dish + sand + rod + resin (after 120 min at 135°C) = W_3,

therefore solids content of resin solution =

$$\frac{W_3 - W_1}{W_2} \times 100\%$$

Method 3. Determination of resin content and volatile content of impregnated paper.

One 2 in square of untreated paper and another of impregnated paper were cut and weighed (to the nearest mg). The impregnated paper was hung in a forced circulation hot-air oven at 150°C for 5 min, then removed and weighed immediately (to the nearest mg).
weight of untreated paper = W_4,
weight of impregnated paper = W_5 and
weight of impregnated paper (after 5 min at 150°C) = W_6,
therefore resin content of impregnated paper =

$$\frac{W_6 - W_4}{W_5} \times 100\%, \text{and}$$

volatile content of impregnated paper =

$$\frac{W_5 - W_6}{W_5} \times 100\%$$

Method 4. Determination of flash value of impregnated paper.

Four 2 in squares of impregnated paper were cut and weighed together (to the nearest mg). The squares were stacked and placed between 3 in squares of aluminium cooking foil. This pack was then placed between 6 in squares of cellophane film and pressed for 5 min at 150°C and 1000 lbf/in^2 in a hand operated laboratory hydraulic press. The pack was then removed from the press, allowed to cool and the cellophane and

foil removed. Flash was removed from the edge of the test laminate by scraping it lightly, twice, with the edge of a piece of rejected laminate. The test laminate was then weighed (to the nearest mg).

weight of the four squares = W_7 and

weight of the laminate = W_8,

therefore flash value of the impregnated paper =

$$\frac{W_7 - W_8}{W_7} \times 100\%$$

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APPENDIX 3.

SUPPLEMENTARY INFORMATION ABOUT THE LAMINATES USED IN THE EXPERIMENTAL WORK.

Full details of each material used have not been given in the body of the thesis. The following information is therefore set out for completeness.

Chapter 4.

Thickness of hot-punching laminate (in x 10^{-3}) :

63.2 - 64.8

Thickness of cold-punching laminate (in x 10^{-3}) :

65.4 - 65.7

Chapters 5 and 7.

Thickness of commercial series (in x 10^{-3}),

A : 61.8 - 62.5
B : 59.9 - 60.1
C : 63.6 - 64.3
D : 59.7 - 60.3
E : 59.7 - 60.0
F : 64.3
G : 63.1
H : 64.9 - 65.1
I : 66.4 - 66.8
J : 62.0 - 62.4
K : 56.8 - 57.7
L : 61.4 - 61.9
M : 64.7 - 64.8
N : 58.7 - 58.8
O : 64.2 - 64.7
P : 64.5 - 64.7

MATERIAL	RESIN CONTENT %	VOLATILE CONTENT %	FLASH VALUE %	THICKNESS IN X 10^{-3}	NO. OF PLIES
Drying time.					
0 min	42.9	11.7	42.9	-	-
10 min	45.9	7.6	34.9	51.7	7
20 min	47.9	6.4	33.4	54.0	7
40 min	47.5	5.6	30.6	56.9	7
60 min	48.1	5.4	30.6	62.5	7
80 min	46.9	5.4	28.3	61.2	7
100 min	46.6	4.8	27.2	61.2	7
Resin content.					
38.0%	-	4.9	13.5	52.8	7
38.0%	-	4.9	13.5	61.5	8
48.1%	-	5.4	30.6	62.5	7
51.9%	-	4.6	31.8	64.8	7
Drying temp.					
70°C	47.9	5.3	30.3	59.1	7
85°C	48.1	5.4	30.6	62.5	7
100°C	46.9	5.1	26.6	59.3	7
Laminating temp.					
135°C	48.8	5.0	26.9	60.1	7
150°C	48.1	5.4	30.6	62.5	7
165°C	48.2	5.1	30.4	61.5	7
Laminating press.					
750 lbf/in^2	48.0	5.3	29.2	63.9	7
1000 lbf/in^2	48.1	5.4	30.6	62.5	7
1250 lbf/in^2	48.8	5.0	29.3	60.0	7
Laminating time.					
30 min	47.1	5.2	28.2	61.0	7
60 min	48.1	5.4	30.6	62.5	7
90 min	48.1	4.9	27.6	61.6	7
Laminates.					
B. Kraft	46.1-48.1	5.1-5.4	21.2-30.6	61.4-62.5	7
C. Linter	48.2-48.5	5.2	27.8-29.8	56.5-57.9	7
Consolidated papers.					
B.Kraft	-	-	-	61.5-63.6	11
C.Linter	-	-	-	62.1-64.0	11

CHAPTER 7.

Laminates prepared by BXL Plastics Materials Group:

PAPER	RESIN CONTENT %	VOLATILE CONTENT %	THICKNESS in x 10^{-3}
Bleached kraft	45.6	3.0	62.8-64.5
Unbleached kraft	46.3	3.5	60.1-61.3
Cotton linter	47.2	3.7	64.3-64.9
Alpha Cellulose	45.6	3.0	61.6-62.5

CHAPTER 8.

RESIN	REFLUX TIME, MIN	VAC. DIST'N FINAL TEMP., ^{o}C	NO. OF IMPREGNATIONS 50%	25%
1/1.15	30	80	1	2
1/1.45	70	30	1	2
p-Cr/P	40	80	1	3
C.N.S.L.	65*	30	1	1

*C.N.S.L. added after reflux

LAMINATE	DRYING TIME, MIN	RESIN CONTENT %	VOLATILE CONTENT %	FLASH VALUE %	THICKNESS in x 10^{-3}	NO. OF PLIES
1/1.15	90	48.5	2.4	12.0	64.7-65.0	8
1/1.45	35	48.0	3.4	8.9	62.6-63.4	7
p-Cr/P	110**	46.2	1.1	14.8	61.8-63.7	8
C.N.S.L.	5	46.0	4.6	13.5	65.0-65.5	8

** 55 min at 103°C, then 55 min at 123°C

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APPENDIX 4.

THE MAJOR ITEMS OF EQUIPMENT USED IN THE EXPERIMENTAL WORK.

Power Press: Hordern, Mason and Edwards Limited,
Type L.M.6.

Punch and die: N.B.Drew and Sons, Aston, Birmingham,
made to University of Aston specification.

Transducer meters: Boulton Paul Aircraft Limited,
Direct reading transducer meter, Type C52.

Transducers: Boulton Paul Aircraft Limited,
Load gauge, Type D58
Displacement transducer, Type F53.

Oscilloscope : Telequipment Limited,
Type D43R

Polaroid Camera: D. Shackman and Sons,
Model No. P.L.1.

Tensile testing machine: Tensometer Limited,
Type E.

Impregnator: N.B.Drew and Sons, Aston, Birmingham,
made to University of Aston specification.

Ovens: 1) Funditor Limited,
Type F.C.1. (used for paper drying)
2) Laboratory Thermal Equipment Limited,
Type F (used for all other purposes).

Hydraulic presses: 1) Apex Construction Limited,
Type 341-2, 10 tons
(used for flash test).

2) T.H. and J. Daniels Limited,
Mk. 2 100 ton downstroke
(used for pressing laminates).

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The figures and tables in this paper may be found in the thesis :

Paper.	Thesis.
Figure 1	pp. 112-115 (Fig. 45a - 45d)
Figure 2	pp. 124-127 (Fig. 47a - 47d)
Figure 3	p. 144 (Fig. 51)
Table 1	pp. 116 and 123 (Tables 10 and 11)

PUNCHING PAPER-BASED PHENOLIC LAMINATES : THE EFFECT OF RESIN COMPOSITION.

by G.S.Learmonth, Ph.D., B.Sc., F.R.I.C., F.P.I., and K.L.Watson, B.Sc., A.R.I.C. (Department of Chemistry, The University of Aston in Birmingham)

ABSTRACT

The effect of resin composition on punching characteristics has been investigated using laminates based on bleached kraft paper. The results suggest that the punching quality of these materials may be improved by decreasing the cross-link density of the resin. Hydrogen bonding may also be partly responsible for poor punching quality but this appears to be reduced by the presence of unsaturated hydrocarbon chains in the cross-linked structure.

1. INTRODUCTION

This paper is the last in the present series on punching paper-based phenolic laminates. The first paper[1] concluded that optimum conditions for punching these materials have been established in commercial practice and that there was some understanding of the physical nature of the punching process. However, there was still a need for a greater understanding of the effect of structural features of the resin, fibre and finished laminate upon the punching process. A technique was therefore developed[2] to determine the stress/strain characteristics of the materials during punching. A material could be characterised by values for stress and strain at break, time to break and a visual assessment of punching quality. In the light of observations of other workers a hypothetical fracture mechanism was advanced to interpret the shape of the stress/strain curves obtained. A

determine which paper was the most suitable for emphasising resin effects. BXL Plastics Materials Group most generously provided four laminates for this purpose. These were prepared from papers of the same general types encountered in the commercial series but using the same resin. Having found the most suitable paper, the way was then clear to examine the effect of four different resins on punching characteristics .

2. EXPERIMENTAL

2.1. Preparation of laminates

2.1.1. Laminates based on different papers.

The type of papers employed were unbleached kraft, bleached kraft, alpha cellulose and cotton linter. These were impregnated and dried at 150°C to a volatile content of between 3.0 - 3.7% (determined by heating a sample at 150°C for 5 min). The resin contents ranged between 45.6 - 47.2%. The resin was a simple ammonia catalysed cresol/formaldehyde composition.

2.1.2. Laminates made from different resins.

The first two resins were simple phenol/formaldehyde compositions having P/F values of 1/1.15 and 1/1.45. The third resin was made from phenol/formaldehyde (P/F : 1/1.15) and p-cresol/formaldehyde (p-Cr/F: 1/1) mixed to give a ratio p-cresol/phenol of 3/1. The final resin was a phenol/formaldehyde composition (P/F : 1/1.45)incorporating Cashew Nut Shell Liquid (25% $^{W}/_{W}$ based on phenol). The phenol and p-cresol were general purpose laboratory grade materials and the formaldehyde was in the form of formalin (35.8% $^{W}/_{W}$). Since electrical properties were not to be investigated crude Cashew Nut Shell Liquid (C.N.S.L. was used. All four resins were catalysed with barium hydroxide (4g $Ba(OH)_2.8H_2O$ per mole of phenol or p-cresol). The resins were neutralised to pH 6-7 with 10% sulphuric acid before vacuum distillation.

carried out as has previously been described[4]. The resin content of all the laminates ranged between 46.0 - 48.5%.

The impregnated paper was dried in a forced draught hot-air oven controlled at 103 ± 2°C. The higher temperature, compared with that previously used[4], was necessary to advance the lightly condensed resins satisfactorily although the p-cresol resin required yet a further drying period at 123 ± 2°C. The original intention was to dry all the papers to a flash test value[4] of 10-15%. In practice, the range was 8.9 - 14.8%. Since different resins were being used on the same paper it seemed sensible to control the drying stage by using a flow test rather than drying to a fixed volatile content.

7 or 8 plies (to give a nominal laminate thickness of $\frac{1}{16}$ in) of the dried impregnated paper were then pressed between stainless steel plates at 150°C and 1000 lbf/in^2 for 60 min followed by 10 min cooling under pressure.

2.2. Measurement of punching characteristics

Each of the laminates was punched at ~~25~~ 20, 55, 90, 125 and 160°C (10 min heating time) as has been described previously[2].

P.Q. values and visible defects have been tabulated in Table 1. Features noted in the stress/strain curves have also been noted in this table.

Figures 1 and 2 show punching characteristics plotted against punching temperature for the paper type and resin type experiments respectively.

3. RESULTS.

3.1. Laminates based on different papers.

The alpha cellulose and cotton linter based laminates tended to show higher stress and strain at break and time to break than the unbleached kraft and bleached kraft materials. Although they punched better at low temperatures they showed a peak in

P.Q.

The 1/1.45 material showed inferior punching quality over the whole temperature range whereas the 1/1.15 behaved similarly to the p-cresol material. C.N.S.L. had a markedly beneficial effect on punching quality especially at low temperatures.

4. DISCUSSION :

4.1. Laminates based on different papers.

It was quite clear that, from the P.Q. results shown in Figure 1, the bleached kraft paper was the most suitable for investigating resin effects since it showed the widest range of P.Q. values and P.Q. increased with temperature over the whole range.

The peak in P.Q. for all materials except bleached kraft appeared to be related to the sharp increase in strain at higher temperatures. This suggested that "yield" defects such as haloing and tensile cracking could arise from high values of strain at break. The bleached kraft material, which showed relatively low values of stress and strain at break, was presumably able to reach its "at break" condition before serious damage had occurred at high temperatures.

4.2. Laminates made from different resins.

The P/F : 1/1.45 resin showed inferior punching quality to the 1/1.15 resin. The lower temperature sensitivity in stress and time was presumably due to a higher cross-link density giving a structure containing elements less capable of rotational freedom. There was, however, little evidence that the temperature dependence of strain at break was less for the 1/1.45 material.

Up to 90°C the p-cresol resin showed similar behaviour to

Jones[11] studied the melt viscosity of a series of phenol/formaldehyde novolaks over a temperature range of 100 - 250°C. It was shown that the energy of activation for viscous flow fell rapidly as the temperature increased and tended to steady values at higher temperatures. The steady values were almost linearly related to molecular weight. The rapid fall in energy of activation as the temperature increased was attributed to the breakdown of association, mainly consisting of hydrogen bonds. It was believed that, at high temperatures, flow took place by the movement of single molecules, but at low temperatures the large energies of activation suggested that flow took place by associated dimers, trimers etc. breaking away from the general association field that surrounded them. It is also perhaps significant that precautions were taken to remove as much water and phenol as possible since these both appreciably altered the viscosity of resins containing them (1 per cent of water having been found to decrease the viscosity of a novolak by five times!).

Freeman and Traynor[12,13] plasticised phenolic resins by introducing substituents into the phenol molecule which, they suggested, prevented the close approach of polar centres by steric hindrance with consequent reduction in hydrogen bonding. There have been other suggestions that the properties of phenolic resins might be modified by hydrogen bonding. Sprengling[14], discussing the results of some solution studies, suggested that resins essentially linked by o-methylene bridges would be relatively rigid since the tendency to hydrogen bonding which he had postulated would hold adjacent phenolic nuclei in fixed positions relative to each other thus :

higher strength of the 1/1.15 resin compared with 1/1.45 at lower temperatures. Little significance could be attached to the punching quality of the p-cresol laminate above 90°C because of its apparent "thermoplastic" characteristics.

The effect of C.N.S.L. in reducing the overall stress at break and increasing strain at break at low and high temperatures raised some interesting points. If it could be assumed that, by 160°C, the effect of secondary forces was slight, then the properties at this temperature were mainly indicative of the primary structure. The somewhat low stress and possibly the higher strain at break at 160°C compared with the simple resins therefore suggested a lower cross-link density. This was consistent with the presence of the linear hydrocarbon chains in the meta position of the phenolic components of C.N.S.L.[17]. These substituents would be likely to hinder addition at the ortho and para positions. This, however, was not the complete explanation for the superior punching quality of the C.N.S.L. laminate since the apparent lack of cross-links in the p-cresol resin did not have the same effect.

Sprengling and Traynor[18] incorporated nitrile rubber into phenolic resins resulting in improvement of their cold punching properties. They suggested a reduction in hydrogen bonding resulting from the presence of a flexible chain "diluent" and by the elimination of phenolic hydroxyl groups by chemical reaction between phenolic o-methylol groups and carbon-carbon double bonds in the nitrile rubber.

The side chains in C.N.S.L. provided both a potential chain diluent and carbon-carbon double bonds and it, therefore, seemed likely that similar arguments were applicable.

seems to be some evidence that hydrogen bonding might, in part, be responsible for the brittle behaviourof phenolic resins.

6. ACKNOWLEDGEMENTS

The authors wish to express their gratitude to Midland-Yorkshire Tar Distillers Limited for financial support, to BXL Plastics Materials Group for the four laminates based on different papers and to B.P. Chemicals Limited for the Cashew Nut Shell Liquid.

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Punching paper-based phenolic laminates: the effect of temperature

G.S. Learmonth PHD, BSC, FRIC, FPI **and K.L. Watson** BSC
University of Aston in Birmingham

Abstract: *There is a requirement for a greater understanding of the effect of the structura features of paper-based phenolic laminates upon their punching characteristics. With this object in view, a small power press has been instrumented to enable stress/strain characteristics of these laminates to be investigated. Samples of commercial hot-punching and cold-punching materials have been used to establish experimental technique and to obtain information regarding the effect of temperature upon their punching properties. Marked differences in the shape of the stress/strain curves are observed at different temperatures. These differences are related to variations in punching quality. In the light of observations of other workers a hypothetical mechanism for the punching process may be advanced in which, after an initial settling stage, the shear stress builds up until microcracks form, leading to yield. The stress/strain slope will then increase if the crack propagation energy exceeds the crack initiation energy, after which an apparent yield due, to eg, delamination would appear in materials of inadequate punching quality, but where quality is satisfactory the crack propagation stage proceeds smoothly until fracture is complete.*

1 Introduction

There is a considerable variety of paper-based phenolic laminates used in the electrical industry. Materials with attractive physical and electrical properties may be made by proper formulation of resin and choice of paper and by the judicious selection of impregnating and laminating conditions. These materials are comparatively cheap and in sheet form may be punched to produce a wide range of electrical and electronic components.

The authors have already reviewed the punching of paper-based phenolic laminates[1] and concluded that optimum punching conditions have been well established in industrial practice. It was shown that there was some understanding of the physical nature of the process, but that there was a need for a greater understanding of the effect of the structural features of the resin, fibre and finished laminate upon the punching process.

This paper describes equipment and procedures suitable for the investigation of this problem and evaluates them by reference to two well-known commerical materials. A small power press was used which was instrumented to measure shear stress and strain during the punching process. Two paper-based laminates were used to explore the effect of test variables on the results. A hot-punching proprietary brand was selected to represent grades for recommended punching temperatures between 80° and 100°C and another brand by the same manufacturer to represent a cold-punching material. Both were used in $\frac{1}{16}$-in thickness.

2 Apparatus

A photograph of the apparatus is shown in FIGURE 1. FIGURE 2 shows the press table layout. The press guard was removed for clarity.

The punch diameter was 1·502 in and the clearance between punch and die was less than 0·001 in. The combined stripper plate and compression pad was driven by the press ram through rubber buffers.

Punching load was measured against time by means of a load transducer comprising a proof ring which incorporated a differential-inductance displacement transducer. The load transducer was used in conjunction with a transducer meter, the output of which was fed into one channel of a double-beam oscilloscope.

Punch penetration was measured against time by means of a displacement transducer used in conjunction with a second transducer meter. The displacement output was fed into the other channel of the oscilloscope. The transducer armature was mounted on a support arm clamped directly to the punch.

In operation, the oscilloscope was triggered by the signal from the displacement transducer meter and a photographic record of the trace was obtained by means of an oscilloscope camera. An example of a photographic record is shown in FIGURE 3.

A heating block was used which could be maintained at the correct temperature in a hot-air oven until shortly before the test. A rectangular slot through the block contained the test piece. The block served to maintain the laminate at the test temperature from the time it was removed from the oven until the punching operation. A trigger and spring mechanism activated by the press ram ensured that the test piece was projected into the toolset within 0·2 s of the punching operation.

3 Procedure

Five test-pieces were punched under each set of experimental conditions. Average plots of stress against time and strain against time were obtained. These plots were combined to give stress/strain curves. Stress was defined as load per unit area of sheared surface (ie peripheral length of punched contour × sheet thickness). Strain was defined as the percentage ratio of penetration to sheet thickness.

Assessment of the punching quality of the material under given conditions was made by visual examination of the pierced hole. Points, from 0 to 6, were awarded for each test-piece by reference to a set of standards

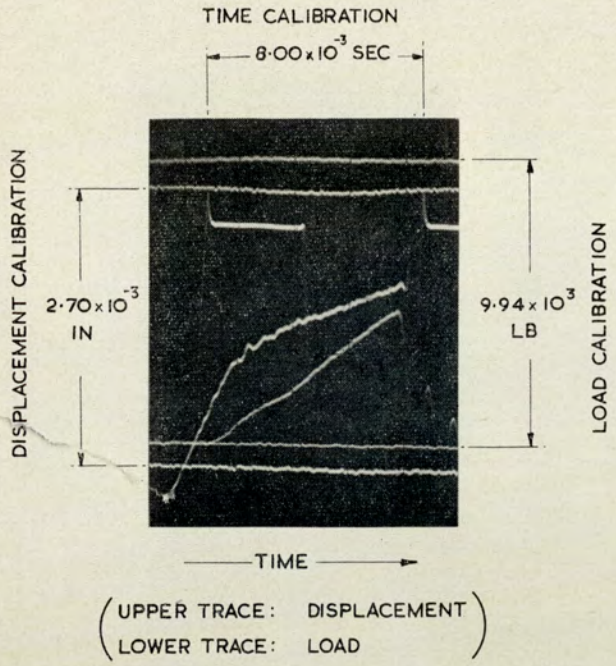

FIG 3 Example of a photographic record

(see FIG 4). The total number of points for the five test-pieces represented the punching quality (PQ) of the material. As a rough guide PQ values of 10, 15, 20 and 25 were regarded as bad, poor, good and excellent, respectively.

The variables examined were heating time, punching temperature and the elapsed time between heating and punching.

4 Results

4.1 Heating time

It was first necessary to determine the time for the laminate to reach the required temperature. The hot-punching material was used at 55°, 90°, 125° and 160°C. Stress/strain curves with corresponding PQ values for various heating times are shown in FIGURES 5, (a) to (d). The results are summarized in TABLE 1.

Significant differences were observed only at 160°C. Heating times of 5 and 10 min at this temperature gave similar results, although yielding appeared to be slightly less at 5 min. Heating for 20, 30 and 60 min appeared to result in increasing degrees of overcure.

4.2 Maximum permissible heating time

To confirm that overcure occurred for heating times of 20 min and above at 160°C, test-pieces were heated at this temperature for 10, 20, 30 and 60 min and allowed to cool at room temperature. Stress/strain curves for these test-pieces punched at 21°C were compared with that of the same material which had not been pre-heated. Examination of FIGURE 6 shows that there was no significant difference between the results for 0 and 10 min, but after 20, 30 and 60 min an increasing degree of overcure resulted.

Table 1

HEATING TIME	EFFECT OF HEATING FOR PUNCHING AT			
	55°C	90°C	125°C	160°C
min				
1	Sufficient	Sufficient	Sufficient	Insufficient
5	—	—	—	Sufficient
10	Sufficient	Sufficient	Sufficient	Sufficient
20	—	—	—	Excessive
30	Sufficient	Sufficient	Sufficient	Excessive
60	—	—	—	Excessive

4.3 Punching temperature

In view of the results stated in Sections 4.1 and 4.2, a heating time of 10 min was used to compare the effect of punching temperature for the two materials. To check that no significant overcure took place with the cold-punching brand, test-pieces were heated to 160°C for 10 min and punched at 25°C, and the results were compared with those for unheated material punched at the same temperature (see FIG 7). FIGURES 8 and 9 show the results of punching the two materials at 25°, 55°, 90°, 125° and 160°C. FIGURE 10 shows the effect of temperature on peak stress, peak strain and time to peak. Significant features in the stress/strain curves are summarized in TABLE 2.

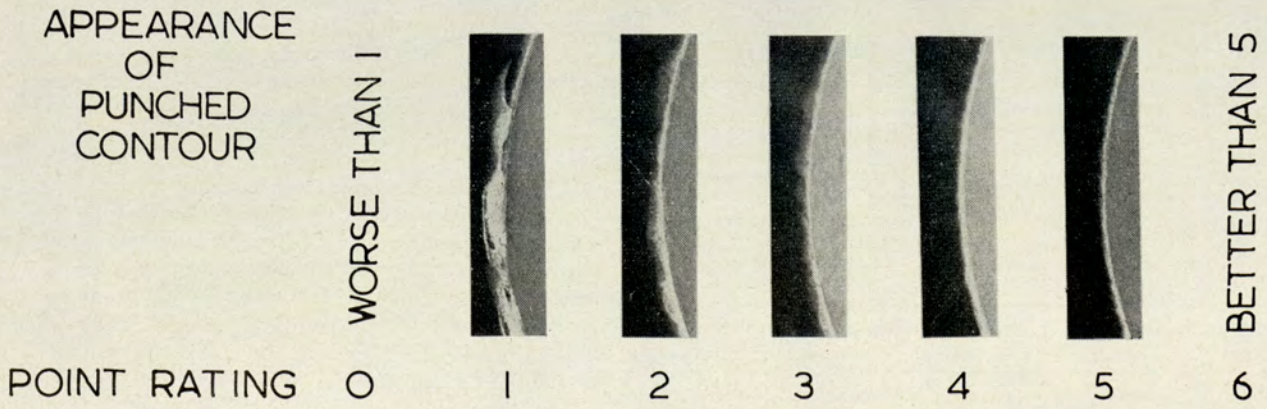

FIG 4 Point rating for visual assessment of punching quality

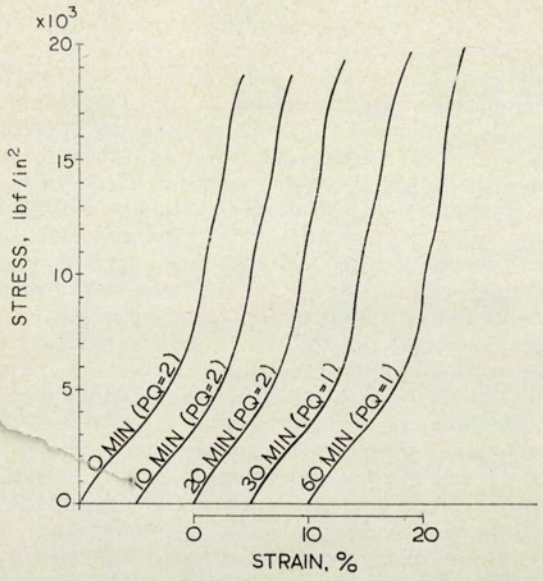

FIG 6 Stress/strain curves for hot-punching laminate at 21°C after preheating at 160°C for 0, 10, 20, 30 and 60 min

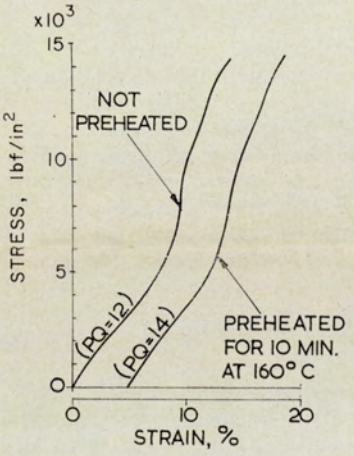

FIG 7 Stress/strain curves for cold-punching laminate at 25°C

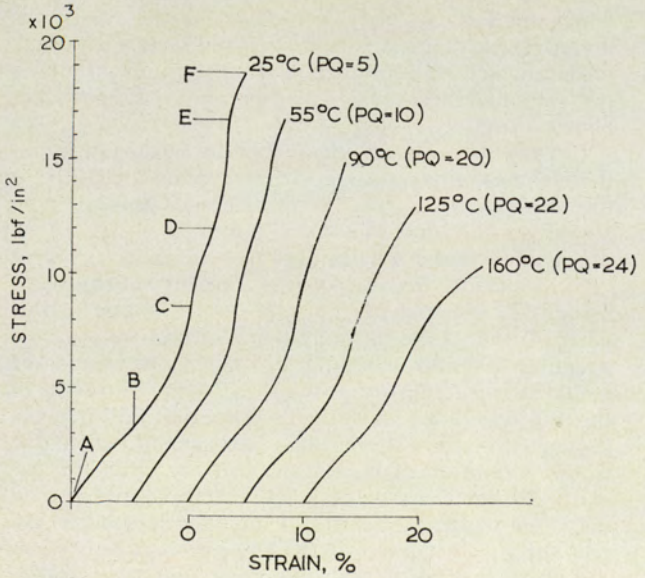

FIG 8 Stress/strain curves for hot-punching laminate at 25°, 55°, 90°, 125° and 160°C
Heating time 10 min

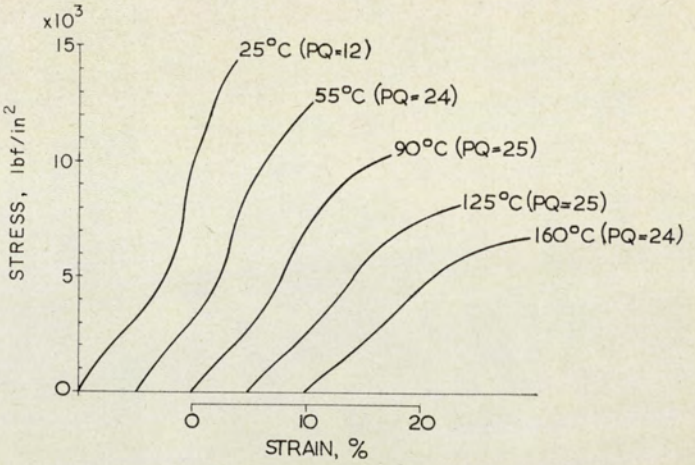

FIG 9 Stress/strain curves for cold-punching laminate at 25°, 55°, 90°, 125° and 160°C
Heating time 10 min

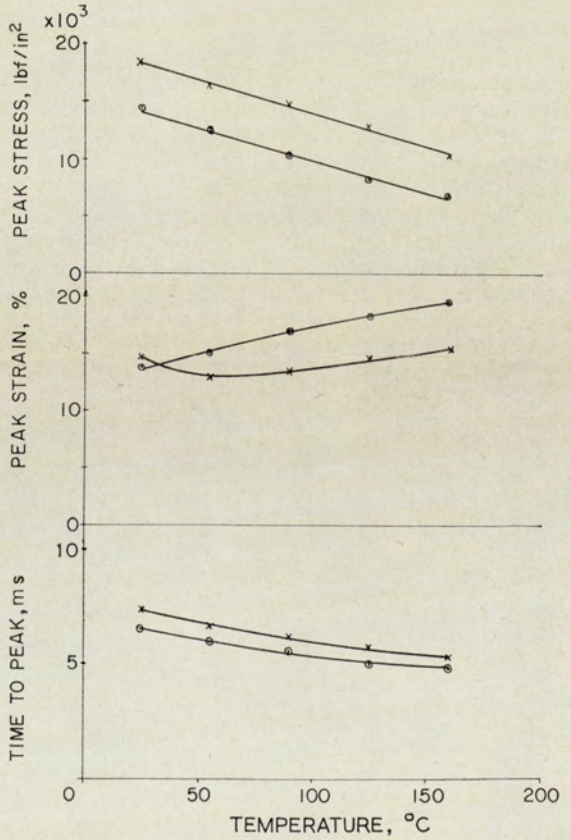

FIG 10 Effect of temperature on peak stress, peak strain and time to peak
× Hot-punching laminate
○ Cold-punching laminate
Heating time 10 min

quality remained the same. Peak stress was slightly increased. From 30 to 200 s delay, punching quality decreased and the stress/strain curve altered considerably. After 200 s delay the material showed similar behaviour to that at 25°C.

5 Discussion

5.1 Shape of stress/strain curves

The stress/strain curve for the hot-punching brand at 25°C is divided into regions (see FIG 8). After an initial increase in stress with increasing strain (AB) a region

results in severe damage to the test-piece. The 55°C curve in FIGURE 8 is assumed to result from the same processes which occur at 25°C. In the 90°C curve, secondary yield (EF) is absent and punching quality is satisfactory. It is suggested that the crack propagation stage in this case proceeds smoothly until the fracture process is complete. At 125°C the reduction of crack propagation energy to an order similar to that of the crack initiation energy would result in extension of the yield from C onwards. Owing to softening, and hence toughening, of the material, crack propagation might be somewhat hindered although the force requirements would be less, leading to increased extension at break. This argument is consistent with the fact that once conditions for adequate punching quality are achieved the peak-strain/temperature curve assumes a positive slope (see FIG 10).

5.4 Potentiality of the method

It is clear that the factors influencing the shape of the stress/strain curve are also reflected in punching quality. There is the possibility that this fact could form the basis of a punchability test.[1–3]

The technique certainly provides a potential method for assessment of the relationship between punching characteristics and structural features of paper-based phenolic laminates. Further work is envisaged to investigate the effect of chemical structure of the resin.

6 Conclusions

A technique has been developed whereby the stress/strain characteristics of paper-based phenolic laminates may be determined during the punching process. The effect of temperature upon punching characteristics of hot- and cold-punching laminates has been examined.

The effect of heating times of 1, 10 and 30 min for the hot-punching grade at 55°, 90° and 125°C has been shown to be similar at each temperature. At 160°C, 1 min was insufficient, whereas 20 min resulted in significant overcure. The effect of cooling at room temperature after heating the hot-punching grade for 10 min at 90°C has been examined. A delay of 10 s could be tolerated with little change in punching characteristics, but after 30 s significant deterioration occurred.

It is clearly possible to relate punching quality to the shape of the stress/strain curves, and a potential method for relating the structure of laminates to punching characteristics is thus provided.

Acknowledgements

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Punching paper-based phenolic laminates

G.S. Learmonth PHD, BSC, FRIC, FPI **and K.L. Watson** BSC
Department of Chemistry, University of Aston in Birmingham

Abstract: *The nature of paper-based phenolic laminates is determined by the chemical structure of the resin, the type of paper and the interaction between these two components. A variety of hot-punching techniques are used in industry. Preliminary investigations by the authors indicate that these laminates exhibit an increasing tendency towards ductile behaviour at higher temperatures. Various other workers have investigated the physical nature of the punching process and have gained some understanding of the fracture mechanism involved. Consideration should be given to the special nature of the materials when designing tools and punched components. Standard tests are available for the assessment of punching quality, although various workers have made independent efforts to devise alternative methods. Although punching techniques are well established in industrial practice and there is some understanding of the physical nature of the process, there is a need for greater understanding of the effect of structural features of the resin, fibre and finished laminate on the punching process.*

1 Introduction

Plastics are available for engineering applications in two distinct forms: either as fully moulded components or as semi-finished stock such as sheet, tubing or rod for fabrication by normal engineering operations. In particular, laminated plastics have become irreplaceable materials in the electrical industry. These laminates are composite materials made from paper, cloth or felt bonded with a suitable resin. Phenolic resins are the most usual, although amino resins, epoxides and silicones are sometimes used.

One of the most useful methods of fabrication is high-speed shearing by guillotining or by punching in a power press or hydraulic press. Punching may involve either the piercing of holes or the blanking of individual components.

A considerable amount of empirical knowledge exists as a result of accumulated experience of this process, and also methods of assessment of materials and of calculation of fabrication conditions. However, these do not lead to much knowledge of the fundamentals of the process, and considerable scientific study is necessary to enable soundly based development work to proceed.

2 Nature of the laminates

The basis of the manufacture of laminates is simple, although the practice of producing successful materials is somewhat involved. The fibrous filler (paper, cloth or felt) is dipped into a solution of resin which soaks into it. The solvent is removed in a hot-air oven, leaving a predetermined proportion of filler and resin. The material is cut into sheets which are assembled into packs and pressed at <4000 lbf/in^2 and <160°C (phenolic resins) to give a consolidated cured board. This may be up to 10in thick but punching stock is usually about $\frac{1}{16}$in thick. The properties of the board are controlled by the types and relative amounts of resin and filler and by the interaction between resin and filler. This interaction depends upon the extent to which the filler is wetted and impregnated by the resin.

2.1 Phenolic resins

Cured phenolic resins possess a three-dimensional network structure in which the constituent molecules are cross-linked by primary chemical bonds. These are permanent in nature and their removal would result in total destruction of the resin. They are partly responsible for the rigid, brittle nature of cured resins, but the phenol has a strong ring structure which also assists in this. Other chemical bonds may also be present, and these are secondary bonds of an electrostatic nature. The physical properties (ie strength and stiffness) of the cured resin depend, to a degree, on the relative number of primary and secondary bonds or the extent to which cross-linking has occurred. Hence, some degree of flexibility can be introduced by heating or by plasticization. This may be due to reduction of secondary forces, reduction of steric effects or possibly a combination of both. The extent of cross-linking and the mechanism of plasticization are somewhat uncertain. Plasticization may be achieved both by the addition of natural oils or other conventional plasticizers to the laminating varnish (external plasticization) or by modification of the cross-linked structure (internal plasticization). Internal plasticization may be achieved either by increasing the length of cross-links, by reducing the frequency of cross-linking or by introducing substituents into the phenolic ring which effect steric hindrance.

The chemical structure of the resin largely controls its solubility, and both hydrophilic resins (which are often water-soluble) and hydrophobic ones (which require organic solvents) are used. This factor largely controls the relation between fibre and resins, as described later.

2.2 Fillers

The fillers (ie the fibrous component) are usually cellulosic, although glass, asbestos or synthetic fibres may be used. The cellulose fibres may be hollow and are usually cellular. Most punching laminates are paper-based. Some are cloth-based, but with these impregnation is rather more difficult and they are used only for special purposes. Felts and non-woven fibres are also used, notably from asbestos, and are potentially important.

The papers used are many and varied. They usually contain no size or adhesive and tend to consist of pure cellulose held together by jackstraw arrangement with some degree of hydrogen bonding (semi-chemical bond).

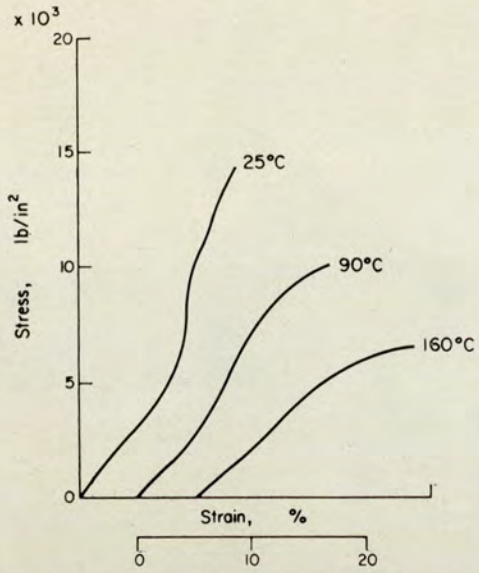

FIG 2 Stress/strain curves obtained in punching a plasticized phenolic laminate at 25°, 90° and 160°C

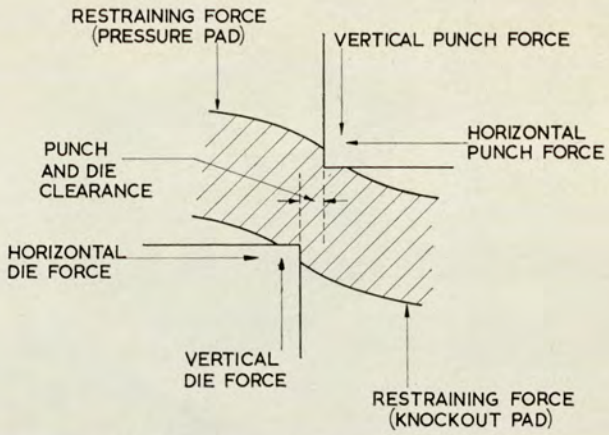

FIG 3 External forces involved in punching (taken from Reference 11)

The method is clean and continuous and output is considerably improved. An oil mist may be blown on to the laminate, although in this case a degreasing stage is necessary.

In some preliminary experiments, Learmonth & Watson[9] have shown that during the punching process the stress/strain relationship exhibits an increasing tendency towards ductile behaviour at higher temperatures. In this case, stress is defined as punching load per unit area of sheared surface (ie peripheral length of sheared contour × sheet thickness) and strain as percentage ratio of penetration to sheet thickness. As may be seen by comparing FIGURES 1 and 2, plasticization of the resin gives a similar effect to heating and there appears to be a plasticization/temperature relationship. This work is still in progress and may serve as a basis for comparison with the time-temperature transform characteristic of plastics.

4 Analysis of the punching process

Before considering practical details in punching paper-based phenolic laminates some of the scientific principles involved in the process are now examined.

The punching process is essentially one of high-speed shearing. The external forces involved are illustrated in FIGURE 3. A downward restricting force may be applied by means of a combined pressure pad and stripper plate. Sometimes a knockout pad is used to apply an upward force to the blank. When closed contours are punched internal restricting forces also occur in the laminate.

Basically, a force is applied by the punch and restriction of the material is provided by the die below. In order to achieve shearing it is necessary to initiate cracks within the material which propagate until the cutting process is complete. This is dealt with more fully below.

Frerichmann[2] investigated the punching of several sheet plastics by arresting the punch travel at various penetrations and examining the cut edges. He found that a paper-based thermosetting laminate exhibited mainly elastic behaviour up to a penetration of 14 per cent of the thickness of the sheet. Microcracks then appeared which were followed by macrocracks. The process terminated in brittle fracture after 28 per cent penetration. The existence of brittle fracture was also indicated by the shape of the force/penetration curve. Chen[3] described what appeared to be part of the same work. He included force/penetration curves for laminated paper at different temperatures, demonstrating the tendency towards brittle behaviour at lower temperatures.

Nakano[10] tentatively suggested a similar mechanism to that of Frerichmann when investigating the effect of degree of cure on punching quality of paper-based phenolic laminates. He concluded that first cracking occurred after about 7 per cent penetration, and maximum load after about 25 per cent.

Hojo[11] divided the process into four stages. Initial flattening of the sheet was followed by elastic deformation during the second stage. The third stage was characterized by the formation of numerous fine cracks in definite directions in the sheared zone. Second cracking occurred during the final stage and, when this was completed after about 25 per cent penetration, final cutting took place. Stages three and four were characterized by the material. He found that propagation of the first cracks and the mode of the second crack were influenced by restriction of the sheet, by punch and die clearance and by the shape of the punched contour. At increased temperatures the force tending to bend the laminate upwards around the punch decreased, as did the shearing force. The side forces hardly varied, however, and were mainly affected by the restricting conditions and the clearance. By applying a compressive axial force in the plane of the sheet[12] Hojo found that the first crack angle decreased to give improved quality of the sheared edges.

Considerations such as these are of prime importance in the study of punching and it is proposed to return to them in a later paper.

5 Tool design

Press tools for laminated plastics are very similar to those used for metals. The modifications in design have been well established by industrial practice. Basically, the tool-set consists of a punch and die. The die may be provided with a stripper plate or compression pad, or a

Depending on the grade of material, thickness and punched shape, this distance may often be reduced until it is equal to the thickness; even half the thickness can be achieved with some cold-punching grades, especially if they are slightly heated. Bobrynin[16] described investigations into minimum bridge sizes. He provided Tables and formulae to enable the minimum bridge size to be obtained for a variety of combinations of holes and thicknesses and grades of materials.

The corners of square or rectangular holes should have a slight radius. This helps to relieve stress, improves the quality of the punchings and decreases tool wear.

7 The punchability test

Different laminates vary in their ability to be punched cleanly without chipping, cracking or delamination. It is important, from the point of view of both the laminator and the fabricator, to be able to assess this property reproducibly on a quantitative basis to facilitate inspection and control.

7.1 Standard tests

Standard methods of assessing punchability exist in Germany, the United States and Britain.

The German Standard DIN 53 488[17] employs a carefully specified die-set which produces a test piece having nine diamond-shaped holes with apices spaced progressively closer together. The shortest distance remaining uncracked divided by the nominal thickness of the material forms the basis of the evaluation. Either warmed or cold test pieces may be used.

The American method is given in ASTM Standard D 617–44[18]. A standard die-set is again employed and test pieces are punched at room temperature and at 135°C. A separate numerical rating is assigned to each punched test-piece in respect of quality of edges, surfaces and holes. Ratings are assigned by reference to a prescribed set of standards. The average of the three values constitutes the measure of punching quality. A hardness test provides a control test on uniformity of punching quality.

British Standard 2076:1954[19] contains a piercing test in which a standard pattern is punched in a paper-based thermosetting laminate not exceeding $\frac{3}{32}$in in thickness. A blanking test is included in which a 1in diameter blank is punched from material not exceeding $\frac{1}{8}$in. The quality of the punched test piece is assessed visually. In British Standard 1137:1966[20] an optional punching test involves the piercing of a $\frac{1}{4}$in diameter hole in phenolic paper-based laminates not exceeding $\frac{1}{8}$in in thickness. Assessment is again visual. It is laid down that these tests should be carried out according to the manufacturer's recommendations.

It should be noted that the German test is the only one that gives a quantitative assessment not dependent upon the judgment of the operator.

7.2 Other tests

The ideal punchability test should be quantitative, should be reproducible and should give a true representation of the ability of the material to be punched. Additionally, the test should be cheap and simple to perform without the operator requiring any special technical skill.

Stel, Jacobs & Shriek[1] reported that they had examined the connexion between hardness of laminated plastics and quality of parts punched from them. They concluded that the hardness test provided a good method of assessing punchability.

Radovsky, Kendall & McHerron[4] described a technique in which strain gauges were attached to the punch. Forces involved in punching laminates were plotted against time using an oscilloscope. This method was proposed as a potential technique for measuring ease of punching and for obtaining a 'machinability index' for a given material. Different materials gave different punching curves. Warming the laminates gave smoother curves which showed less punching force and less binding of the punch on withdrawal. The method was envisaged as a quantitative non-operator-controlled test which could be used on a standard, industry-wide basis.

In a later paper, Radovsky[21] considered progress in defining a punchability test. 'Round Robin' punching tests with various dies had been carried out using the ASTM D 617-44 die as a control. A needle penetration test of the Vicat type, apparently similar to that used by Stel, Jacobs & Shriek,[1] had been examined together with the strain-gauge method above. No real corrrelation was observed, however.

'Round Robin' testing with the German standard die gave fair correlation with cold-punched but not with hot-punched samples. The results were compared with those obtained from punching oscillograms. Work had started towards a mathematical analysis of punching oscillograms.

8 Conclusions

It is clear that optimum conditions for punching paper-based phenolic laminates have been well established in industrial practice. There is also some understanding of the physical nature of the process. There is, however, a need for a greater understanding of the effect of the structural features of the resin, fibre and finished laminate upon the punching process.

Acknowledgements

Acknowledgement is made to Midland Tar Distillers Limited for financial support enabling research into the punching of phenolic laminates to be carried out at the University of Aston in Birmingham. Figure 4 appears by courtesy of Tufnol Ltd.

Copies of British Standards can be purchased from the British Standards Institute, 2 Park Street, London W 1.

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Punching paper-based phenolic laminates: punching characteristics of a series of commercial materials

G.S. Learmonth PHD, BSC, FRIC, FPI **and K.L. Watson** BSC
Department of Chemistry, The University of Aston in Birmingham

Abstract: *The punching characteristics of a series of sixteen commercial paper-based phenolic laminates, at their respective recommended punching temperatures, have been investigated by a technique described in an earlier paper. When satisfactory punching quality is obtained none of the materials shows in its stress/strain curve the secondary yield region that has previously been associated with severe defects. Trends in the type of minor defect and properties at break with the temperature at which individual materials are punched indicate that, on the whole, the materials tested are essentially similar. This work provides a general picture of punching characteristics as observed under typical production conditions.*

1 Introduction

It has already been pointed out that there is a need for a greater understanding of the effects of structural features of paper-based phenolic laminates upon the punching process.[1] In a second paper[2] equipment and a technique suitable for the examination of punching characteristics were described.

One difficulty in any investigation into punching these materials is the establishment of standards by which punching quality can be quantitatively evaluated. It is concluded[2] that it is possible to relate punching quality to the shape of stress/strain curves obtained during punching. Thus, in FIGURE 1, the stress/strain curve

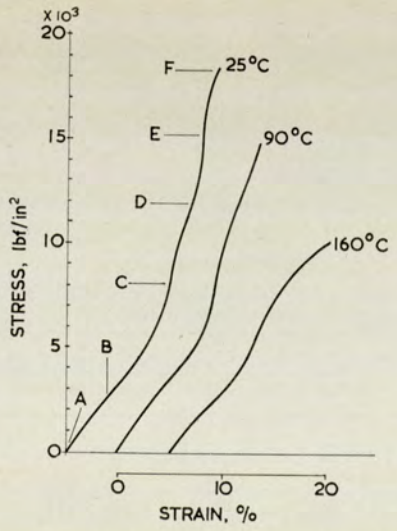

FIG 1 Stress/strain curves obtained in punching a paper-based phenolic laminate at 25°, 90° and 160°C

Key to regions in 25°C curve:
AB – Bedding-down of test piece
BC – Build-up of shear stress
CD – Primary yield (formation of microcracks)
DE – Hardening region (crack-propagation energy greater than crack-initiation energy)
EF – Secondary yield (catastrophic failure)

at 25°C is divided into regions. The secondary yield region is present when the temperature is such that punching quality is inadequate. Secondary yield might be due to stress relief by some process such as delamination which results in severe damage to the test piece. If the temperature is raised to 90°C the secondary yield disappears and punching quality is good. The hardening region is still present, implying that, although the crack-propagation energy is greater than the crack-initiation energy, crack propagation proceeds smoothly until the fracture process is complete. At 160°C, where punching quality is very good, it seems probable that the crack-propagation energy is reduced to an order similar to that of the crack-initiation energy, although the propagation process may be hindered by toughening of the material at the higher temperature. These conclusions, however, have been based on an investigation of only two commercial materials.

The work described in this paper involved the punching of a series of commercial laminates at temperatures recommended by their manufacturers. Thus it was hoped to obtain a general picture of punching characteristics as obtained under typical production conditions. This would also provide a background against which further work on structural features of laminates could be more usefully carried out.

2 Materials

Sixteen commercial materials, all nominally of $\frac{1}{16}$-in thickness, were used in these investigations. Since the tool-set used was essentially similar to those encountered in production and provided a simple punched contour (a 1·5-in-diameter circle) the mid-point of the recommended punching temperature range was used. This value was rounded off to the nearest 5 deg C.

The materials were coded alphabetically in order of recommended punching temperature and were divided into three classes. Materials having room temperature as their lowest recommended punching temperature were classified as cold-punching. Materials having their entire recommended temperature range above 100°C were classified as hot-punching. The remainder were classified as medium-punching.

Material A was found to punch unsatisfactorily at the mid-point of its recommended punching

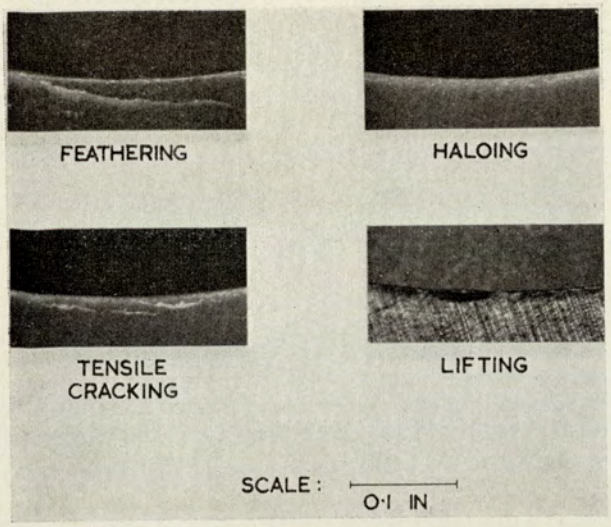

FIG 3 Types of visible defects

Only material A, punched at 40°C, showed evidence of defects sufficiently severe to render the punching quality inadequate. In this case 'feathering' was the main defect (see FIG 3).

The minor defects associated with materials having good rather than excellent punching quality (ie PQ values between 20 and 35) were 'haloing', 'tensile cracking' and 'lifting' (FIG 3). These defects were, at worst, only slight and did not always appear in all five test pieces obtained from each material.

4.3 Property values at break

FIGURE 4 shows stress at break, strain at break, time to break and PQ plotted against the temperature at which the different materials were punched. Material A deviated in the stress/temperature and time/temperature plots and material O deviated in the stress/temperature and strain/temperature plots. In the strain/temperature plot, material O, together with B which also deviated, fell on a line XX′ of almost constant strain which was shared by all materials showing a hardening region. There seemed to be no clearly defined relationship between PQ and temperature. If A, B and O were ignored, however, then there appeared to be a tendency for PQ to improve with increasing temperature, especially if F was also ignored.

FIGURE 5 is a plot of stress at break against strain at break. Materials H and A appeared to deviate.

5 Discussion of results

5.1 Stress/strain curves

All the materials, excluding A at 40°C, showed adequate punching quality and none showed the secondary yield which had previously been associated with inadequate punching quality.[2]

It is interesting to note that A at 40°C punched inadequately and that sudden yield was seen in the stress/strain curve. However, this sudden yield was not preceded by a hardening region as observed previously.[2] It was assumed that in this case crack initiation and unrestricted propagation (the resin not being toughened by elevated temperature) occurred virtually simultaneously. This implied a close relationship between filler and resin, since otherwise the resin/filler interfaces would be expected to hinder the propagation stage. This was consistent with the fact that A was a material with good electrical properties and low water absorption.

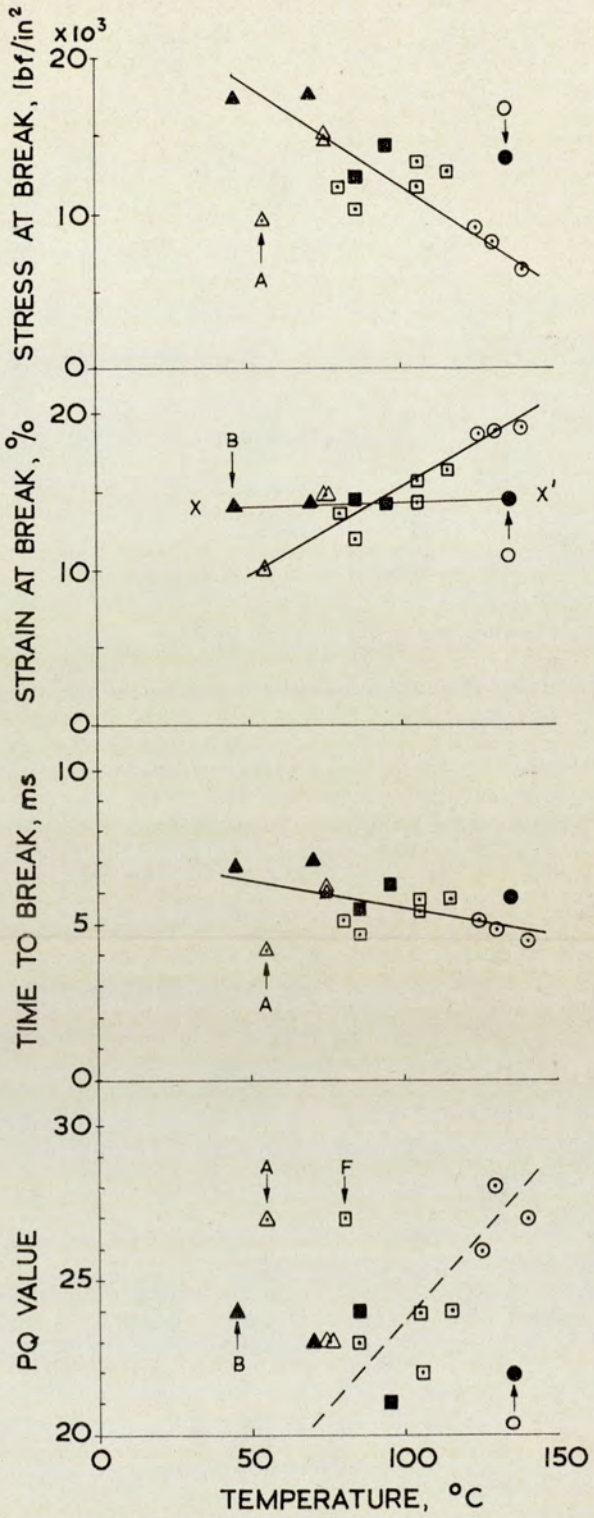

FIG 4 Stress at break, strain at break, time to break and PQ values for individual materials plotted against their respective punching temperatures

△ Cold-punching materials
⊡ Medium-punching materials
○ Hot-punching materials

(solid points represent materials showing a hardening region)

K.L. WATSON

LIST OF COURSES ATTENDED

From M.Sc. Course in the Chemistry and Technology of Polymers:

Polymer processing, viscoelasticity and engineering design with polymers	18¾ hours
Chemistry and technology of plastics	29¾ hours
Mechano-chemistry of polymers	2½ hours
Surface-coating technology	6¼ hours
Synthetic rubbers	8¾ hours

From Chemistry Department postgraduate lectures:

Aspects of polymer science and technology	5 hours
Crystallisation of polymers	5 hours
Computer programming	9 hours

From Chemistry Department postgraduate seminars (polymer group):

13 hours

TOTAL 98 hours

THE UNIVERSITY OF ASTON IN BIRMINGHAM

Regulations and Procedures for Higher Degrees by Research

CONTENTS

Amendments since September 1966 are indicated by a line in the margin of the text.

Regulations and details of procedure for

the degree of Master of Science by research

and the degree of Doctor of Philosophy

1. INTRODUCTION

1.1 Members of the University who have shown ability to carry out independent and original work may be admitted to the higher degrees of Master of Science (M.Sc.) or Doctor of Philosophy (Ph.D.). Those candidates wishing to proceed to a higher degree must first be accepted and registered under the following regulations. Registration is, in the first place, as a **research student** for a higher degree by research and thesis. After the first year of the course, a student may then be recommended as a **candidate** for either the degree of Master of Science or the degree of Doctor of Philosophy.

1.2 The course of research for these degrees may be pursued on a full-time internal, full-time external or part-time internal basis. However, part-time students are not normally recommended to proceed to the degree of Doctor of Philosophy without first being admitted to the degree of Master of Science.

1.3 The degree of Master of Science may be awarded to a candidate whose postgraduate research work represents a useful contribution to knowledge and shows a critical appreciation of the relevant literature. The candidate's work must have developed coherently from the origins of the problem and his thesis or dissertation must present his work in a literary and orderly way. M.Sc.

1.4 The degree of Doctor of Philosophy may be awarded to a candidate whose postgraduate research work represents a useful and original contribution to knowledge and shows a critical appreciation of any relevant literature. The candidate's experimental work must have developed coherently from the origins of the problem; his thesis must present his work in a literary and orderly way and his work, where appropriate, must show evidence of adequate analysis of experimental results. Ph.D.

2.3 Senate shall examine these documents and, if it is deemed that the applicant is capable of following and will profitably pursue the proposed course of study, it shall admit the applicant for registration as a research student on a course leading to a higher degree by research. The applicant will be registered as a research student with effect from the beginning of the term in which the submission is made to Senate. After 12 months, the registration may be transferred either to that for the M.Sc. or for the Ph.D. degree. Senate may require an applicant to pursue such special courses of instruction as it may specify and may require him to pursue his complete course for a period which is longer than the minimum prescribed by these regulations (regulations 3.1, 3.2 and 4.6). ALL

2.4 In order to be considered for admission to a course, an applicant must have at least one of the following qualifications: ALL

(*a*) A suitable honours degree of the University.

(*b*) Another approved honours degree.

(*c*) A qualification deemed by the Senate to be equivalent to (*a*).

In appropriate cases, an applicant may be registered subject to his attaining a suitable standard in a special examination.

2.5 The acceptability of any academic award of any University or College, or National Council, or professional body, for purposes of admission shall be determined by Senate, but conditional registration for a period of one term may be given, pending a decision by Senate. ALL

3. COURSE OF RESEARCH

3.1 A candidate for the degree of M.Sc. by research shall pursue a full-time course of research under the direct supervision of a member of the Acacemic Staff of the University, within the University (subject to regulations 3.3 to 3.7) for a period of one year exceptionally, normally two years and not more than three years (subject to regulation 4.6) after registration for a higher degree. F.T. M.Sc.

3.2 A candidate for the degree of Ph.D. shall pursue a full-time course of research under the direct supervision of a member of the Academic Staff of the University, within the University (subject to regulations 3.3 to 3.7) for a period of not less than two years exceptionally, normally three years, and not more than four calendar years (subject to regulation 4.6) after registration for a higher degree. F.T. Ph.D.

3.9 At the end of the first year the supervisor shall submit to the Academic Registrar a statement on the performance of the student which shall conclude with a recommendation of the degree for which the student shall be a candidate and of the special title of the thesis. ALL

3.10 The Academic Registrar shall lay the documents before the Senate and if approved shall register the candidate as proceeding to the appropriate degree. ALL

3.11 At the end of each year, the supervisor shall submit to the Academic Registrar a statement on the performance of each internal or part-time student. This statement shall include details of the formal course work undertaken by the candidate during that year. If the supervisor is of the opinion that such performance is unsatisfactory, and that the student is unlikely to complete the requirements for the degree, he shall report this through the Academic Registrar to Senate and registration may be withdrawn. P.T. INT.

3.12 At the end of each year, the internal supervisor of each external student shall submit to the Academic Registrar a declaration that the student has been fully engaged in the research for which recognition has been requested and that the working conditions have not deteriorated. He shall also submit a full report on the progress made during the year. If in the opinion of Senate either the declaration or the report is unsatisfactory, registration may be withdrawn. EXT.

4. SUBMISSION OF THESIS OR DISSERTATION

4.1 Within the appropriate period (regulations 3.1 and 3.2) after his registration as a research student, the candidate for a higher award shall present at the office of the Academic Registrar: ALL

(*a*) Three copies of a thesis on his research, each containing a summary, not exceeding 300 words, which must be bound in with each copy of the thesis immediately after the title page.

(*b*) A further copy of the summary of his thesis.

(*c*) A certificate, signed by his supervisor that he has been occupied on full-time research since his registration as a research student, and listing the periods for which he has been so occupied.

or A certificate signed by his supervisor that he has followed a part-time course in research for the requisite time, together with a statement from the

The outer binding case shall carry clearly ($\frac{1}{4}$ inch to $\frac{1}{2}$ inch letters) on the spine, the candidate's name and initials, degree for which the work is submitted, and the year. If desired, the front of the binding case may carry the title of the thesis or dissertation.

4.3 Three copies of the thesis or dissertation shall be submitted, unless the permission of Senate has previously been given to submit only one. The top copy will be retained by the University (and placed in the Library if the thesis or dissertation is accepted for the award of a degree) *; the second copy may be retained by the Department concerned; and the third copy will be returned to the candidate after Senate has approved, or otherwise, the award of the degree.

4.4 A candidate who wishes to submit only one copy of his thesis shall apply in writing to the Academic Registrar, stating the reasons for his application.
Permission to submit a single copy only of the thesis or dissertation may be granted only on grounds of extraordinary expense or difficulty of reproduction. In view of the delays inherent in examining a thesis or dissertation, only one copy of which is available, permission so to submit cannot be given to any candidate who has also sought to have his examiners appointed in advance of submission (see regulation 4.7).

4.5 A candidate may also submit with his thesis or dissertation three copies of any published work which he deems to support his application, and such work shall be considered by the examiners.

4.6 A candidate who is unable to submit a thesis or dissertation within the appropriate period as stipulated in 3.1 and 3.2 may apply for permission to submit late. Such application shall be placed before Senate by the Academic Registrar and shall show good reason why the thesis or dissertation cannot be submitted. The application of the student shall be accompanied by a statement from his supervisor. Extension of time for submission of up to one year may be granted by Senate.

4.7 A candidate may apply to have his examiners appointed in advance of the submission of his thesis or dissertation provided that he makes a normal submission including summary, but includes in place of his thesis or dissertation a statement that he wishes to have his examiners appointed in advance and an explanation of the reason for this. He shall also include a firm declaration of the date before which the thesis or dissertation will be in the hands of the Academic Registrar.

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*The candidate's attention is drawn to the University Library regulations concerning availability of theses.

5.8 After the examiners have prepared and signed their reports upon the thesis or dissertation, an oral examination shall be held, at which the candidate shall be tested upon his knowledge of the subject of his thesis or dissertation and of cognate subjects having regard to the courses attended by the candidate. At the discretion of the examiners a written examination may in extraordinary circumstances be substituted for the oral examination. If this is done, the examiners shall make a full report to Senate of the circumstances which led them to make this substitution.

5.9 If, after the oral examination, the examiners are agreed that the candidate should be admitted to the degree sought, they shall jointly sign a declaration to this effect.

5.10 If the examiners are satisfied with the thesis but not with the oral examination, they may set the candidate a written examination in specified fields, and shall make a final recommendation in the light of his performance in this examination.

5.11 If the examiners are not satisfied that the thesis or dissertation and oral examination are of a standard which would merit the award of the degree of M.Sc., they may agree to make one of the following recommendations: M.Sc.

(*a*) That the candidate be permitted to submit a revised thesis or dissertation.

(*b*) That the candidate be permitted to repeat the course entirely, being registered as starting afresh.

(*c*) That the candidate be not permitted to submit a revised thesis, and be not permitted to proceed to a degree.

5.12 If the examiners are not satisfied that the thesis and oral examination are of a standard which would merit the award of the degree of Ph.D. they may agree to make one of the following recommendations: Ph.D.

(*a*) That the candidate be permitted to submit a revised thesis for the degree of Ph.D.

(*b*) That the candidate be permitted to proceed to the degree of M.Sc.

(*c*) That the candidate be permitted to submit a revised thesis for the degree of M.Sc.

(*d*) That the candidate be permitted to repeat the course entirely, being registered as starting afresh.

(*e*) That the candidate be not permitted to submit a revised thesis, and be not permitted to proceed to any degree.

5.21 If the examiners cannot agree on a recommendation, Senate shall send the thesis or dissertation to an independent referee examiner, who shall report upon the thesis or dissertation, and upon any questions which the Senate may put.

5.22 When Senate has decided that the candidate has reached the appropriate standard, he shall be informed that he may proceed to admission to the appropriate degree.

6. GENERAL

The Senate may at its discretion waive any part of these regulations in such circumstances as it may deem fit.

Regulations for the Degree of Doctor of Science

1. The degree of Doctor of Science may be conferred upon graduates of the University or members of the staff or other persons whose work has been significantly associated with the University, who shall be adjudged by the Senate to have distinguished themselves by their substantial and original contributions to the advancement of knowledge, which indicate that the candidate has an authoritative standing in his subject.

2. The application for the degree of Doctor of Science must be based either wholly or to a substantial extent on original work of distinction carried out by the candidate. If any of the work submitted has been produced jointly with others, the candidate shall include a written statement indicating the share which he personally has taken in the work. He must also indicate whether or not the work or any part of it has been submitted successfully or unsuccessfully, for a degree in this or any other University.

3. Applications shall be made in writing to the Academic Registrar and must be accompanied by copies of published work on which the candidate bases his claim for the degree.

4. The work shall be submitted to two external assessors appointed by the Senate. The assessors may, at their discretion, require the candidate to present himself for interview. In the event of the assessors disagreeing, a referee shall be appointed by the Senate. The Senate shall decide, after consideration of the reports of the assessors and referee, whether a degree shall be awarded.

5. The University Library may retain one copy of the work approved for the award of the degree, or require a list of publications submitted by a successful candidate to be retained in the University Library.

6. The candidate shall, at the time of submitting his application, pay the appropriate fee (£50).

Reference 40.
Plastics & Polymers, in press.

The figures and tables in this paper may be found in the thesis :

Paper.	Thesis.
Figure 1	p. 102 (Fig. 40)
Figure 2	p. 104 (Fig. 41)
Figure 3	p. 107 (Fig. 42)
Figure 4	p. 109 (Fig. 43)
Figure 5	p. 110 (Fig. 44)
Table 1	p. 105 (Table 9)

PUNCHING PAPER-BASED PHENOLIC LAMINATES: THE PUNCHING CHARACTERISTICS OF A SERIES OF COMMERCIAL MATERIALS CLASSIFIED ACCORDING TO PAPER TYPE.

by G.S.Learmonth, Ph.D., B.Sc., F.R.I.C., F.P.I., and K.L.Watson, B.Sc., A.R.I.C. (Department of Chemistry, The University of Aston in Birmingham).

ABSTRACT:

The series of sixteen commercial paper-based phenolic laminates previously investigated has been re-examined with special reference to the type of paper from which they were made. Clear separation in punching characteristics is observed between unbleached kraft and bleached kraft paper based materials. By punching these at one temperature and by reference to a special tensile testing procedure there are indications of resin content variations within the two paper types which appear to influence punching quality. Anisotropy in tensile behaviour is also related to punching quality.

1. INTRODUCTION:

Learmonth and Watson have developed a technique for examining the punching characteristics of paper-based phenolic laminates by reference to their stress/strain characteristics during the punching process (Ref. 1.). A hypothetical fracture mechanism, based on the observations of other workers, was advanced to explain the shape of the stress/strain curves. It was suggested that, after an initial "bedding-down" stage, shear stress built up on the material until microcracks developed, leading to a yield region. If the crack propagation energy exceeded the crack initiation energy, then an apparent hardening region was observed after which, if the material showed

materials at the same temperature, which for convenience was fixed at 55°C.

Pepper and Barwell (Ref. 4.) have described a method of assessment of brittleness based on the comparison between the normal ultimate tensile stress of a phenolic laminate and the ultimate tensile stress of a test-piece with a hole in its centre. The resulting "stress concentration factor" was used to assess the brittleness of the material. A similar approach was adopted in the present work to help interpret the results from punching the series of materials at the same temperature.

2. PROCEDURE :

2.1. Measurement of punching characteristics:

This procedure has already been described in an earlier paper (Ref. 1.). A punching temperature of 55°C and a heating time of 10 min. was used in all cases.

Punching quality was assessed visually as has already been described (Ref. 1.) and the type of defects observed (Ref.2.) was noted.

2.2. Tensile Tests:

2.2.1. Preparation of test pieces.

For each material, ten rectangular test-pieces measuring 4.0 in x 0.75 in were cut in the lengthwise and crosswise directions, parallel to the edges of the boards. A circular saw was used for this purpose. The long edges of each test-piece were carefully sandpapered.

"Notched" test-pieces were prepared by drilling a 0.25 in diameter hole in the centre of five test-pieces from each direction.

2.2.2. Tensile testing procedure.

The tensile testing machine was provided with a hot air box enclosing the clamps. The temperature was controlled at

3.2. Punching characteristics at 55°C:

It was hoped to isolate the property or properties associated with punching quality by plotting the punching characteristics at a fixed temperature against the temperature at which the materials should have been punched (i.e. recommended punching temperature). This has been done in Figure 2.

Separation between unbleached kraft and bleached kraft materials was again clear. Stress and time to break for the unbleached materials appeared to be constant although the bleached kraft materials did tend to show a very slight increase in stress and decrease in time. Punching quality fell with increasing recommended temperature, especially with the bleached kraft materials. The interesting point was that strain at break decreased for both classes.

On the whole, the two cotton linter materials still appeared to be more closely associated with the unbleached kraft materials, the third remaining exceptional. The alpha cellulose material appeared to behave as the bleached kraft materials except in strain at break.

The visible defects shown by each group of materials have been tabulated in Table 1. The most significant point emerging seemed to be that only unbleached kraft materials showed lifting and that no unbleached kraft material showed feathering.

3.3. Ultimate tensile stress at 55°C:

The decrease in strain at break at 55°C at apparent constant stress at break as punching quality deteriorated suggested a corresponding increase in "brittleness" (i.e. a decrease in work of fracture). This led to the adoption of the tensile testing procedure based on the work of Pepper and Barwell.

U.T.S. (unnotched) by U.T.S. (notched) in each case. P.Q. values have been plotted against stress concentration factor in Figure 4. There appeared to be a significant decrease in P.Q. value with increasing stress concentration factor in the weaker direction. The unbleached kraft laminates were closely grouped but the bleached kraft exhibited a wide range of stress concentration factors. There appeared to be no significant trend in the stronger direction.

The fractured edges of the unnotched tensile test-pieces in the weaker direction were cleaner and straighter than in the stronger direction for all materials. The edges for the stronger direction were uneven and cracks were present which tended to turn towards the weaker direction (e.g. as in Figure 5).

4. DISCUSSION:

There were five main points arising from the results at 55°C

1) Strain at break and punching quality decreased as the recommended punching temperature (at which the materials should have been punched) increased.
2) Punching quality showed an increase with increasing ultimate tensile stress.
3) Punching quality increased as tensile anisotropy increased.
4) Punching quality decreased as the stress concentration factor increased in the weaker direction.
5) Unbleached kraft and bleached kraft materials showed a clear division in properties, unbleached kraft being generally stronger and better punching.

Learmonth and Watson have already demonstrated that increasing resin content gave a reduction in strain at break with a corresponding decrease in punching quality while stress at

propagation process. This was consistent with the decrease in punching quality with increasing stress concentration factor or brittleness in the weaker direction.

The gross differences between the unbleached kraft and bleached kraft laminates were thought to be due to the better crack stopping properties of the longer, stronger unbleached kraft fibres leading to the increased strength and improved punching quality of these materials. Only the unbleached kraft materials showed lifting, which implied a reduction in interlaminar strength. This was consistent with the more coherent and less soft, fluffy appearance of unbleached kraft paper. There would presumably be less involvement of unbleached kraft fibres with those of an adjacent ply. The absence of feathering could have been associated with superior crack stopping properties or with the difficulty in observing visual defects because of the opaque nature of most of the unbleached kraft materials.

There was little to be noted about the cotton linter or alpha cellulose materials because of insufficient data. One of the cotton linter materials had exceptional, and desirable, properties which might have been associated with the resin system used or with resin/paper interaction.

5. CONCLUSIONS:

The results suggested that, at 55°C, the punching characteristics of the commercial laminates examined primarily depended upon the paper used.

Without direct evidence, there were indications that resin content was a secondary factor.

Comparison of tensile properties in the weaker and stronger directions of the laminates suggested that fibre orientation might play some part in determining punching quality.

Reference 38.

Plastics & Polymers, in press.

The figures and tables in this paper may be found in the thesis :

Paper.	Thesis.
Figure 1	p. 74 (Fig. 25)
Figure 2	p. 77 (Fig. 26)
Figure 3	p. 78 (Fig. 27)
Figure 4	p. 81 (Fig. 28)
Figure 5	p. 84 (Fig. 29)
Figure 6	p. 85 (Fig. 30)
Figure 7	p. 86 (Fig. 31)
Figure 8	p. 87 (Fig. 32)
Figure 9	p. 88 (Fig. 33)
Figure 10	p. 89 (Fig. 34)
Figure 11	p. 90 (Fig. 35)
Figure 12	p. 91 (Fig. 36)
Figure 13	p. 92 (Fig. 37)
Figure 14	p. 95 (Fig. 38)
Figure 15	p. 96 (Fig. 39)
Table 1	p. 82 (Table 7)
Table 2	p. 93 (Table 8)

PUNCHING PAPER-BASED PHENOLIC LAMINATES : THE EFFECT OF PROCESSING VARIABLES AND TYPE OF PAPER

by G.S.Learmonth, Ph.D., B.Sc., F.R.I.C., F.P.I. and
K.L.Watson, B.Sc., A.R.I.C.
(Department of Chemistry, The University of Aston in Birmingham)

ABSTRACT:

The effect of impregnating and laminating variables on the punching characteristics of paper-based phenolic laminates has been investigated by a previously described technique using an instrumented power press. Resin content of the laminate, laminate thickness, state of cure of the resin and, possibly, the presence of voids have been shown to influence punching quality and the stress/strain characteristics during punching. Comparison between laminates made from bleached kraft and cotton linter papers has suggested that cotton linter fibres had a greater effect in suppressing the propagation of cracks during the fracture process than bleached kraft fibres.

1. INTRODUCTION

Learmonth and Watson have pointed out that there is a need for a greater understanding of the effect of the structural features of the resin, fibre and finished laminate upon the process (Ref.1.). They have also described a technique whereby the punching characteristics of these materials may be examined at different temperatures (Ref. 2). They have applied this method to a series of commercial materials to obtain a background picture of punching characteristics under conditions that typify those encountered in industrial practice (Ref. 3). The method depended upon examination of the stress/strain characteristics obtained using

cresol/formaldehyde resin, dissolved to ~~30~~ 50% solids in industrial methylated spirits, was used throughout the investigation.

2. IMPREGNATING AND LAMINATING VARIABLES

2.1. Preparation of Laminates

2.1.1. General Method

The paper was impregnated in a laboratory scale continuous impregnator which is illustrated in Figure 1. Apart from the resin content experiments, the paper was impregnated twice and the resin content was maintained between 45.9 and 48.8%. The air temperature was controlled at 95-100°C to flash off most of the solvent. The residence time in the oven of any point on the paper was $1\frac{3}{4}$ min. Except for the drying temperature experiments the paper was then dried at 85°C in a forced circulation air oven for the required length of time. Although this temperature was lower than that normally used in commercial practice, the need for precise control of the state of the dried paper outweighed the disadvantage of the extra time involved. The dried paper was then cut into sheets and seven plies, unidirectionally stacked, were pressed between matt finish stainless steel plates in a 100 ton hydraulic press equipped with steam heated/water cooled platens. The standard pressing conditions used were 1 hour at 150°C and 1000 lbf/in^2 followed by cooling under pressure for 10 min.

2.1.2. Drying Time Experiments

Samples of the impregnated bleached kraft paper were dried for 10, 20, 40, 60, 80 and 100 min. and pressed under the standard conditions. Volatile and resin contents were determined by heating 2in squares of the dried, impregnated paper at 150°C for 5 min in a hot air oven. A sensitive version of the flash test was also used in which four 2 in squares of dried, impregnated paper were pressed for 5min at 150°C and 1000 lbf/in^2. The weight of the flash was expressed as a percentage of the weight of the

2.2. Measurement of Punching characteristics

This procedure has already been described in an earlier paper (Ref. 2). A punching temperature of 55°C and a heating time of 10 min. was used in all cases.

2.3. Experimental Results

Property values at break, together with density values, have been tabulated in Table 1 and the stress/strain curves are shown in Figures 4 to 10.

2.3.1. Drying Time Experiments (Figure 4)

After an initial decrease the punching quality levelled off after 60 min. The 10 and 20 min stress/strain curves showed no secondary yield and punching quality was good in these cases only. Stress at break remained constant whereas strain tended to decrease very slightly. Time to break appeared to increase very slightly initially and to level off after 60 min.

The levelling of density and thickness, together with punching quality and time to break, indicated that this respresented the time after which drying was essentially complete, although flash and volatiles continued to decrease slowly up to 100 min.

2.3.2. Resin content Experiments (Figure 5)

Increasing resin content was accompanied by a marked decrease in punching quality. The stress/strain curve for the 38.0% material showed no secondary yield and punching quality was good. Stress at break remained constant but strain decreased and time increased with increasing resin content. Density decreased and thickness increased also. A comparison between the stress/strain curves for the seven and eight ply laminates of the paper impregnated to 38.0% resin content are shown in Figure 6. Although there was no significant difference between stress and strain at break the thicker laminate showed increased time to

Both papers were dried at 85°C, samples being taken at 10 min. intervals until the volatile content was between 4.9 and 5.3%. Resin content was maintained between 46.1 and 48.5%.

3.2. Measurement of Punching characteristics.

The laminates were punched at 25, 55, 90 125 and 160°C using a heating time of 10 min in all cases.

3.3. Experimental Results.

The stress/strain curves for the bleached kraft laminate are shown in Figure 11 and for the cotton linter laminate in Figure 12. The punching characteristics for both laminates are plotted against punching temperature in Figure 13.

Both materials showed the expected decreasing stress and time to break and increasing strain to break with increasing temperature, although the bleached kraft laminate showed an initial decrease in the strain/temperature curve. The cotton linter material became increasingly stronger and took increasingly longer to punch than the bleached kraft, though the effect was small in both cases. From 55°C upwards, the cotton linter laminate showed between 1-2% greater breaking strain than the bleached kraft.

The bleached kraft material, which was considerably inferior in punching quality at 25°C, showed more rapid initial improvement than the cotton linter paper as the temperature was increased, until, above 100°C it was significantly better.

The nature of the visible defects is indicated in Table 2.

4. COMPARISON BETWEEN THE TWO PAPERS CONSOLIDATED WITH NO RESIN.

4.1. Preparation of consolidated papers

Eleven plies of paper, in both cases, were pressed for 1 hour at 150°C and 1000 lbf/in^2 with 10 min cooling under pressure. This procedure gave boards 1/16 in thick.

4.2. Measurement of Punching characteristics.

The consolidated papers were punched at 25, 90 and 160°C using a heating time of 10 min.

for the 48.1% laminate compared with 61.5 x 10^{-3} in for the 38.0% laminate).

5.2. Drying Temperature Experiments.

The evidence for an improvement in punching quality for the 100°C material was only very slight. Since there was no significant change in density and the decrease in time and strain to break were not accompanied by a decrease in stress it was assumed that the slight effects observed were the result of an accumulation of experimental scatter. This might have been associated with the difficulty of control at the higher drying temperature.

5.3. Laminating Temperature Experiments.

The trends in properties at break with increasing laminating temperature and the improved punching quality of the 135°C material indicated that a less advanced state of cure had a beneficial effect on punching quality.

5.4. Laminating Pressure Experiments.

The low density of the ~~700~~ 750 lbf/in^2 laminate suggested that the improved punching quality and reduction in stress and time to break resulted from the presence of voids.

5.5. Laminating Time experiments.

The slight reduction in property values at break and possible improvement in punching quality for the 30 min laminate indicated that cure at 150°C was incomplete.

5.6 . Comparison of Effect of Temperature upon Bleached Kraft and Cotton Linter laminates.

The greater stress, strain and time to break of the cotton linter material over the bleached kraft material at higher temperatures suggested that the cotton linter fibres tended to act as better crack stoppers than the bleached kraft fibres.

that the paper alone was capable of supporting a surprisingly large proportion of the stress at break of the finished laminate. It might be supposed that the independent strength of the paper would be even greater in a resin matrix where, with proper support, the fibres would be able to exhibit their full mechanical strength.

It was interesting to note that although the consolidated cotton linter paper was weaker than the bleached kraft, its laminates were stronger than bleached kraft laminates at higher temperatures. The crack stopping properties of the cotton linter paper had presumably outweighed its inferior strength.

5.8. General Comments.

The time available for this work did not permit an investigation into the general applicability of the results. The investigation of processing variables did not reveal any surprising effects, although the experiments were essential to clear the ground for future work on resin variables. It should be emphasised that this work was only directed towards the punching characteristics of the materials with no reference to other property requirements.

The comparison between laminates made from bleached kraft and cotton linter papers was interesting. Data from a wider range of papers with different resins would undoubtedly be of value. Although there are no immediate plans to obtain this information, it is hoped to return to this area later.

6. Conclusions.

Processing variables, on the whole, showed the effects that might have been expected although the punching characteristics of the laminates were somewhat surprisingly insensitive to these variables.

The effect of drying time of the impregnated paper was