WATER TRANSMISSION THROUGH
POLYESTER/GLASS LAMINATES

A study of the behaviour of polyester resins and laminates when exposed to water at 50°C

by

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SUMMARY

This thesis is an investigation of the relationships between unsaturated polyester resin composition and permeability to water. The permeabilities of cured unreinforced resins (castings) and glass reinforced polyesters (G.R.P.) made with different resins were studied at 50°C. In addition, the effect of applied strain on the permeability of castings and laminates made from a single resin was investigated. Six commercial resins were examined in all. Three variables were studied:

1. The effect of chemical constitution of the resin on the transmission rate of water.

2. The effect of glass reinforcement on permeability.

3. The effect of applied strain on the permeability of castings and laminates made from a single resin.

It was shown that, in the absence of any external strain, the castings made from various resins behaved differently. Castings made from a moderately crosslinked resin showed the highest resistance to water transmission. Castings made from resins with either higher or lower unsaturation showed a higher permeability to water. The diethylene propylene fumarate isophthalate resin has an advantage over the propylene fumarate isophthalate resin in having a lower water transmission rate. The permeability of the polyester resin increases with increase in the acid value of the resin.

Another feature observed in the study is the decrease in the rate of transmission of water as the volume fraction of glass fibres in the laminates increases. This effect becomes more pronounced for laminates made from resins with high unsaturation. Results show that the observed transmission rates of water through laminates are always less than the product of resin volume fraction and resin permeability. The difference between the calculated and observed values of permeability become larger as the fibre orientation changes from random to bidirectional. This suggests that fibre orientation, as well as fibre volume fraction, is an important factor affecting water transmission through laminates.

The effect of external strain on resins and laminates depends on the nature of the resin used. In general, applied strain increases water transmission rates, both in castings and laminates. An exception to this rule was found with laminates made from a moderately crosslinked resin. Glass laminates made from this resin allow the passage of less water when under low strain than when unstrained. However, permeability increases when the applied strain is higher.

* * *

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THE PROBLEM

Since their development glass reinforced polyester resins (G.R.P.) have been used in many applications, notably in the chemical, marine, aircraft, automobile, electrical and building industries. The weathering characteristics and water resistance of fibre reinforced polyesters have been the subjects of many investigations.

From practical experience and laboratory experiments it is known that hot water adversely affects many polyester resins. This results in various surface defects, causing concern about the long term effect on mechanical properties. Gel coat permeability is also an important parameter. It is, therefore, necessary to study the transmission of water through polyester resins and laminates.

Since the G.R.P. industry is relatively young, attempts have been made to develop accelerated test methods to predict the long term behaviour of resins and laminates. While these methods have proved useful, they do not reproduce actual situations. Results obtained by reproducing test conditions similar to those in which G.R.P. materials are normally used could reveal some facts about the process of water transmission in laminates.

Polyester resins do not possess particularly good water resistance because of the presence of hydrophilic ester groups. The extent to which water permeation occurs depends on the structural elements of the polyester chain, the degree of crosslinking, crosslinking monomer and molecular weight distribution. A comparative study of the permeabilities of castings of various polyesters would be useful in determining the relative importance of some of these factors.

These resins can be reinforced with glass fibres to make glass reinforced polyesters. The highly anisotropic nature of laminates renders the study of these materials complicated. However, the effect of glass fibres may be examined using laminates made from the same series of resins as those studied in the form of castings. Further to this, the study of the effect of applied strain on the permeability should also throw some light on the structural changes induced by mechanical strain.

The production of polyester resins is carried out by a batch process. This results in a number of variables in the properties of the resins between batches and makes it more difficult to obtain reproducible and well characterised products. However, variables, such as crosslink density, resin structure and the molecular weight distribution, were examined as far as possible within these limitations.

CHAPTER ONE

INTRODUCTORY SURVEY

1.1 INTRODUCTION

One of the most important uses of thermosetting resins is in reinforced plastics.

Of the various synthetic thermosetting resins used in the manufacture of fibre reinforced plastics, unsaturated polyesters are the most widely used. These resins are usually reinforced with glass fibres in various forms, although other materials, such as asbestos and carbon fibres, are used. Glass fibre reinforced polyesters offer the advantages of high specific strength and modulus with good chemical resistance. Other properties which make reinforced plastics attractive for industrial use as substitutes for more traditional materials of construction are easy fabrication of complicated shapes, ease of handling and repair.

The substitution of G.R.P. for conventional materials is often limited by the heterogeneous nature of reinforced plastics and their tendency to degrade in the presence of moisture, especially at elevated temperature. The present work is directed towards understanding the relationship between materials structure and penetrant transport. An investigation of the chemical and physical processes by which water is transported through reinforced and unfilled polyester resins at elevated temperature has been carried out. This is done both in the presence and absence of applied strain.

1.1.1 Nature of the Components of a Glass Reinforced Polyester Resin

a) Resin

Unsaturated polyesters are thermosetting resins produced by the condensation polymerisation of saturated acid and unsaturated dibasic acids with glycols. The nature of the unsaturation in these polyesters is usually fumarate and, to a lesser degree, the isomeric maleate. Cost and process considerations make it desirable to employ maleic anhydride in the manufacture of polyesters. At normal process temperatures the maleate groups are largely isomerized into the fumarate homologues. The final resin usually contains 10 - 30% maleate unsaturation and 70 - 90% fumarate unsaturation (1).

The polyester so formed is capable of subsequent cross-linking by addition reaction, through an unsaturated bond in a monomer such as styrene. The liquid styrene also serves as a solvent for the otherwise highly viscous unsaturated polyesters. Such a solution of linear molecules with intermittent unsaturated sites dissolved in an unsaturated monomer constitutes an unsaturated polyester resin. The proportion of the monomer present is about 30 - 40% by weight. Several text books describe the manufacture of polyester resins and explain why certain constituents are preferred (1, 2, 3). The crosslinking reaction may be initiated by methyl ethyl ketone peroxide (M.E.K.P.) or cyclohexanone peroxide in the presence of cobalt naphthenate or cobalt octoate.

The mechanism of radical initiation is given below (4):

$$\mathrm{ROOH} + \mathrm{Co}^{++} \xrightarrow{\text{fast}} \mathrm{RO.} + \mathrm{OH}^{-} + \mathrm{Co}^{+++}$$

$$\mathrm{ROOH} + \mathrm{Co}^{+++} \xrightarrow{\text{slow}} \mathrm{ROO.} + \mathrm{H}^{+} + \mathrm{Co}^{++}$$

$$\mathrm{ROO.} \longrightarrow \mathrm{R.} + \mathrm{O}_2$$

The cured polyester network is made up of polyester chains and copolymer chains with fumarate links common to both. The number of styrene links between the fumarate crosslink points is uncertain, but thought to be about two. Variation in properties of the cured resins can be made by altering the ratio of saturated acid to unsaturated acid, by introducing long chain acids or glycols and/or by altering the styrene content. These changes have been discussed by Boenig and Parker et al. (1, 5).

b) Glass Fibre

Fibres are available in several different glass compositions. They are as follows:

1. "A" glass, a soda-lime glass
2. "E" glass, a low alkali borosilicate glass
3. "C" glass, an alkali-borosilicate which is claimed to be chemically resistant (6).

The compositions of these glasses are shown in table 1 (a). Table 1 (b) gives comparative chemical resistance data measured on glass filaments in standardised tests. It has been found that laminates fabricated from "E" glass materials are more resistant to water than the equivalent "A" glass products (6). Hence "E" glass is used in such applications.

Table 1(a) Glass Compositions (6)

% by weight	"A" glass	"E" glass	"C" glass
SiO_2	72.0	54.3	64.6
Al_2O_3	0.6	14.8	4.1
CaO	10.0	17.3	13.4
MgO	2.5	4.7	3.3
B_2O_3	-	8.0	4.7
Na_2O	14.2	0.6	7.9
K_2O	-	0.6	1.7
BaO	-	-	0.9
SO_3	0.7	-	-
As_2O_5	trace	-	-
Fe_2O_3	-	0.4	-
F_2	-	0.1	trace

Table 1(b): Chemical Resistance Data for Glasses (6)

TYPE OF GLASS	% WT. LOSS - 1 HR. BOIL IN WATER	% WT. LOSS - 1 HR. BOIL IN 1.0N H_2SO_4	% WT. LOSS - 1 HR. BOIL IN 0.1N NaOH
"A" glass	11.1	6.2	12.0 - 15.0
"E" glass	1.7	48.2	9.7
"C" glass	0.13	0.10	-

The strands made from filaments are used to produce chopped strands and rovings.

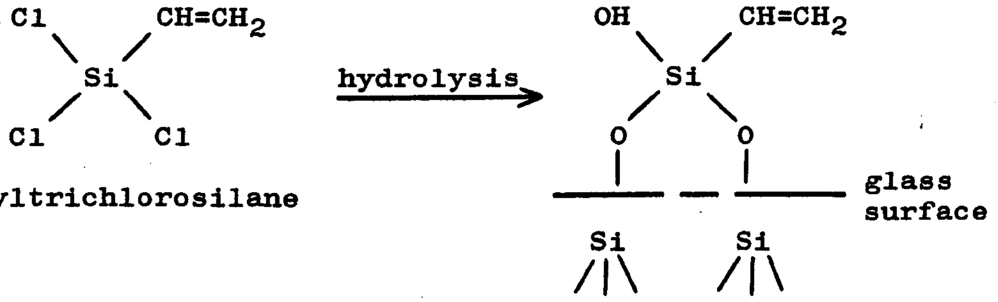
Chopped strand mats are non-woven and the strands distributed in a random pattern to ensure consistency of strength in all directions.

Woven roving fabrics are made from rovings which contain practically no twist, so both ends and picks lie flat in the fabric. They are manufactured in both plain and twill weaves.

c) Coupling Agents

Mixtures containing coupling agents are normally used for surface treatment of glass fibres for resin reinforcement. The coupling agent in the mixtures improves the bond of resin to glass. The improved bond has been shown to have an influence on the strength of the final laminate (6, 104), in particular on the wet "strength" of the laminate in a standard boiling test.

The type of finish used in the present work is based on the silane compounds. Studies have shown that R SiX_3 type structure is most effective for glass reinforced polyester resins (8). The organo functional group (R) is selected to react with the resin and the X groups may be halides. The reaction of such finish is represented below:



Vinyltrichlorosilane

The unsaturated vinyl group subsequently will be able to crosslink with unsaturated groups in the resin.

d) Size

Besides coupling agents treatment mixtures also contain a binder/lubricant and is called "size". This is applied to newly formed fibres as they come together just below the bushing, from which the fibres are extruded, and is necessary to protect the filaments and to bind them in a strand. Size prevents fibres abrading one another and sticks fibres together weakly and maintains them in the form of a strand.

e) Glass Fibre Reinforced Plastics

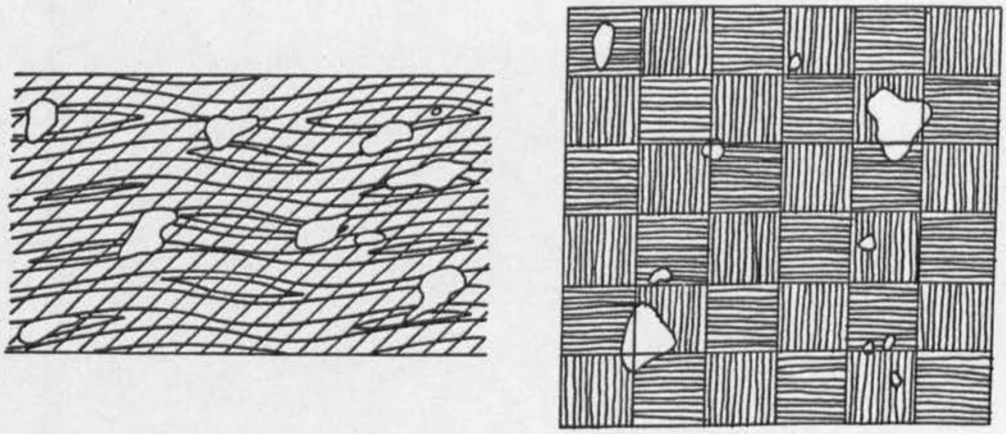
Glass fibre reinforced plastics are composite materials consisting of fibres bonded by a resin matrix, each component contributing to the overall properties of the laminate.

With water resistant laminates it is usual to have a resin rich layer on the exposed surface. This is to prevent exposing fibres to water attack and to stop the wicking of water along the fibre. The surface layer may be reinforced with a very light "C" glass tissue. The outer layers may contain a combination of different types of glass orientation (e.g. chopped strand, woven roving, continuous etc.) to give maximum strength with minimum wall thickness. The specifications for laminate preparations are reviewed by Parkyn (2). Penn (7) has described different modes of manufacture in some detail and points out the faults that may occur with each.

Many of the faults are caused by gel coat problems. The main exceptions are concerned with delamination of the mats due to imperfect wetting of the mats and to voids.

Inadequate wetting can be reduced by impregnating the fibre mats in the resin, reducing the viscosity of the resins and protecting the fibres from accumulation of dust on their surfaces before use.

Voids, on the other hand, are difficult to eliminate. These arise from volatile materials, trapped air and formation and growth of microvoids during curing. The size of the voids varies considerably. They can range from two to several hundred times that of a filament diameter (9). In badly made laminates a single void could extend almost from one surface to the other. Capillary voids along the fibres can also be formed (fig. 1).



Cross Section

Plan

Fig. 1 Voids in Laminates

The use of vacuum technique can produce laminates with low void content. However, this is not practical in large scale operation. In addition, the loss of monomer during laminating may be enough to offset the benefits.

Faults occurring in the gel coat may be grouped under three headings:

1. Faults occurring during application
2. Imperfections produced immediately after curing
3. Damage developing after some time

Faults occurring in wet gel coats are: crating (fish eyes), dewetting at certain areas leaving a few spots with no gel coat; sagging of too thick films on sloping or vertical surfaces; fibre pattern caused by either too thin a gel coat or rolling before the gel coat hardens.

Problems occurring immediately after curing are: togging, caused by clouding of the gel coat; softness, due to undercuring; wrinkling, normally caused by laminating before the gel coat is fully cured.

Damage developing after exposure to environment: blistering, usually caused by trapped air, dirt or solvent; crazing, by impact or flexing of the gel coat; pinholes, created by trapped dirt, air or solvent bubbles; chalk-like appearance or deposit on the surface by degradation of the resin, incorrect proportion of curing agent.

1.2 DEFINITIONS AND TERMINOLOGY

"Penetrant" is a term given to molecules diffusing into a phase adjacent to that phase the molecules already occupy. Other terms used for diffusing molecules are diffusant and permeant. There are two possible mechanisms whereby small molecules can penetrate super cooled liquid glasses. At high concentrations the penetrant may condense on the surface of the solid. The "surface of the solid" in this sense includes not only the external surface, but capillaries and/or voids present at the interface. This is called adsorption.

Absorption is the second mechanism which involves distribution of molecules in a solid as a result of intermolecular action between the two components. The uptake of the penetrant by a solid has been termed sorption, adsorption and absorption, being regarded as special cases. There is no sharp dividing line between absorption and adsorption. One or the other dominates during certain phases of sorption. In many systems the overall sorption process is best represented by a composite of the two methods.

The process of water transmission in an amorphous polymer can be conceived qualitatively in terms of the movement of penetrant molecules through a tangled mass of polymer molecules. Diffusion takes place by the movement of a penetrant molecule from hole to hole under the influence of a concentration gradient, by a co-operative action of the surrounding complex of molecules. In fact, there does not need to be a hole formed for diffusion to occur. The penetrant molecule and its surrounding polymer segments may share the same common volume before and after the diffusion jump. However, certain Van der Waals type polymer-polymer or polymer-penetrant forces must be overcome to allow rearrangement of the local structure for passage of the diffusing molecules.

The mathematical theory of diffusion is based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section.

$$\text{i.e. } F = -D\frac{\partial C}{\partial x}$$

when F is the rate of transfer per unit area of section, c the concentration of diffusing substance, x the space co-ordinate measured normal to the section and D is the diffusion coefficient. Desorption is the reverse of sorption. During the process of desorption the sorbed molecules leave the solid through the exposed surface and evaporate into an adjoining medium.

The permeability of a polymer film at a given temperature is the quantity of permeant which passes through unit area in unit time under unit pressure difference. However, the precise definition of permeability is governed by the test conditions. In the present investigation temperature and pressure are held constant. The permeability of the polymer to water is then defined as the mass of water transmitted through unit area and thickness of the film per unit time.

$$\text{i.e.} \quad P = \frac{Ql}{At}$$

where P is the permeability coefficient, Q the mass of water transmitted through an area A of thickness l for a period t. In this expression the permeability can also be described as transmission rate or permeation rate.

In transmission experiments, from the instant the diffusant is first admitted to one side of the sheet and prior to the establishment of a steady state, both the rate of flow and the concentration at any point of the sheet vary with time. The time taken to reach the steady state of permeation is termed the time-lag.

1.3 THE PROCESS OF WATER TRANSMISSION

The transmission process may be considered as a series of jumps by the penetrant molecule through spaces in the polymer network. The free volume, activated zone and transition state theories all explain the nature of the diffusion process using this original concept (10, 11, 12). Each theory considers from a different point of view how the polymeric chain segments move to form spaces to allow penetrant movement.

The movement of gases through polymer membranes proceeds by the condensation and solution of gas at one surface followed by diffusion through the matrix and evaporation to the gaseous state at the other surface (13). The diffusion of permanent gases (e.g. H_2, O_2, N_2) in high polymers follows a much simpler process than that of water or organic vapours. This is mainly because of the comparative lack of interaction between the simple gases and the polymer. Furthermore, the diffusion constants of gases are independent of concentration and their solubility in polymers is proportional to the pressure (i.e. Henry's Law is obeyed).

The diffusion of vapours is more complex and their diffusion constants are highly dependent on the concentration of the penetrant in the polymer (i.e. Henry's Law is not obeyed) (13).

Several studies of the diffusion of liquid water in a variety of polymers have shown features not found in the diffusion of most gases or organic vapours.

A difference between vapour and liquid water permeabilities has been observed for several systems (14, 15). Yet for a number of polymers for which the water permeability varied linearly with pressure, both permeabilities were identical (16, 17). It is thought that the differences between liquid and vapour permeabilities are largely due to experimental difficulties in making the vapour phase at unit relative pressure.

In the liquid state water is strongly associated through hydrogen bond formation. While diffusion coefficient generally increases with concentration for an organic vapour, marked decreases have been observed with water in several polymers (18).

Values for the enthalpy of formation of the hydrogen bond in the range 14 - 28 kJ /mole^{-1} suggest strong localised interaction between the water molecule and suitable polar groups of the polymer. In relatively non-polar materials clustering of the sorbed water is encouraged. Evidence has been presented suggesting that water molecules absorbed in polymeric media exist in two or more different states (19 - 21). Some water molecules are bound to polymer molecules through hydrogen bonding and are immobilised, while others are relatively free to move.

The exact bonding mechanisms vary from one polymer to another and are not clearly established in most cases. However, the relative distribution and the structure of each of these states can have profound effects upon the absorption and permeation of water.

1.3.1 Principles of Diffusion

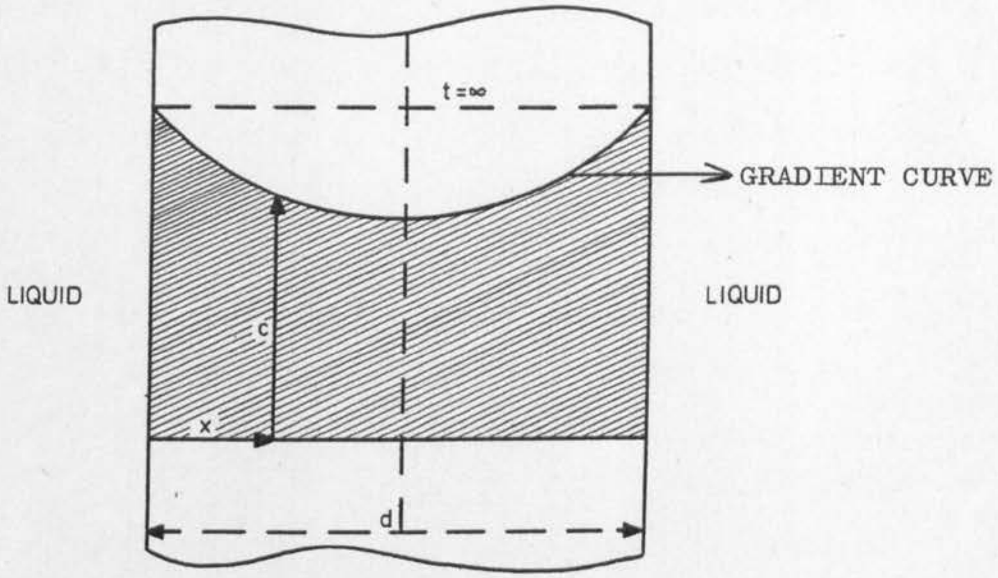


Fig. 2: Flat Specimen Immersed in a Liquid

a) Activated Diffusion

When a flat specimen is immersed in a liquid, a quantity Q of the liquid passes in time t from the area with greatest concentration to the area of the least concentration, until a dynamic equilibrium of the liquid in the specimen is established. Classical diffusion theory is based on Fick's Laws which state that the rate of transfer of diffusing molecules through unit area is proportional to the concentration gradient measured normal to the area.

$$Q = -D\frac{\partial C}{\partial X} \quad \ldots\ldots\ldots\ldots\ldots \quad [1]$$

C is the concentration of diffusing material; x is the distance in the direction normal to the plane, and the coefficient of proportionality, D, is the diffusion coefficient. Equation [1] is commonly referred to as Fick's first Law. The following assumptions apply:

1. The liquid enters by active diffusion
2. No physical or chemical change occurs to alter the diffusion rate
3. The external surface is saturated instantaneously
4. The water enters by the major surfaces of the specimen

By considering the mass balance of an element of volume, the fundamental differential equation of diffusion takes the form (22).

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \quad \ldots\ldots\ldots \quad [2]$$

Frequently, diffusion occurs effectively in one direction only. In such cases,

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \quad \ldots\ldots\ldots \quad [3]$$

Equation [3] is commonly referred to as Fick's second Law. In 1924 Andrews and Johnston (24) succeeded in deriving a general equation for water absorption from Fick's Law. This was especially suitable for cases when the thickness of the slab is low in comparison with its area. The equation derived by Andrew and Johnston (24) is as follows:

$$Q_t = Q_\infty \left[1 - \frac{8}{\Pi^2} \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} e^{\frac{-\Pi^2 D(2n+1)^2 t}{d^2}} \right] \quad .... [4]$$

$$Q_t = Q_\infty \left[1 - \frac{8}{\Pi^2} \left(e^{\frac{-\Pi^2 Dt}{d^2}} + \frac{1}{9} e^{\frac{-9\Pi^2 Dt}{d^2}} + \frac{1}{25} e^{\frac{-25\Pi^2 Dt}{d^2}} \right) \right] \quad .... [5]$$

Qt is the total weight of diffusant sorbed after a time t, and Q_∞ the corresponding quantity at saturation.

Equation [5] is suitable for both moderate and large times. It is very practical in that it can also be applied to non-Fickian behaviour (25).

This equation was also derived considerably later by Irany (25).

In this form the equation describes a series; however, so long as $\frac{Dt}{d^2}$ is greater than 0.1 (corresponding to values of $\frac{Q}{Q_\infty}$ greater than 0.36), all terms except the first may be neglected.

With this limitation equation [5] reduces to:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} e^{\frac{-\pi^2 Dt}{d^2}} \quad \ldots\ldots \quad [6]$$

A similar relationship is derived for the swelling of cylindrically shaped samples (25). The applicability of equations [4], [5] and [6] to the water absorption of rubber (24) and polyvinyl acetate, polyvinyl acetal and other polymers has been shown (25).

Equation [4] can be simplified if the linear portion of the reduced sorption curve extends to the time $\frac{Q_t}{Q_\infty} = \frac{1}{2}$, then the value of $\frac{t}{d^2}$ for which $\frac{Q_t}{Q_\infty} = \frac{1}{2}$, conventionally written as $(\frac{t}{d^2})_{\frac{1}{2}}$ is given by (13).

$$\left(\frac{t}{d^2}\right)_{\frac{1}{2}} = -\frac{1}{\pi^2 D} \ln \left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right] \quad \ldots\ldots \quad [7]$$

or, with an error of 0.001 per cent, it can be written as:

$$D = \frac{0.0494}{(t/d^2)_{\frac{1}{2}}} \quad \ldots\ldots \quad [8]$$

Unfortunately, equation [8] cannot be applied for sorption which does not give an initial linearly reduced sorption curve. It would be applicable to hydrophobic materials, and only in a limited number of hydrophilic cases.

Once D is determined, P can be calculated from:

$$P = D \times S \quad \begin{pmatrix}P \text{ is permeability} \\ S \text{ is solubility}\end{pmatrix}$$

again, only if the system obeys Henry's Law.

Assuming that D is constant, equation [6] can be written as:

$$\log_e \frac{Q_\infty - Q_t}{Q_\infty} = \log_e \frac{8}{\pi^2} - \left(\frac{\pi^2 D}{d^2}\right)t \quad \ldots\ldots \quad [9]$$

Equation [9] represents a straight line. To plot a curve for calculating the diffusion coefficient, it is essential to know Q_∞. This is usually reduced experimentally by prolonged immersion of specimens in the liquid until equilibrium is reached. Judd and Sedov et. al. (27, 28) have used equation [9] to analyse data obtained from polyester resins immersed in water.

Using this equation for water diffusion in rubber sheets, Andrews and Johnston (24) found that the diffusion coefficients were independent of sheet thickness. This was confirmed by Steinhaus (26) for polyester resin films between 0.5 mm and 1.5 mm thick.

b) Law of Capillarity

Penetration by water molecules is thought to take place by two different mechanisms. The first is by active diffusion and the second is by capillary penetration. In the latter case, water is assumed to progress as a separate phase through pores in the matrix.

From Poiseuille's law of flow through small diameter tubes, it has been shown that the passage of water molecules by capillary penetration proceeds as a parabolic function of the time.

$$\text{i.e.} \quad Q = c\sqrt{t} \quad \ldots\ldots\ldots \quad [10]$$

where, Q is the water absorption per unit area, t the time and c is a constant depending on the material.

If a plot of Q versus $t^{\frac{1}{2}}$ is linear, capillary flow is indicated.

1.3.2 Principles of Permeation

There are two main mechanisms whereby gas or vapour can pass from one side of a polymer material to the other. In the first, the gas or vapour can flow through holes in the material, the material then being described as porous. In the second, if such holes are not present a process of absorption and diffusion occurs.

In the absence of cracks, pores or other gross defects, the transport of a fluid penetrant through a polymer film is usually considered to occur by the following process (29):

Step (1) Molecules in phase I adjoining one film surface, penetrate and disperse rapidly into the surface layer, producing a concentration gradient. The conditions under which this sorption process occurs are generally such that the concentration of penetrant at the surface is maintained at a constant value.

Step (2) The penetrant passes through the film by molecular diffusion. Molecules of penetrant diffuse by random thermal molecular jumps, whose driving force is produced by local differences in the chemical potential of the penetrant.

Step (3) A desorption of the penetrant into an adjoining phase II occurs. Generally, this is carried out in such a way that the concentration at the desorption surface is also maintained at a constant value.

For all materials investigated so far the second step is by far the slowest of the three and consequently, the rate controlling step of the whole process of permeation (29).

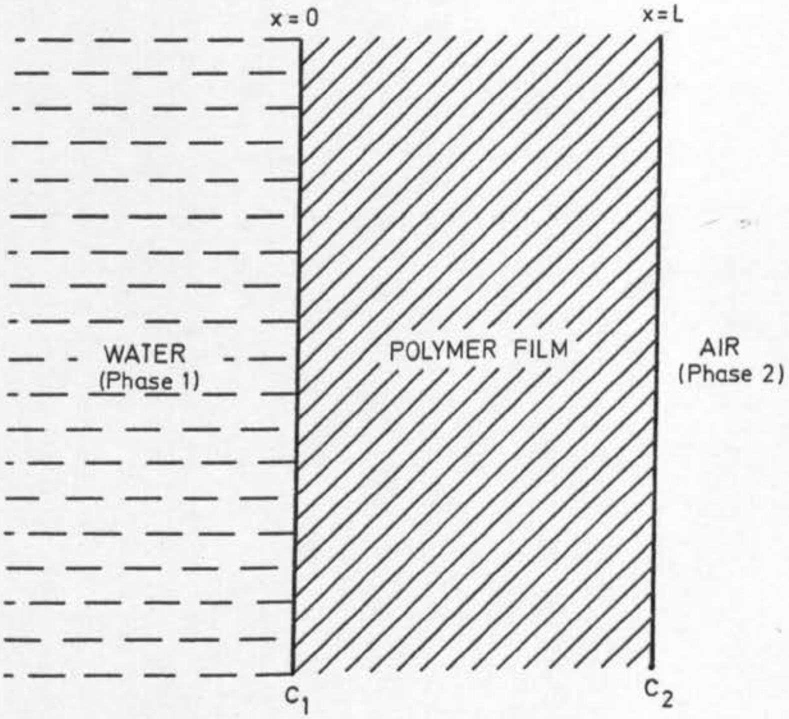


Fig. 3: Polymer Film Subjected to One Sided Exposure

The rate of permeation J is defined as the weight of penetrant passing, during unit time, through a surface of unit area normal to the direction of flow, independent of the rate of aggregation of the medium.

It follows that: $J = Q/At$ ...... [11]

where Q is the total weight of penetrant which has passed through area A during time t.

Consider a unit area of film of thickness L, as shown in fig. 3, exposed to a gaseous penetrant at pressure p_1 at one side and a lower pressure p_2 at the other. Let the concentration of penetrant in the first layer of film ($x = 0$) be C_1 and in the last layer ($x = L$) be C_2. After a time a steady state is reached, in which J is constant and the rate of permeation is directly proportional to the concentration gradient as expressed by Fick's first Law of Diffusion: $J = - D \frac{dc}{dx}$ .... [12]
where D is defined as the diffusion coefficient and assumed constant.

On integration, this gives:

$$J \int_{x=0}^{x=L} dx = -D \int_{C}^{C_L} dC$$

$$J = D (C_0 - C_1)/L \quad .... \quad [13]$$

The equilibrium concentrations C_1 and C_2 of penetrant in the surface layers can be related to the partial pressures p_1 and p_2 by an expression of the form:

$$C = S\Delta p$$

where S is the solubility coefficient of the penetrant in the polymer. When Henry's Law is obeyed, there is a linear relationship between concentration and pressure. S is then constant and it follows that:

$$J = DS\ (p_1 - p_2)/L \quad \ldots\ldots \quad [14]$$

$$= P\ (p_1 - p_2)/L \quad \ldots\ldots \quad [15]$$

where P is defined as the permeability constant

$$\text{i.e. } P = DS \quad \ldots\ldots \quad [16]$$

Thus, an observation of J yields the permeability from equation [15] and D follows from equation [16], provided the solubility is known.

It has already been demonstrated (30 - 32) that these equations are invalid if there is interaction between the film and the penetrant. Previous investigations (33) of water permeation through polar polymers showed that in this case P, S and D are not constants, but functions of the concentration of the penetrant.

Similar behaviour would be expected for the unsaturated polyester resins used in the present work. Thus, a complete investigation requires the determination of the concentration dependence of all three factors. For the sake of simplicity, the above treatment is limited to the isothermal case and to a steady state. In this manner, P, D and S are independent of temperature.

Diffusion coefficients can also be calculated from permeation experiments by the "time lag" method (22). From the instant water is first admitted to one side of the sheet, and prior to the establishment of a steady state, both the concentration and the rate of flow of the penetrant at any point of the sheet vary with time. If the diffusion coefficient is constant, the sheet is initially completely free of penetrant and the permeant is continually removed from the low concentration side, where $C_2 = 0$, the quantity of water Q_t, which passes through the sheet in time t, is given by:

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) \quad \ldots\ldots \quad [17]$$

As t increases the steady state is reached and the exponential terms become negligible.

Thus: $$Q_t = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \quad \ldots\ldots \quad [18]$$

which is a straight line with intercept $\frac{l^2}{6D}$

1.3.3 The Measurement of Permeation Rates and Permeabilities

Methods for determining the permeability of diffusing penetrant have been reviewed by a number of authors (22, 34, 35, 36).

One of the earliest techniques used for measuring water permeability was the dish or weight-cell method. This was later standardised by TAPPI (37, 38) and is the one most generally used in the packaging industry.

The method involves partially filling a dish with desiccant and then sealing the top with the film under test. The whole unit is placed in a preset thermostatically controlled humidity cabinet. The rate of transmission of water vapour is measured by periodic weighing. The most obvious drawback of this method is the difficulty of establishing a satisfactory seal between the film and the desiccant. This should be kept as small as possible in order to minimise the error because of a vapour-pressure gradient forming in the static air space.

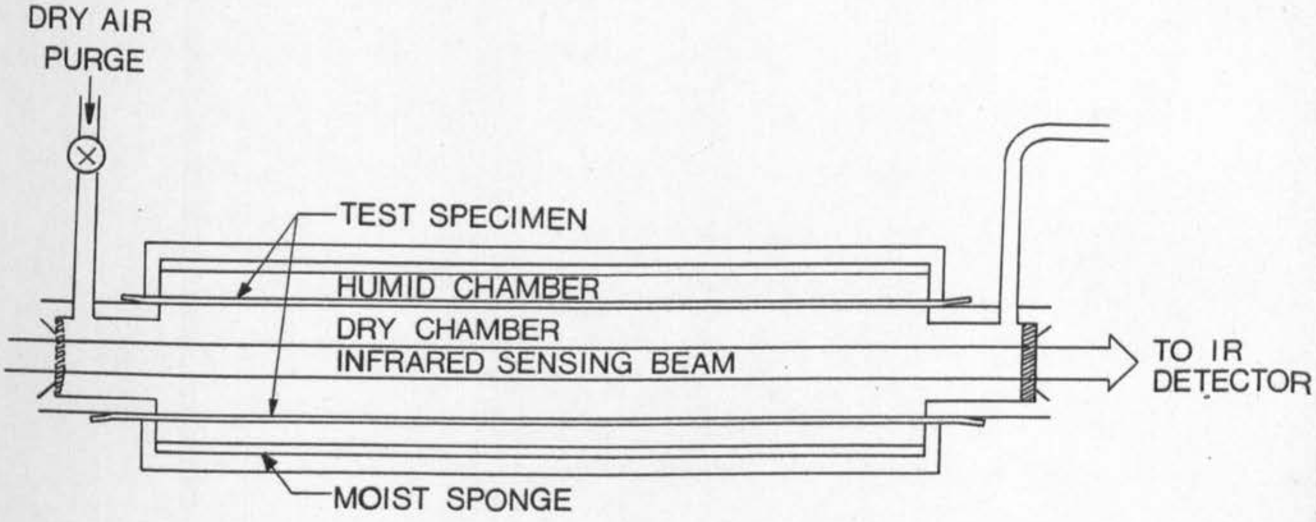
For more accurate measurement, the partition-cell method has been used by several workers. This cell consists of two chambers: one "wet" and the other "dry", separated by the test film. The cell can be used for gases, vapours or liquids with slight modifications. In the case of liquid water the feed is introduced into the upper compartment from a nearby reservoir (39, 40). The diffused water vapour through the film is measured as a function of time.

Water transmission rates for polymer film may be measured by the high vacuum technique commonly used for gas permeability determinations, provided that a modified McLeod gauge is used, in which the compression capillary is jacketed with hot water to prevent condensation of water vapour inside the gauge (41, 42). In some diffusion studies a second high vacuum technique has been described (43), in which the vapour diffusing through the film is frozen and subsequently re-vapourised into a known volume which is connected to a manometer. A further technique makes use of an absorbent to maintain near zero vapour pressure, and the mass transmitted is obtained by weighing the absorbent (39, 40, 44).

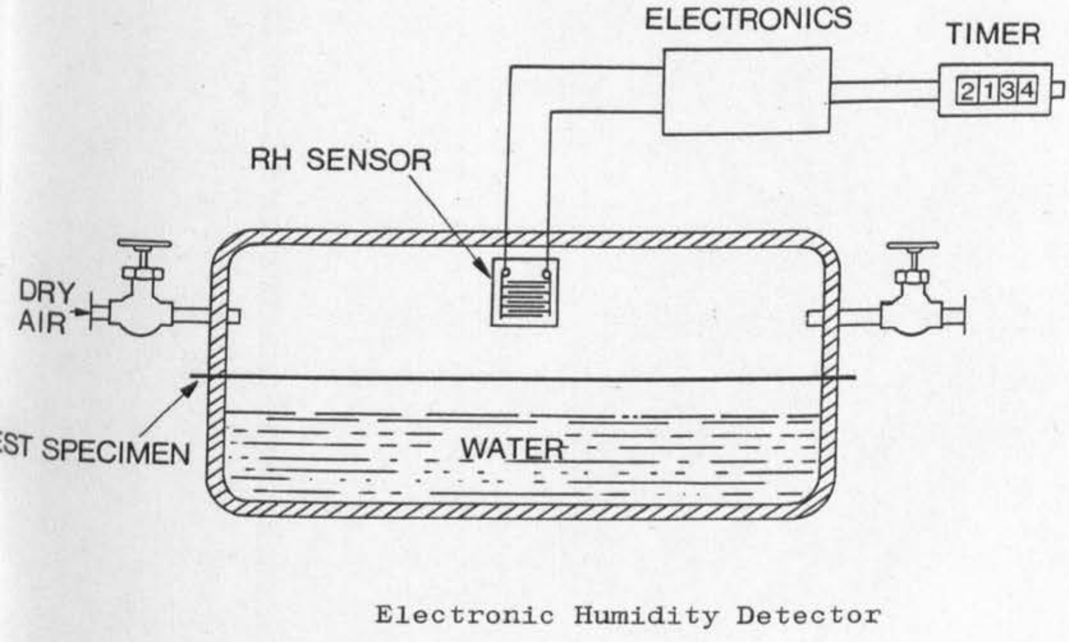
Several methods based on electronic humidity detectors have also been described (45, 46, 47). These methods are claimed to yield more reproducible results than the ASTM method. Also, these methods require only minutes to determine a rate, whereas standard techniques require several hours. Similarly, absorption-spectra analysis (48) has been used to measure the weight of moisture in a chamber. In this case, the sensing element picks up IR radiation of a particular wave length, susceptible to attenuation by water vapour.

In either of these methods to make a measurement, the flow of dry gas through the sensing cell is stopped, which signals the start of the conditioning period. The build-up of water vapour in the dry cell is then monitored. The time required for a specified increase in relative humidity or for a specified amount of water vapour to pass through the film is measured.

The instruments are calibrated with a standard film or test plate, the permeability characteristics of which have been established by the gravimetric test. Conditions affecting the permeation rate, such as pressure and temperature gradient, can be closely controlled. Fig. 4 shows schematic diagrams of the instruments for each of the methods.



Absorption Spectra Analysis



Electronic Humidity Detector

Fig. 4: Apparatus for Measuring Permeability of Films to Water

Other quantitative methods have also been devised. In one of these methods the polymer sheet is used as the membrane in an electrolytic cell (49, 50). A thin metal, such as nickel-phosphorus, is used as a sensor. The Ni-P deposit is extremely sensitive to the presence of moisture when an electrical potential is applied between two areas of the film. It is probably an electrolytic process that takes place in the Ni-P layer and results in the destruction of the original structure. In the absence of water, the electrical resistance of the film changes insignificantly. However, in the presence of a minute amount of water the resistance of the film increases and in the limit becomes an open circuit. There is no correlation between the original resistance and the resistance change, and for this reason the same film should be used in comparative experiments.

The measurement of the mass of water transmitted through the materials may be measured by a number of methods. Modified McLeod gauge, high vacuum, hygrometers, absorption spectra techniques and the use of powerful absorbents are some of the methods used for measuring water transmission rate. The latter was used in the present work and comparative water absorbing figures for various absorbents are given in table 2 (51, 52).

Table 2: Drying Agents Depending on Absorption for their Efficiency

Substance	Residual Water mg/l of dry air	Temp. °C	Ref.
Liquid N_2	1.6×10^{-23}	-196	51
P_2O_5	2.5×10^{-5}	25.0	51
BaO	6.5×10^{-4}	30.5	51
Al_2O_3	3.0×10^{-3}	30.5	51
H_2SO_4	3.0×10^{-3}	25.0	52
KOH fused	2.0×10^{-3}	30.0	52
$Mg(Cl\,O_4)_3$	2.0×10^{-3}	25.0	51
Silica gel	0.03	30.5	51
$CaCl_2$ granular	1.5	30.5	52

1.4 WATER TRANSMISSION THROUGH RESINS

1.4.1 Effect of Structure

The properties of crosslinked polyester resins depend on:

1. The chemical structure of the main chain (backbone).

2. The chemical structure of the crosslink monomer.

3. The crosslink density of the copolymer.

4. Molecular weight distribution.

5. Unreacted materials present.

1.4.2 Backbone

The backbone of the polyester chains consists of glycols, unsaturated and saturated acids. The unsaturated acids provide double bond for the crosslink reaction and the type of saturated acid modifies the properties of the final resin in certain ways (e.g. hardness, water resistance, H.D.T. etc.). The most commonly used unsaturated acid is maleic, which undergoes partial isomerization to the fumaric form during polyesterification reaction. The higher reactivity of the fumarate conformation compared with the maleate results in polyesters that contain a larger proportion of crosslinking and great water resistance.

The larger heat of polymerization of fumarates with styrene results in large exotherm during the crosslinking reaction. Volume shrinkage on copolymerization with a fumarate configuration is greater than with a maleate configuration (28). Copolymers containing a mixture of maleate and fumarate appear to contain a larger number of microcracks (possibly due to uneven heating and shrinkage during cure) than those containing either maleate or fumarate alone (28).

The properties of polyester resins made with aliphatic dicarboxylic acids have been investigated by several authors (5, 53, 54). These polyesters are more flexible and absorb more water than those containing phthalic acids. The "weakest link" in a crosslink polyester is the ester group, at which hydrolysis occurs. The use of acids and/or glycols with a ring structure improves chemical resistance, screening the ester group and hindering the hydrolysis reaction.

The water resistance of polyester resisns is greatly improved when aromatic dicarboxylic acids (e.g. phthalic, isophthalic or terephthalic acids) are used. Long term exposure to a number of chemicals has confirmed that isophthalic polyester resins have a higher resistance to water than those containing orthophthalic (39). This is considered the result of different stereochemistry.

A comparison was made of the water sorption at constant styrene content but varying maleic-saturated acid molar ratios (1, 5). It was observed that an increase in maleic : phthalic ratio produced an increase in water sorption. The lowest value for water sorption was found in the region of 20 to 30 mole % maleic anhydride (5, 55, 56).

It was suggested that this may be due to the effect of increased proportion of the saturated acids.

The contribution of the glycol components to the properties of the cured products is as important as that of the unsaturated and saturated acids (1). Most of the general purpose polyester resins presently marketed contain propylene glycol as the major glycol component.

Greater flexibility in the crosslinked polyester can be achieved by using diethylene glycol, triethylene glycol or glycols with longer chains. It has been observed that the chain length of the glycol affects water absorption in both rigid and flexible resins (table 3).

Diethylene fumarate phthalates absorb slightly more water than propylene fumarate phthalates and this effect becomes more pronounced as the unsaturation becomes very low (below 35% mole unsaturation) (5).

Replacement of ethylene glycol by 1,4 butylene glycol (1,4 butane diol) increases the water absorption of the polyester. An addition of a methylene link (1,5 pentane diol) causes a further increase. Certain structural features in glycols also tend to promote water absorption; e.g. if one pendant methyl group is added to ethylene glycol, the water absorption of the resin is increased from 0.15% to 0.25%. Another pendant methyl group (2,3 butylene glycol) increases this value to 0.50%.

In going from 2,3 - butylene glycol to 1,3 - butylene glycol, the loss of one pendant group is more than compensated for by the addition of one more methylene linkage in the glycol component of the casting. Replacement of a methylene link in 1,5 - pentanediol by an oxygen bridge causes an increase in water absorption. This is probably due to two effects: increased flexibility and additional hydrophilicity imparted by the increased polarity of the ether - oxygen bond (1). The chemical resistance can be improved further by partial or total substitution of the straight chain glycols by cyclic diols, such as hydrogenated bisphenol A and cyclohexanediol (39, 57, 58). The water resistance of a polyester was said to be improved when N - bis - B - hydroxyethylaniline was substituted for ethylene, diethylene and propylene glycol (59). This may be because of the presence of aromatic ring, which gives rigidity and increased hydrophobic character to the resin.

Table 3: Effect of Glycol on Water Absorption

GLYCOL COMPONENTS	SAT. ACID/ UNSAT. ACID	STYRENE % WEIGHT	WATER ABSORPTION (%)			REF.
			PHTHALIC/ MALEATE	SUCCINATE/ MALEATE	ADIPATE/ MALEATE	
Diethylene Glycol	1 / 1	33	2.6	7.5	-	(1)
Dipropylene Glycol	1 / 1	33	1.0	2.5	1.8	(1)
1,5 - Pentane Diol	1 / 1	33	0.8	1.3	0.6	(1)
1,3 - Butylene Glycol	1 / 1	33	0.6	1.8	1.5	(1)
2,3 - Butylene Glycol	1 / 1	33	0.15	0.9	1.0	(1)
1,4 - Butylene Glycol	1 / 1	33	0.35	-	-	(1)
Propylene Glycol	1 / 1	33	0.25	1.4	1.6	(1)
Ethylene Glycol	1 / 1	33	0.5	-	-	(1)
Propylene Glycol	1 / 1	30	0.22	-	-	(5)

1.4.3 Crosslinking Monomer

The physical properties of cured polyesters also depend on the type and concentration of the monomers that have been used in the crosslinking reaction. Styrene is preferred for general purpose resins. However, methyl methacrylate, diallyl phthalate, vinyl toluene and many others have been used for special purposes. The factors influencing the choice of monomers are discussed by Smith (61). Styrene satisfies most of the requirements and is also fairly inexpensive.

The effect of styrene concentration on the water absorption of cured polyester resins prepared from maleate/phthalate polyesters of propylene glycol at mole ratios of maleate : phthalate, ranging from 10 : 60 to 60 : 40, and at styrene contents ranging from 20% to 50%, has been investigated (5, 56, 60). It would appear that the optimum styrene content to produce minimum absorption for the system is 30 - 33%. However, the effect of the amount of styrene in the range investigated is very marginal (5, 56) and the water absorption varies with varying maleate/phthalate ratio. A reduction of styrene to below 20% causes considerable deterioration in water resistance of the copolymers as a result of a reduction in the crosslink density and a decrease in the quantity of the hydrophobic aromatic component (60).

It is generally believed that in most commercial resins, short crosslinks of one to three styrene units are formed (1, 62, 63).

1.4.4 Crosslink Density

Two of the most important variables in the structure of a crosslinked unsaturated polyester, with respect to water resistance, are the number of crosslinks per polyester chain and the number of vinyl monomer units present between crosslinks.

The factors influencing the number and length of styrene bridges between the polyester chains have been discussed by Funke (62), Park (63) and Boenig (1). The average crosslink consists of two styrene molecules. The crosslink density in different polyester systems depends upon the distance between two reactive groups (i.e. double bonds) in the uncured polyester chain. This distance is defined as the least chain length.

Polymers with high crosslink densities are obtained by having the reactive groups on the backbone closely arranged. By spacing out the reactive groups, polymers with varying crosslink densities can be made. The least chain length therefore depends on the type of glycol and saturated acids which are employed, and on the concentration of fumarate (or maleate) groups along the polymer chains.

In practice, not all fumarate groups take part in the crosslinking reaction. Boenig (1) blended various proportions of styrene with a polyester. The cured castings were hydrolysed and the products analysed. The values of both reacted and unreacted styrene and fumarate unsaturation in their molar fractions are listed below:

Table 4: Composition of Polyesters Before and After Cure

MOLAR RATIO OF STYRENE TO FUMARATE	MOLE % STYRENE REACTED DURING CURE	MOLE % FUMARATE REACTED DURING CURE
0.29 : 0.72	85.8	38.13
0.39 : 0.61	93.34	57.80
0.48 : 0.52	93.36	74.54
0.55 : 0.45	97.00	84.22
0.61 : 0.39	95.40	94.61
0.71 : 0.29	93.00	93.83
0.79 : 0.21	91.81	97.97
0.87 : 0.13	91.81	94.42
0.92 : 0.08	90.84	99.22
0.94 : 0.06	91.65	99.33

Maximum cure appears to be attained at a molar ratio (of styrene to fumarate) of about 2 : 1. If the molar ratio is reduced to 1 : 1, only about 75% of all fumarate groups will be reacted.

1.5 PRACTICAL CONSIDERATIONS

Fabrication methods and conditions of use are important in determining the water resistance of G.R.P. materials. The formation of defects will now be considered.

1.5.1 Flaws

Evidence has been presented for the presence of a microporous structure in certain amorphous polymers below or near the glass transition temperature (28, 65). The presence of micropores and flaws in the polymer structure allows the permeant to pass through the material by means distinct from normal activated diffusion. Simultaneous activated diffusion and viscous flow have been observed in some polymer penetrant systems (65, 66). The consequence of cracks, pores and areas of comparatively low density on the molecular scale have been discussed by Rogers (67). He states that the transport of penetrant through the polymer may depend on activated diffusion and capillary flow. The prominence of capillary flow will depend on whether or not the defects are interconnecting, how they are distributed and what size they are. The dominant mechanism should be that, which requires the least activation energy. Irany (68) and

Judd (28) show curves for resins which depend, to different extents, on both mechanisms,and the curves are non-Fickian. Ticknov (69), White (70) and Frisch (71) have developed expressions from experimental work to show that the water entering the polymer by activated diffusion, and that entering by capillary flow, is additive with respect to the total water uptake.

Flaws in the polymer structure include shrinkage cracks, pinholing, caused by the venting of volatile resin components during the cure process, voids, created by trapped air and volatile components and cracks, caused by internal stresses as a result of the thermal nature of the polymerisation process.

Other factors which contribute to microflows are leachable monomers and impurities, such as dust and inorganic residues (24, 58) present within the network of the polymer. This becomes apparent when the castings are exposed to water. Several workers have reported visible damage in cast resins by the presence of water (58, 72). Two classes of cracks reported when resins are exposed to water are internal disc cracking (58) and surface cracking (72).

1.5.2 Internal Stresses

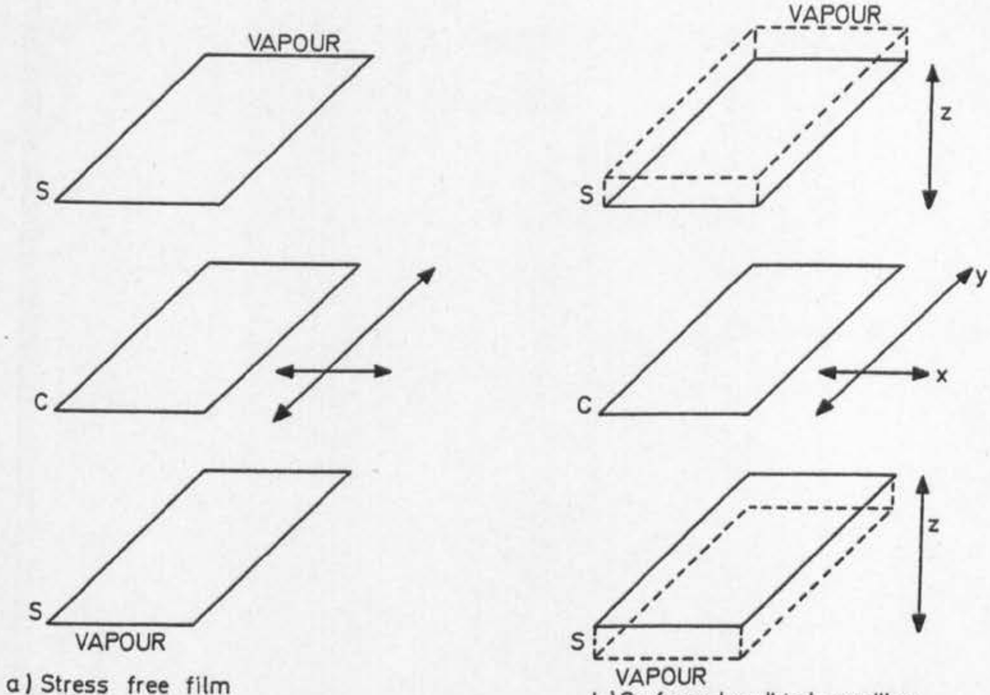
Internal stresses affect water permeation directly and indirectly. There are several reasons why internal stresses are present within a polymer material.

In reality, the three dimensional network of a polyester contains regions of dense and moderate crosslinking (73, 74). This results in uneven shrinkage during curing, thus giving rise to a cured polymer with internal stresses. A major cause of internal stress is the existence of embedded objects (e.g. glass fibres). Another contributing factor is uneven thermal expansion of the chemical constituent (28) and the molecular weight of the uncrosslinked polymer chains (55).

Crank and Park (75) suggested that when a polymer film, free of the above stresses, is exposed to penetrants, such as water, the swelling takes place in two ways. The first involves a differential swelling of different parts of the polymer sheet as the penetrant enters. The second is a slow change in the polymer structure, which relieves some of the stresses incurred by the differential diffusion process. Another theory put forward by Rosen (76) describes a different process, by which a biaxial tension may be produced in the surface layers of films of organic glasses (fig. 5). He points out that, if an initially stress-free film begins to absorb vapour (fig. 5a), the surface-localised swelling, which this produces, is resisted by the bulk of the film (fig. 5b), so producing surface compression and internal tension. The compressions have the effect of increasing the chemical potential of the absorbed vapour and so restricts further absorption. He states that, in order to reach an equilibrium concentration of vapour, organic glasses must frequently await retarded deformations (fig. 5c), acting to reduce these surface compressions and to increase the volume of the surface layers in order to accommodate new vapour. He further believes that the softer surfaces (plasticised by the vapour) find it easier to undergo such an expansion by increasing the film thickness in the vicinity of the surfaces. This produces long ranged macro-molecular extensions in a direction perpendicular to the surfaces. With more relaxation controlled vapour penetration beyond the surfaces, the central dry core undergoes further tensions. This results in still further expansion of the film thickness. As the vapour begins to accumulate at the centre of the film its area is observed to increase. During these latter stages of absorption, a state of tension is induced in the swollen stress-relaxed surfaces, which have already been weakened by the macromolecular orientation. The anisotropic strains are essentially irrecoverable and the film is severely altered in the process of swelling.

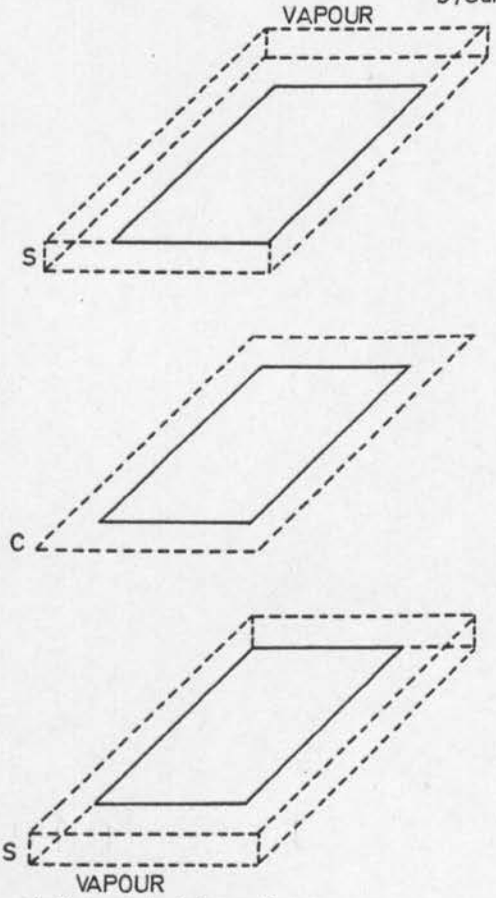
The process which Rosen (76) describes may occur in resin plate specimens exposed to hot water, and if so, this must further increase the stresses present in the polymer.

Alfrey (77) described a detailed model of a time-dependent transmission process of a penetrant in polymers below their glass transition temperatures. They divided the diffusion characteristics into two cases. Case I is a Fickian type diffusion process. Case II is a time-dependent process which is more apparent when the penetrants are either vapours or liquids. Case II transport is rate determining and is osmotically created by polymeric relaxation between the swollen boundary and the unpenetrated region (78 - 80).



a) Stress free film

b) Surface-localised swelling



c) Retarded deformation

FIG. 5 A SIMPLIFIED MODEL OF ROSEN'S THEORY

1.6 EFFECT OF TEMPERATURE ON PERMEABILITY WHEN EXPOSED TO WATER

The temperature dependence of permeability (40) and diffusion coefficient (27, 40, 81, 82) over a small range of temperature can be represented by an Arrhenius type equation:

$$P = P_o \exp(-E_p/RT)$$
$$D = D_o \exp(-E_d/RT)$$

where E_p and E_d are the apparent activation energies for the overall permeation and diffusion processes respectively. The activated energy for diffusion, E_d, is associated with the energy required for hole formation, against the cohesive forces of the medium, plus the energy necessary to force the molecule through the surrounding structure. Such activation energies in polyesters vary from 17 - 42 kJ /mole (27, 40, 82). The pre-exponential factor, D_o, can be thought of as related to the number of holes or "looseness" of the polymer structure in the presence of penetrant. More rigorous interpretations of D_o are derived from specific theories for the temperature dependence of diffusion, such as the transition - state theory and the activated - zone theory (10 - 13, 83).

The permeability coefficients usually decrease with decrease in temperature, as shown in fig. 6 (40, 84). However, there are certain exceptions with vapours. The permeability of nylon 66 and polyvinyl alcohol to water increases as the temperature decreases. The permeability coefficient in such systems is pressure dependent and often exhibits a minimum value (43).

The logarithmic permeability/temperature relationship for gases and vapours can be used only where the equation $P = DS$ holds. In some systems (such as water vapour in various polymers) the dependence of D, S and P on temperature follows Arrhenius theory, as shown in fig. 7 (84). Deviations from Arrhenius theory may arise from the plasticising effects of the absorbed penetrant and from the deviation from Henry's Law at the higher concentration of the absorbed vapour. In addition, the heat involved in the absorption of the vapour during the transmission process helps to counterbalance the activation - energy requirements for diffusion.

The dependence on temperature of the diffusion coefficient for water in cured polyester resin systems follows Arrhenius theory, as shown in fig. 8, according to several workers (27, 40, 82). Evidence of similar behaviour for the permeability coefficient has been studied to a smaller extent (40, 84).

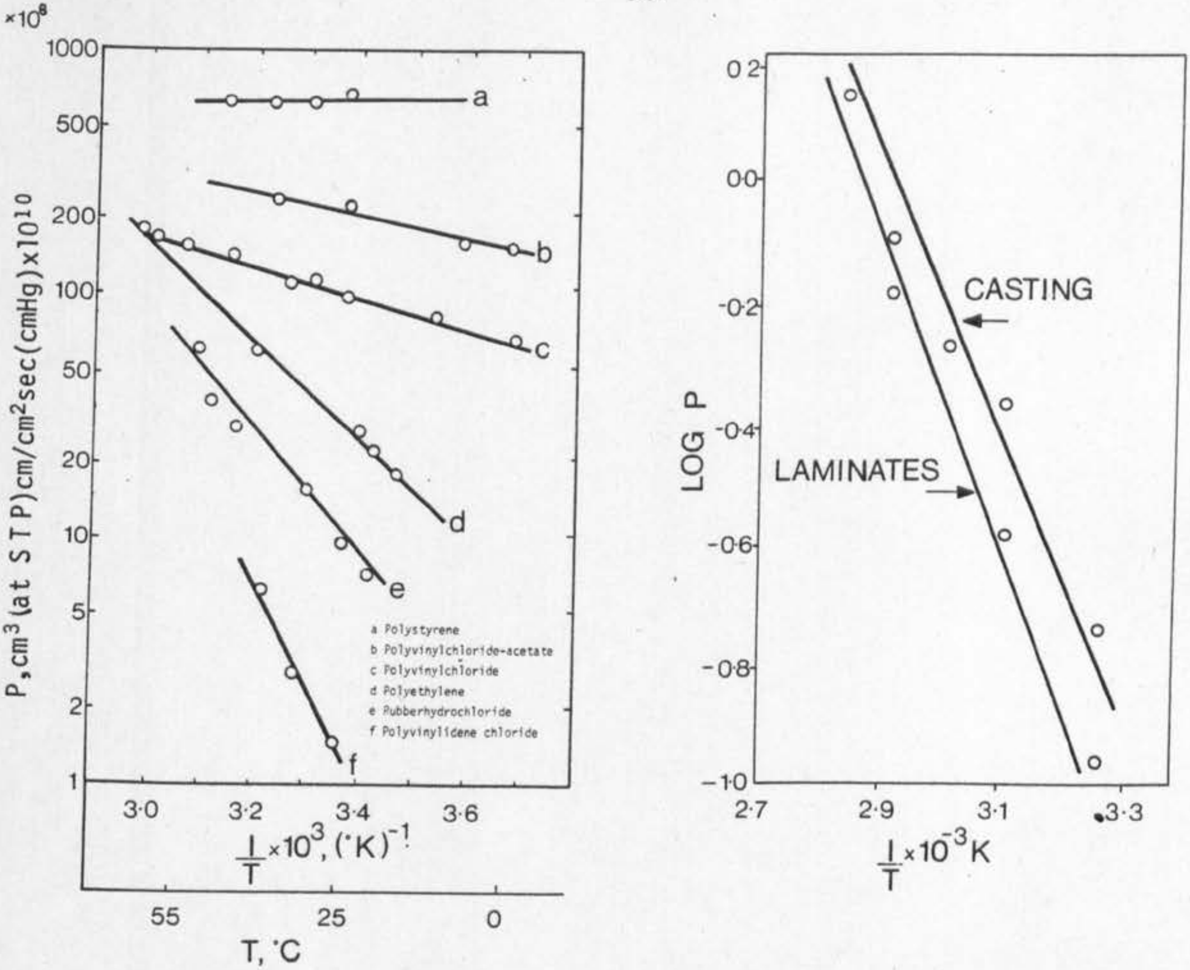


Fig. 6: (a) Dependence of the Water Permeability of Various Polymers on the Temperature (84)

(b) Effect of Temperature on Permeation Coefficients (40)

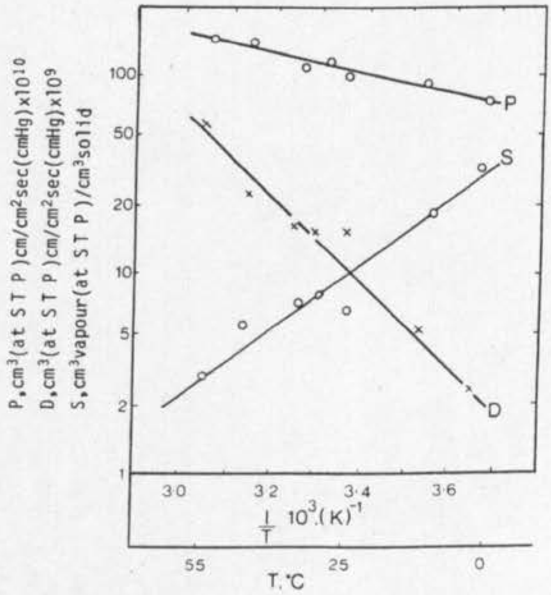
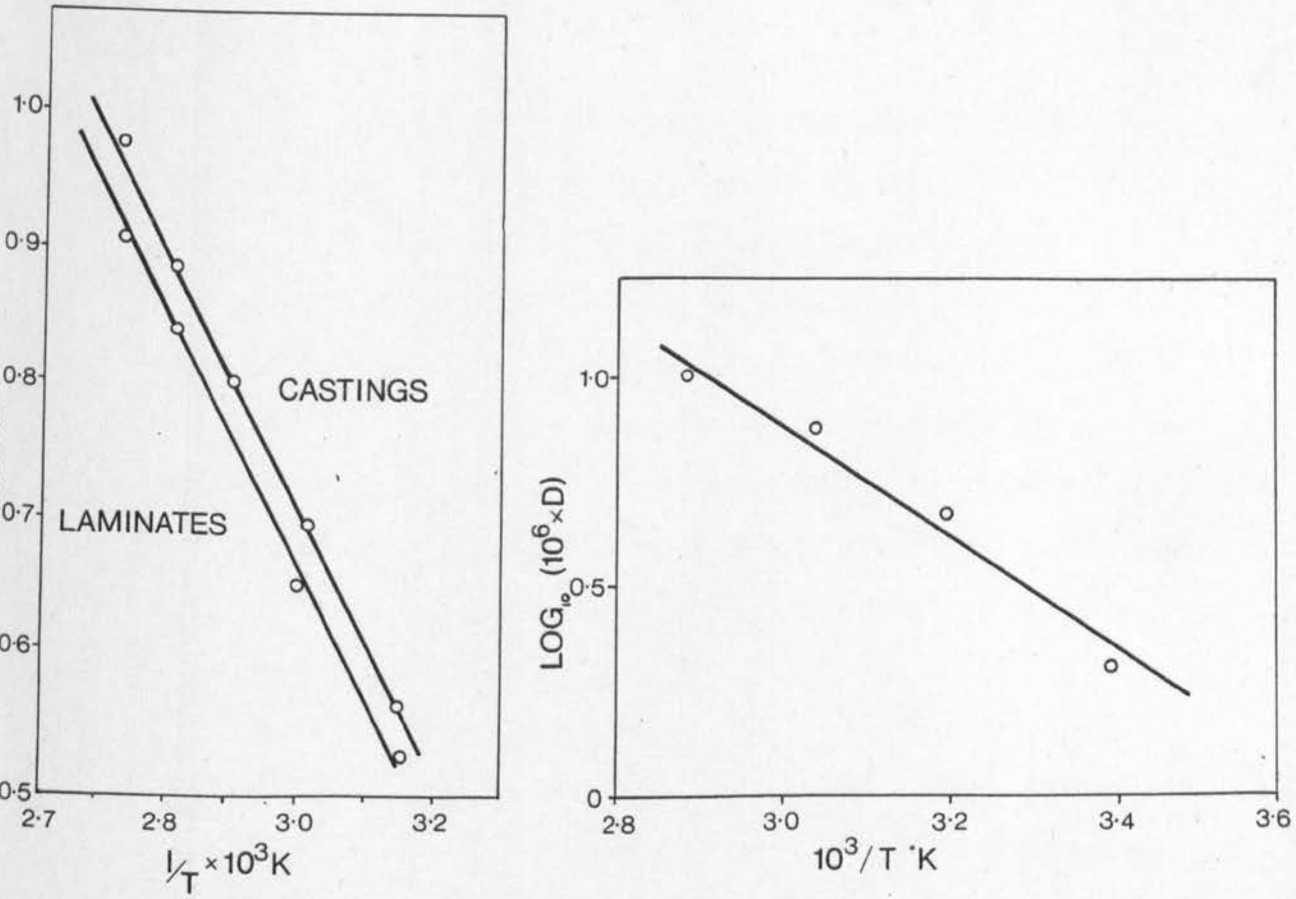
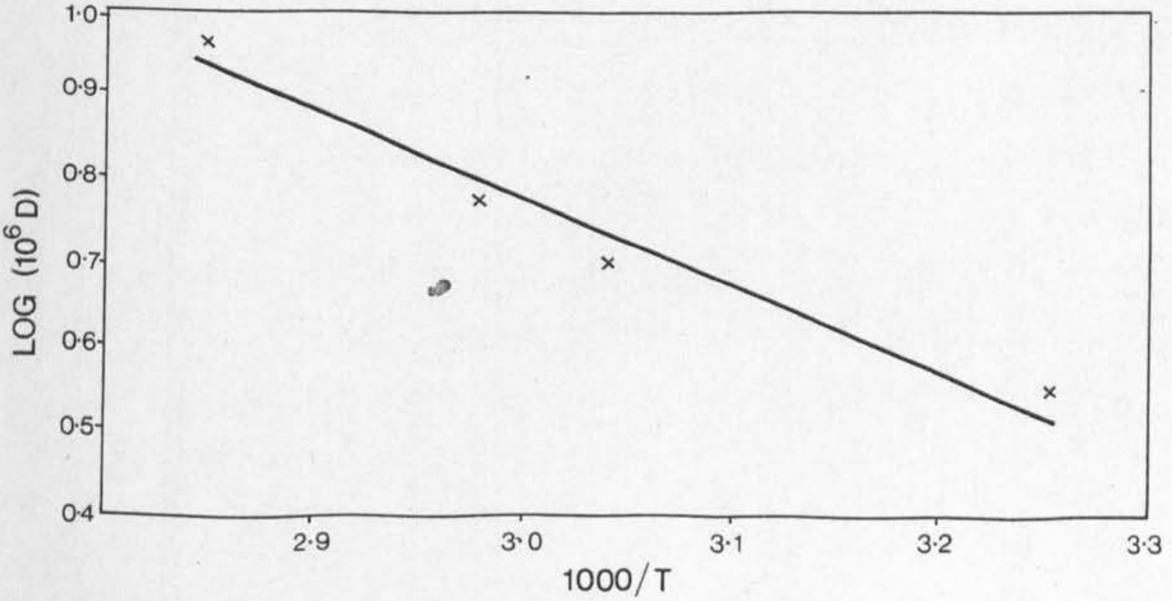


Fig. 7: The Dependence of the Permeability (P), Diffusivity (D) and Solubility (S) of Water Vapour in Polyvinyl Chloride on Temperature (84)



(a) Effect of Temperature on Diffusion Coefficients (40)

(b) Temperature Dependence of Diffusion of Water in Polyester Resin (82)



(c) Diffusion Coefficients of Polyester Resins at Various Temperatures (27)

Fig. 8

Studies carried out into water permeation rates during the exposure of cured polyesters to distilled water at 80°C, 100°C and 125°C show a substantial increase with increasing temperature. This is especially noticeable when the temperature is raised from 100°C to 125°C (85). The increase in permeation rate is accompanied by a comparable increase in the rate of degradation of mechanical properties. A relationship between mechanical property retention and the quantity of water passing through a laminate, independent of the time of exposure, was realised by Regester (39). This relationship can apply only to a single resin or laminate. This observation is the basis of a proposed 125°C accelerated test by him in a previous paper (85).

Studies of castings and laminates exposed to water at above ambient temperatures for extended periods have shown leaching of low molecular weight substance from the polymer and internal cracking in the form of discs. The activation energy for the leaching up to 400 hours over the temperature range 22°C to 75°C is 23 kJ /mole, while over 1000 hours and above 57°C it becomes 84 kJ /mole. The effect of disc cracking can also be represented by an Arrhenius plot which yields an activation energy of 100 kJ /mole (86).

Studies by Yasada et. al. (92) on the transport of water through swollen homogeneous polymer membranes have shown that the difference between the hydraulic permeability under a pressure gradient and the diffusion permeability P under a concentration gradient can be explained by viscous flow of the permeant at a high degree of swelling.

Paul (93), on the other hand, disagreed with Yasada's findings. Though he recognises that viscous and diffusive flows exist in water transport, he points out that the equations used by Yasada et. al. (92) were in error. This, he suggests, might have led authors who used similar equations to suggest viscous flow.

Practical tests carried out on glass reinforced polyesters by Regester suggest that the change in permeation rate of water through the laminates, realised by a substantial increase in pressure (20 atmos.) is less than that obtained by an increase in temperature from 100°C to 125°C (85).

1.7 INFLUENCE OF PRESSURE ON PERMEABILITY OF CASTINGS

The transport of water through polymer barriers can be brought about by either a vapour pressure (87) or an osmotic pressure difference (88).

Thermodynamic considerations indicate that the transport of a penetrant through a membrane is dependent only on the driving forces acting on the film and not on the way in which they are attained. This principle remains valid so long as the film characteristics are not changed by the environmental conditions producing the driving forces. Therefore, it may be possible to correlate the results obtained by means of vapour pressure difference with those obtained by means of osmotic pressure differences.

Preliminary work by Perera (89) using the cup method and involving two systems, seems to suggest that, for the same absolute water activity, different permeability coefficients are achieved. The permeability values are always higher for a system in which the water activity is greater than zero on both sides of the film. Similar results were reported by Neantze Li (90) and Stannett (91) using gases and water vapour respectively. Neantze Li further suggests that the relationship between the permeabilities and the pressures can be described by the following expression:

$$P = P_o e^{A}p$$

when P is the permeability coefficient, p is the pressure and P_o and A are constants.

In further work Perera pointed out that results obtained from osmotic permeation can be considered as an extension of the water vapour measurements.

1.8 EFFECT OF APPLIED STRAIN ON CASTINGS AND LAMINATES

Rosen (72) and McAfee (94) studied the permeability of gases through unoriented and biaxially oriented glassy polystyrene films. The results showed a considerable increase in permeability for oriented films. This was attributed to the development of microcracks by the mechanism of redistribution of the applied strain in the material (fig. 9).

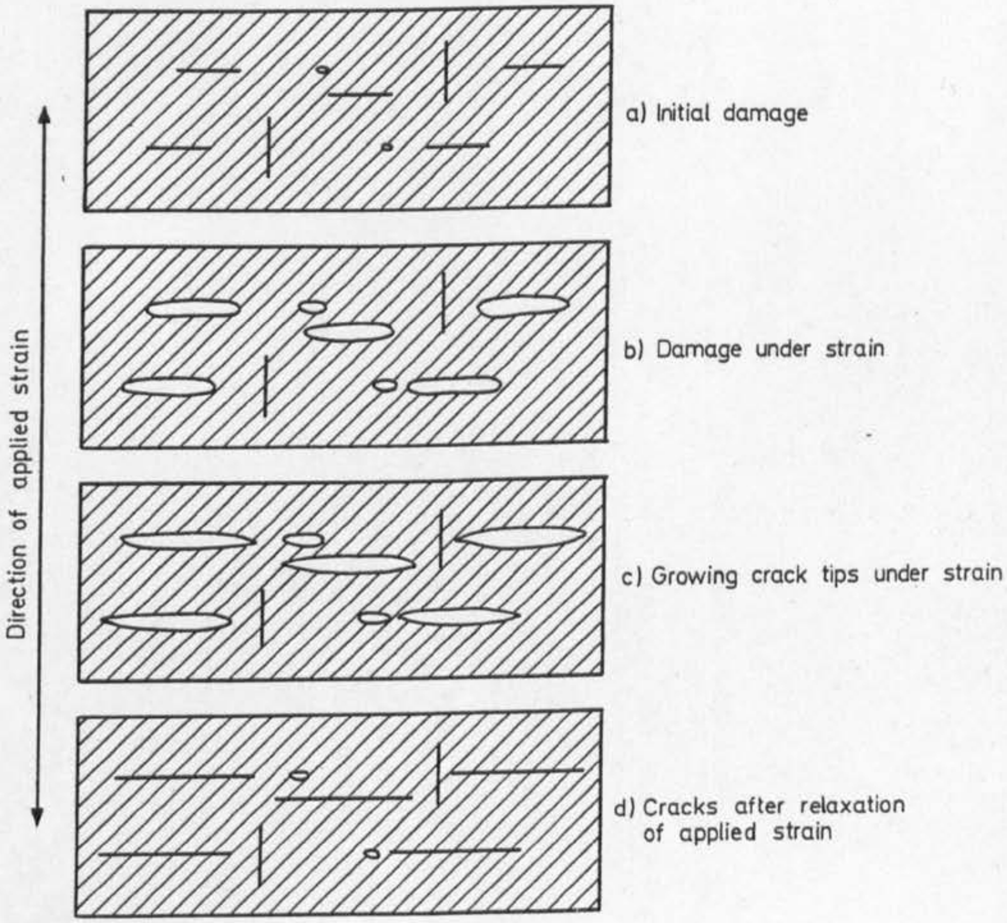


Fig. 9: Effect of Applied Strain on Castings

Baird et. al. (95) have suggested that orientation stresses in addition to swelling stresses increase the rate determining relaxation in the stretched polymers.

Up to now a few workers have investigated the permeability of polyester resins to water when subjected to applied strain. An increase in the permeability of laminates was observed with increased applied strain of up to 0.4% (40). Damage in the laminates caused by cracks in the resin matrix and debonding of fibres aligned transverse to the direction of applied force were attributed to the increase in permeability of the strained laminates.

Owen and Howe (96) have reported the appearance of fibre debonding at lower strains.

The newly formed channels would increase the concentration of water in the laminates. This may increase the permeability of the damaged laminates. However, Poiseuille flow of water along the channels is unlikely since the plane of the fibres lies perpendicular to the direction of flow.

To understand the effect of applied strain on laminates, the dependence of the permeability of castings on applied strain should be studied.

Applied strain in a casting causes reduction of the molecular free volume and increases the energy available for segmental rotation (97). Chain scission and microvoids may also result. It has also been suggested by Christiansen et. al. (98) that occupied volume can change under stress in such a way as to allow the free volume to increase without increasing the total volume.

1.9 TWO-PHASE SYSTEMS

Two-phase systems, where one phase is organic polymer and the other is inorganic particulate filler or fibrous reinforcement, have been studied by several workers (27, 39, 40, 99, 100). The relationship between permeability and volume fraction of each component has been examined. The present discussion is restricted to resin-glass systems.

1.9.1 Effect of Glass Fibres

Glass reinforcement can be achieved using filling materials in widely differing forms, from glass spheres with an aspect ratio of one, to continuous filament reinforcement with an aspect ratio of infinity. The aspect ratio is the ratio of length to diameter.

A simple expression for predicting the decrease in permeation by introduction of fillers given by Nielsen (100) is as follows:

$$\frac{Pf}{Pu} = \frac{\phi_p}{(1 + L/2W\ \phi_f)}$$

? Φ_f

where Pf and Pu are the permeability coefficients of the filled and unfilled resin respectively, and L/W is the ratio of length to width of the fillers.

Values calculated from this equation predict that particles which are approximately cubical in shape are quite inefficient in decreasing permeability. However, thin plates with large aspect ratio can very drastically decrease permeability, provided the particles are parallel to the surfaces of the film.

Permeability through such systems is more complex for a liquid than it is for a gas. Liquids often have an appreciable solubility in the polymer, thus causing swelling. In the glass/matrix interface the solubility may differ from that in the bulk material. The latter may be especially so if the glass filler has been surface treated with a coupling agent.

There is experimental evidence that in glass filled systems there can be an interfacial layer with properties different from the bulk polymer (101, 102). Nielsen (100) developed a model for such a system and discussed how the total permeability of a penetrant through a filled system can be estimated by considering the permeability of liquid through the interfacial part and the saturated bulk polymer.

However, he points out that not too much emphasis can be placed upon the quantitative aspects of this model.

Deviations from predicted sorption and permeation behaviour have been noted for several reinforced polymer compositions. In order to explain such deviations, it was first proposed by Landel (103) and by Kumins and Roteman (104) that even relatively large and low surface area fillers restrict the mobility of polymer segments. Kwei (102) developed a model for the ordering of polymer segments by the filler. This hypothesis was used by Kwei et. al. (101, 102, 78, 79, 105, 106), Galperin (107) and Kumins (108) to interpret the various types of anomalous behaviour mentioned.

In all these reports explaining different anomalies, no consideration has been given to the chemical interaction between the penetrant and the polymer and the effect it has on the permeation rate of the penetrant through the filler-polymer system.

1.9.2 Volume Fraction of Glass Fibres

General expressions for permeation in filler/polymer systems have been derived independently by Nielsen (100) and Higuchi (99). The equation given by Nielsen is as follows:

$$P_{FL} = \frac{P_i P_{PL}}{P_{PL}\theta_i + P_i \theta p} \left(\frac{\phi_{Li}}{r^*}\right) + P_{PL}\left(\frac{\phi_p + \phi_{LP}}{r}\right)$$

where P_{FL}, P_i and P_{PL} are the permeabilities of liquid through the filled polymer, interface and unfilled polymer respectively; θ_i and θ_p are the fractional length of diffusing path through the interface and polymer respectively; ϕ_p is the volume fraction of the polymer, and ϕ_{Li} is the volume fraction of liquid collected in the interfacial region, while ϕ_{LP} is the volume fraction of liquid dissolved in the polymer; r^* and r are the tortuosity factor for the interfacial part and the polymer respectively. It should be noted that the equation proposed for determining permeation rate is based on the assumption that the diffusion path length is the only factor concerned in the reduction of permeation rate.

Using activity rather than the concentration of a diffusing agent as the driving force, Higuchi (99) developed an equation for permeation through a barrier filled with random spheres. The equation is given below:

$$P_m = \frac{2P_1^{2}(1-V_2) + P_1P_2(1+2V_2) - KP_1\left(\frac{P_2-P_1}{2P_1+P_2}\right)^2(2P_1+P_2)(1-V_2)}{P_1(2+V_2) + P_2(1-V_2) - K\left(\frac{P_2-P_1}{2P_1+P_2}\right)^2(2P_1+P_2)(1-V_2)}$$

The respective effective permeability constants of the barrier, polymer and filler, or P_m, P_1 and P_2, V_1 and V_2 are the volume fractions of polymer and filler respectively. K is the distribution function for random spheres and is a function of V_2.

Results published show a definite decrease in permeation rate of water through polymer filled with glass beads with increase in volume fraction. Permeation of liquid water through an epoxy film filled with 0%, 10% and 20% by weight of spherical glass beads was measured at temperatures above and below the glass transition temperature (108).

While collection of water at the interface, chemical reaction between water, polymer and glass, and leaching of monomers that have entered into the crosslinking, cannot be ruled out, results suggest any such effect must be more than compensated for by the specific decrease in permeability due to the filler.

The results for decrease in permeation rate obtained by several workers (103, 104) led them to believe that fillers restrict the mobility of polymer segments and to develop models for the ordering of polymer segments by the fillers (78, 79, 101, 102, 105 - 107).

1.9.3 Effect of Fibre Arrangement

Little has been published about the effect of fibre arrangement on the rate of transport of water through reinforced polymers. The literature shows a variety of reinforcements and fibre arrangements used in laminate fabrication. Some workers used multilayers of a single type mat (49, 109) and some multilayers of different types of mat (85, 110). While results suggest a decrease in permeation rate with increasing filler concentration, no evidence has been presented establishing definite change in permeation rate with fibre arrangements. However, if the theory put forward by Lenk (55) and others (78, 79, 101, 102, 105, 106), that polymer backbone chains are attracted to the glass surface, is confirmed, there may exist an ordering of chain segments due to the introduction of fibrous glass fillers. Thus, further ordering of polymer chains may be achieved by arranging the fibrous fillers from random orientation to unidirection.

Much of the evidence presented for chain orientation due to fibrous fillers is circumstantial and qualitative. To examine the effect of arrangement of fibres on permeation rate, further extensive experimental studies are needed.

1.9.4 Effect of Applied Strain

Applied strain affects the permeability of laminates and castings. To understand the effect of applied strain on the permeation rate of penetrant through glass reinforced polymers, the effect of original stresses present in the laminate should first be examined. Depending on the nature of the polymer, crosslinking does induce internal stresses and strains within the glass reinforced polymer because of uneven heating and shrinkage. Inclusion of foreign particles, such as dust and gas bubbles, increases this strain further. These higher-strain areas of the polymer will attain the maximum strain level for the matrix in the presence of an external strain before the rest of the polymer reaches the same level of strain. This obviously depends on whether the moulded-in strain is in the same direction as that applied externally. Thus, these areas become the focal point for crack initiation.

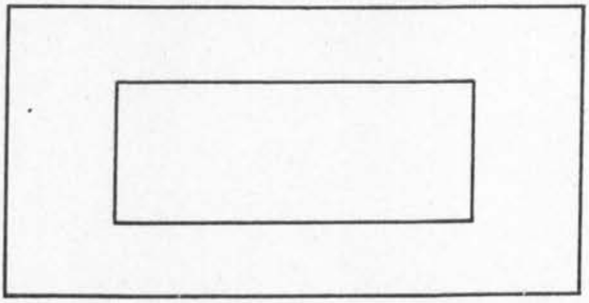
The coefficients of thermal expansion for typical resins and glass are of the order of 70-100 x $10^{-6}C^{-1}$ and 5 x $10^{-6}C^{-1}$ respectively. It is generally assumed (111 - 113) that the temperature attained during the composite postcure process is sufficient to remove most internal stresses. In such a situation, the stresses built up between the fibres and the matrix can be assumed to be zero. On cooling, however, the large difference between the thermal expansion coefficients of the two components leads to an effective resin shrinkage. This exerts compressive stresses, both axial and circumferential (tangential), on the fibre. The resin, on the other hand, is subjected to axial and hoop tensile stresses.

The principal compressive stresses exerted along the fibre axis are due to:

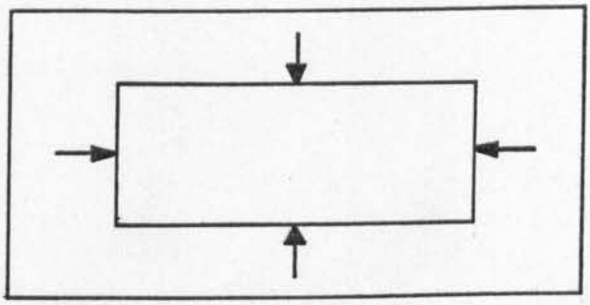
1. the load exerted over the fibre ends, and
2. the load transferred by shear stresses across the fibre/resin interface (fig. 10a - 10d).

Since the magnitude of the latter stress increases from zero at the ends of the fibre to a maximum at the centre, the net axial fibre compression must increase proportionally. Another stress arising from the above two is a tangential compressive stress on the fibre due to radius expansion of the fibre.

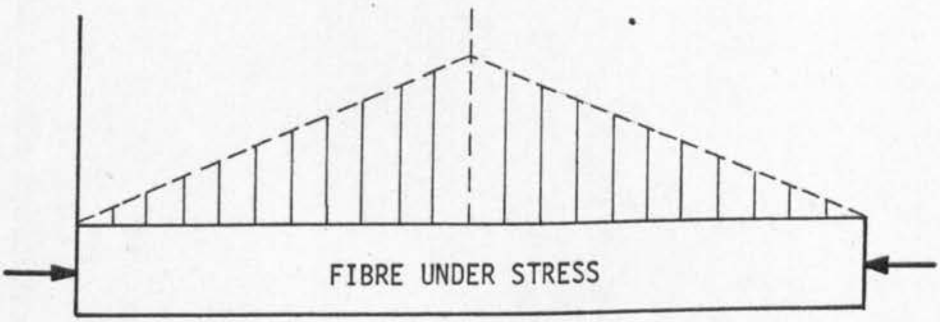
The above compressive stress condition upon the fibres exists only up to a limited value of glass volume fraction in the laminate. Above this value the nature of the stresses may be reversed, thus, instead of the fibres being under pressure from the resin matrix, the fibres experience tensile stresses due to shrinkage of the 'tricorn' of the resin between any trio of glass fibres, as shown in fig. 10e.



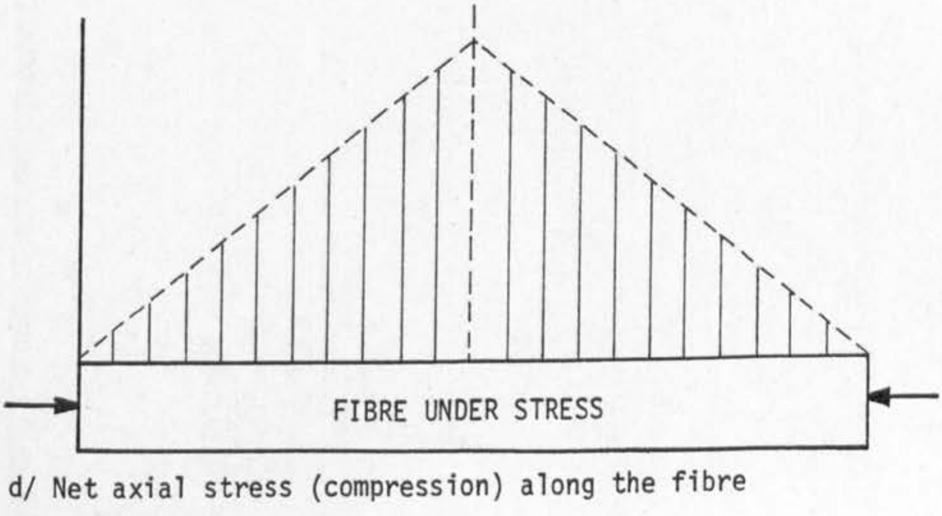
a/ Stress free single filament embedded in resin at postcure temperature



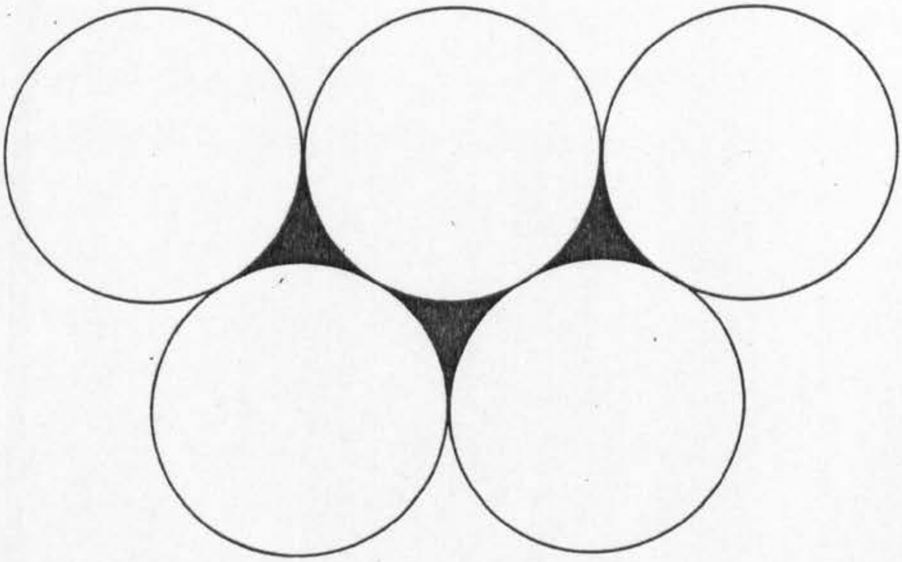
b/ Stresses induced in the system on cooling



c/ Build up of shear stress across the fibre/resin interface along the length of fibre



d/ Net axial stress (compression) along the fibre



e/ Hexagonal packing of fibres

For a thin film composite the aspect ratio of the glass fibres plays a predominent part in determining the magnitude of the induced stresses in the fibres and the matrix. Haslett and McGarry (112) suggested that for an infinite matrix the magnitude of the axial stress is many times that of the radial stress. This, however, is in disagreement with the conclusions reported by Wyatt (58). Wyatt suggests that, as the aspect ratio of the fibre changes, the axial stresses on the fibre remain more or less constant, while those on the resin decrease steadily, with increasing aspect ratio of the fibres. The radial stresses on the fibre (compressive) and on the matrix (tensile) increase steadily with increasing aspect ratio until it reaches 100. Above this the stresses level off and the magnitude of the stresses on the fibres and on the matrix remain constants.

When an applied strain is introduced the whole strain system within the laminate becomes very complex. It is not surprising that several modes of fracture and various paths of crack extension are possible. The applied strain would drastically change the internal stresses and strains originally present. The changes in internal stresses may be reduced in certain areas while in others they may have increased sufficiently to reach the minimum level required for fracture initiation.

Localised fracture initiated at imperfections may occur either in the fibres or in the resin. Once initiated, various paths of crack extension lead to any one of numerous modes of fracture.

1.9.5 Fibre Orientation and Strain

Examining a two dimensional single layer parallel filament/resin system (fig. 11), any static load that is applied to the composite can be resolved into two components, one acting along the fibre length and the other perpendicular to the fibre axis.

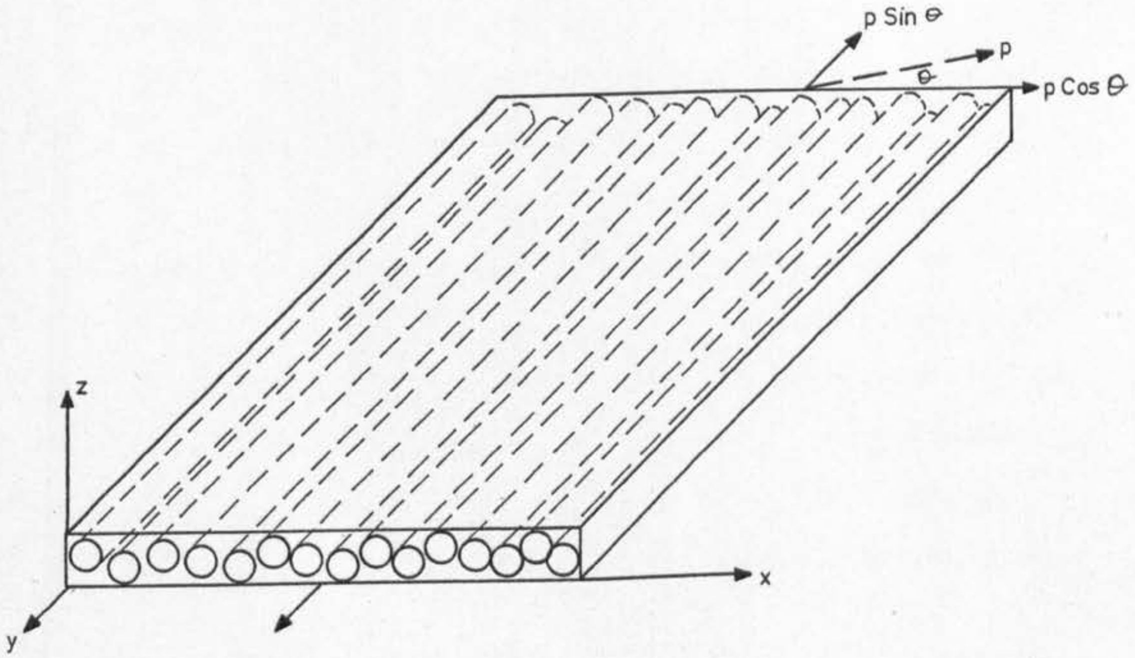


Fig. 11: Direction of Applied Strain on Continuous Filament Laminates

a) Forces acting in the direction parallel to the filaments. Foreign particles, air bubbles and surface scratches constitute imperfections which, because of the associated stress and strain concentration, initiate cracks in the resin at small values of resin stress. Typical origins of resin cracks in pure epoxy resin tensile specimens were reported by Feltner (114). In his report Feltner illustrated examples of all the more common types of crack initiation flows which eventually lead to material failure.

b) Forces perpendicular to parallel fibres: Fibres at right angles to the applied stress constitute discontinuities that produce strain concentration in the resin. The values of strain concentration depend on the moduli of the fibres and resin and on fibre spacing. These strain concentrations produce fracture initiation at composite fracture strain values considerably smaller than that of the pure resin. Thus, in parallel filament composites, the fibres assist rather than retard crack initiation and extension parallel to the reinforcement in the presence of a force perpendicular to the fibres.

ANC-17 Bulletin (115) reported stress strain characteristics for laminates with four types of reinforcement. A polyester resin was used in all laminates and data for three directions of loading were shown for reinforced laminates. Laminates with balanced weave glass cloth reinforcement exhibit high stress to strain ratio in two perpendicular directions. At 45° to the filaments, however, the laminates exhibit lower stiffness and strength.

1.10 EFFECT OF PROLONGED WATER TRANSMISSION ON THE PROPERTIES OF LAMINATES

The most commonly used method of examining the effects of water on glass reinforced resin is by measuring the loss of strength of the composite arising, following exposure to water under a variety of conditions (110, 116 - 123). The loss in strength of a glass reinforced polyester depends on temperature, time of exposure and the method of testing (116, 119, 121, 122).

Varying degrees of recovery of mechanical properties have also been reported for specimens dried after exposure to water (110, 111, 120, 121). However, only a few workers reported the study of the actual mechanism, by which the loss of strength in a composite system is brought about (58).

1.10.1 Mechanisms of Damage

Several possible causes for loss in strength can be postulated, i.e. weakening and/or loss of adhesion between glass fibres and resin, resin deterioration and lowering of strength in the glass fibres. The last of these has been the subject of many investigations and has been reviewed periodically (6, 117).

The importance of the other two will be briefly discussed. It is widely accepted that to achieve good laminate properties, it is essential to have a good interfacial bond between fibres and the resins.

The loss of mechanical strength of polyester resins when exposed to water and the causes thereof are not well documented. Of particular interest are comparisons between resin deterioration and glass fibre/resin composite strength loss. Holland and Turner (119) reported a correlation between the visible damage suffered by cast sheets of various polyester resins and the loss in strength of chopped strand E-glass mat laminates made from the same resins, for water immersion at 60°C. Visible resin damage has also been investigated by Wyatt (58) and Steel (110, 120).

CHAPTER TWO

MATERIALS

AND

EXPERIMENTAL METHODS

EXPERIMENTAL PROCEDURE

2.1 Materials Used

2.2 Preliminary Examination of the Resins

2.3 Specimen Preparation

2.4 Method of Determining Permeability

2.5 Water Absorption Measurements

2.6 Microscopic Examination of the Samples

2.7 Physical and Chemical Tests Carried Out on Specimens

2.1 MATERIALS USED

2.1.1 Resins

Four isophthalic polyester resins, a bisphenol resin and a vinyl ester resin were employed in the present investigation. These resins were selected because of their good resistance to hot water.

Details of the resins used in this work are given in table 5. Some of the properties of the resins as given by the manufactureres are listed in table 6. Three more resins (resins 7, 8 and 9) with increasing acid values were derived from resin 2 by adding low molecular weight propylene glycol - maleate. Properties, such as gel times, solid contents and acid numbers, are subject to variation over a long period of storage. These were checked from time to time to assess any change which occurred. The resins were stored in the dark at -10°C. To avoid variation in properties of resins from batch to batch, only one batch was used for each resin.

2.1.2 Catalysts and Accelerators

Methyl ethyl ketone peroxide was used as an initiator in the form of a 60% solution in phthalate plasticiser. In addition, a paste containing 50% cyclohexanone peroxide in phthalate plasticiser and three types of cyclohexanone peroxide was employed.

Table 5: Constitution of Resins Used

RESIN NUMBER	COMPONENTS USED	MOLAR RATIO
1	Vinylester	
2	Maleic anhydride Isophthalic acid Propylene glycol Diethylene glycol	1 1 1 1
3	Maleic anhydride Isophthalic acid Propylene glycol	1 1 2
4	Maleic anhydride Isophthalic acid Diethylene glycol	1 2 3
5	Maleic anhydride Isophthalic acid Propylene glycol	3 1 4

Table 6: Properties of Resins

Liquid Resins

Resin	1	2	3	4	5	6
Viscosity at 25°C (poise)	5.0	3.5	6.0	8±2	6.0	7.5
Specific gravity at 25°C	1.04	1.21	1.15	1.15	1.10	1.04
Acid value mg KOH/g	8.5	18	11	18	25	13
Volatile content % w/w	45	41	38	32	38	47

Cured Resins

Resin	1	2	3	4	5	6
Barcol hardness (Model GYZJ-934-1)	37	45	45-50	-	50	38
Water absorption (BS2782, 502P)	0.15%	0.17%	20 mg	-	25 mg	17 mg
Deflection temp. °C (BS2782, 102G)	100	75	100	28	130	120
Specific gravity	1.136	1.21	1.2	-	1.20	1.15
Elongation at break at 20°C (BS2782, 301J)	5%	2.3%	-	-	2.0%	4.0%

The accelerators used are:

1. 0.4% solution of cobalt octoate in styrene
2. 6.0% solution of cobalt octoate in styrene
3. 10.0% solution of dimethyl aniline in styrene

Methyl ethyl ketone peroxide, as well as cyclohexanone peroxide, was used in conjunction with cobalt octoate. For curing vinyl ester resin, dimethyl aniline was used in combination with cobalt octoate and methyl ethyl ketone peroxide (table 7).

2.1.3 Glass Fibres

"E" type glass fibres were used, as prepared by TBA Industrial Products Limited, England.

Two types of "E" glass mats were used in the present work. They are chopped strand mat and woven roving mat. The surface treatment used for "E" glass mats was a mixture of silane coupling agent, a combination of polyvinyl acetate (binder) and an emulsion lubricant.

The chopped strand mat was constructed of chopped strands bonded together in a random manner; the usual strand length being 52 mm. Besides the coupling agent and binder, the surface treatment mixture used for chopped strands contained an anti-static agent. The density of the mat was 600 g/m^2.

Woven roving mat used was of a plain weave, in which each warp and weft yarn is passed under one yarn and over the next. It is heavier than the chopped strand mat at 800 g/m^2.

The surface tissue was made of "C" glass and supplied by Fibreglass Limited, Lancs., England. "C" glass fibres were treated with a mixture containg polystyrene binder and a coupling agent.

Other properties of the glass mats are given in table 8.

Table 7: Curing System

RESIN	INITIATOR	PER 100 g OF RESIN	ACCELORATOR	PER 100 g OF RESIN
1	MEKP in phthalate plasticiser 9% active oxygen	2 g	6.0% cobalt octoate in styrene. 10% dimethyl aniline in styrene	0.5 g 1.0 g
2	"	2 g	0.4% cobalt octoate in styrene	1.0 g
3	"	2 g	"	1.0 g
4	"	2 g	"	1.0 g
5	Cyclohexanone in phthalate plasticiser	4 g	"	1.0 g
6	MEKP in phthalate plasticiser 13% active oxygen	2 g	6.0% cobalt octoate in styrene	6.0 g

Cure schedule for the isophthalic and bisphenol polyesters was 24 hours at room temperature followed by 3 hours at 80°C. Cure schedule for the vinylester resin was 24 hours at room temperature followed by 3 hours at 100°C.

Table 8: Properties of Glass Fibres

CODE NO	DENSITY g/cc	FILAMENT DIAMETER	TYPE	FILAMENT LENGTH	SURFACE TREATMENT	MATS	SURFACE DENSITY
P15	2.57	13 μm	C	∞	poly-styrene binder	tissue	31g/m^2
ECM75	2.55	12 μm	E	52 mm	EDR75	chopped strand	600g/m^2
ECK24	2.55	13-14 μm	E	∞	EDR24	woven roving	800g/m^2

2.2 PRELIMINARY EXAMINATION OF THE RESINS

2.2.1 NMR Spectra of the Liquid Resins

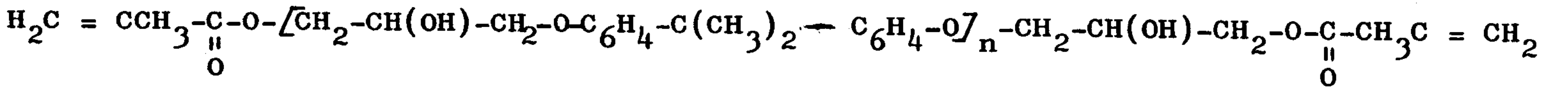
The chemical constituents of the resins are given in fig. 12. Resins 2, 3, 4 and 5 contain isophthalic ester units, propylene or diethylene glycol and maleate or fumarate esters.

The fact that fumarate was a major constituent was confirmed by NMR spectroscopy.

Fig. 13 indicates the structure of the units, and the assignments for the labelled protons are given in table 9. The spectra of the resins are shown in figs. 18 - 22. By comparison of the relative intensities of bands arising from different components of the resins, the molar ratio of the components present was calculated. The results are shown in table 10.

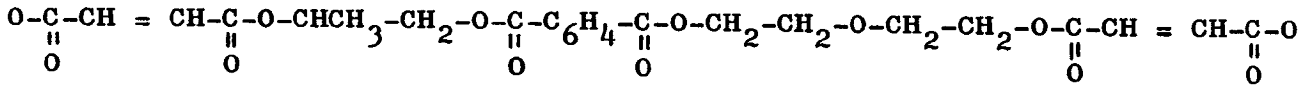
There was always an excess of the glycol component in all the isophthalic resins tested. The percentage excess glycol relative to total acid components is given in table 10.

Resin 1 :



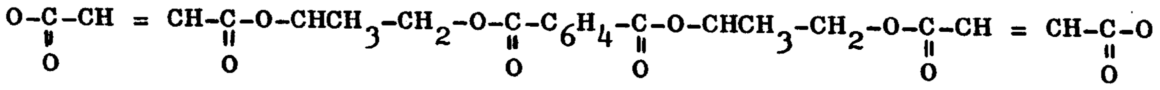
$$H_2C = CCH_3-\underset{\overset{\|}{O}}{C}-O-[CH_2-CH(OH)-CH_2-O-C_6H_4-C(CH_3)_2-C_6H_4-O]_n-CH_2-CH(OH)-CH_2-O-\underset{\overset{\|}{O}}{C}-CH_3C = CH_2$$

Resin 2 :



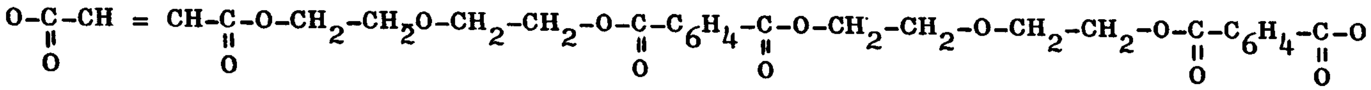
$$O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2-O-CH_2-CH_2-O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O$$

Resin 3 :



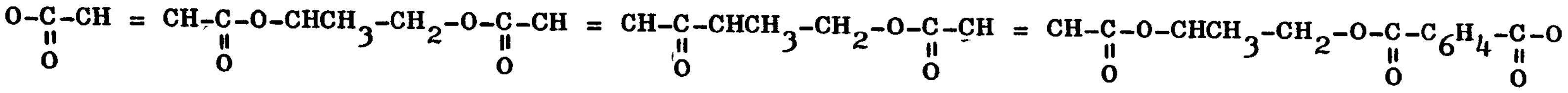
$$O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}-O-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O$$

Resin 4 :



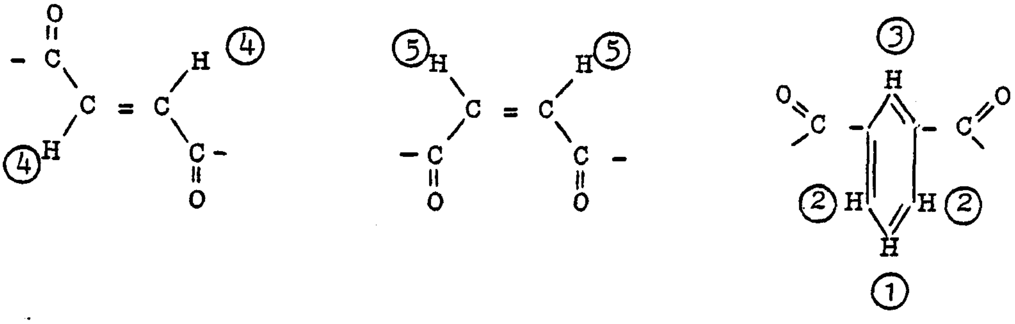
$$O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2O-CH_2-CH_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2-O-CH_2-CH_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}-O$$

Resin 5 :

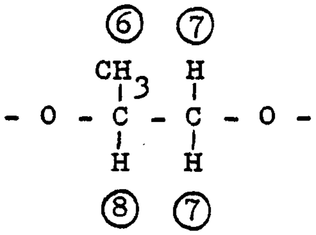


$$O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-CH = CH-\underset{\overset{\|}{O}}{C}-O-CHCH_3-CH_2-O-\underset{\overset{\|}{O}}{C}-C_6H_4-\underset{\overset{\|}{O}}{C}-O$$

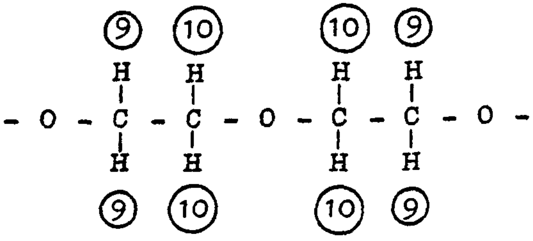
Fig. 12 : Idealised Structure of Resins



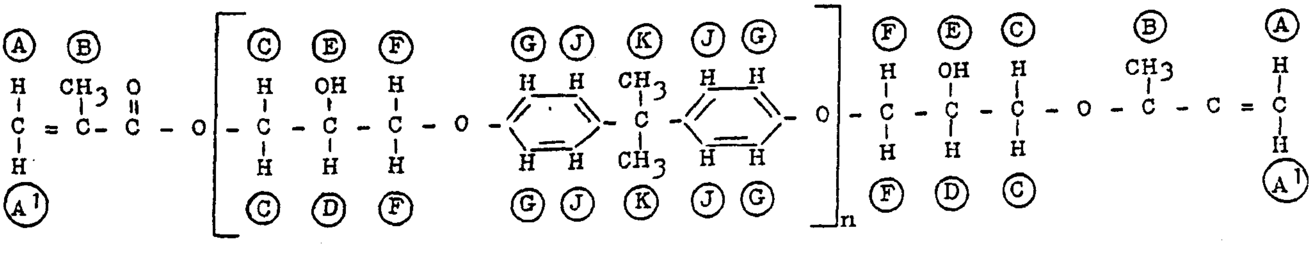
FUMARATE MALEATE ISO PHTHALATE



PROPYLENE GLYCOL



DIETHYLENE GLYCOL



VINYL ESTER

Fig. 13: Identification of Structures of Units for NMR Analysis

The structure of resin 1 is given in fig. 13 with the system used for labelling the protons. Fig. 18 shows the NMR spectrum; the assignments are given in table 9. From the relative intensities of the methyl groups containing the protons (K) and (B), the average number of groups in the repeating unit may be determined. From the first spectrum (60 MH_z) :

$$\frac{(K)}{(B)} = \frac{76}{27} = 2.82$$

From the second spectrum (90 MH_z) :

$$\frac{(K)}{(B)} = \frac{117}{38} = 3.08$$

2.2.2 Number Average Molecular Weight Determination of Resins

The method used for determining the number average molar mass of resins was vapour pressure osmometry.

The apparatus consists of a temperature controlled chamber saturated with solvent vapour at the temperature of measurement ($25^{\circ}C$) and containing two differential matched thermistors. Six syringes, one for solvent and five for solutions of different concentrations, were used to apply a drop of solution of certain concentration to one thermistor, and a drop of solvent to the other. The thermistors form part of a wheatstone bridge. When equilibrium is reached, the temperature difference between the two drops ΔT was recorded as a difference in resistance ΔR.

The molar mass was then calculated from

$$\Delta R/K^{*}C = (1/Mn)\ (1 + \tfrac{1}{2}\Gamma_{2}C)^{2}$$

where K^{*} is the calibration constant. Mn was obtained by extrapolating the data to $C = 0$. The calibration constant was estimated by measuring R for solutions of known concentrations prepared from standard compounds of known molar mass Mk (Benzil in styrene).

Then $$K^{*} = Mk\ (\Delta R/C)$$

2.2.3 Acid Number

Samples of resins were dissolved in acetone and titrated against $\frac{N}{10}$ alcoholic KOH with phenolphthalein as indicator.

The acid number of the resin is the number of mg. of KOH required to neutralise 1 g. of resin.

2.2.4 Heat Distortion Temperature (HDT)

The HDT of cast resin bars was measured by the method of BS 2782 (102 G).

2.2.5 Gel Time

The relationship between gel time and accelerator concentration was established by the preparation of small casting samples.

2.2.6 Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a process which separates polymer samples into fractions, according to their molecular size, by means of a sieving action. This was achieved using a non ionic stationary phase of packed spheres, the pore size distribution of which can be controlled. With a wide distribution of pore sizes in any support gel, a separation by molecular size is obtained. The GPC in the present work was carried out by the Paint Research Association, Teddington, Middlesex.

2.3 SPECIMEN PREPARATION

2.3.1 Cast Sheets

Flat castings (approximately 100 mm diameter) were prepared by pouring the resin into a glass mould. The mould consisted of two glass plates, 150 mm x 150 mm x 3 mm, separated by a circular frame made of rubber with internal diameter 100 mm. The rubber frame mould itself was sprayed with a commercial mould release spray. The shrinkage that does occur in the resin when curing, can usually be taken up by the compression of the rubber frame, so that there is no shrinkage of the resin away from the mould surface. This results in a far better surface finish and a material which contains far fewer inherent moulding stresses than those made from moulds with metal frames.

To avoid adhesion of the resin to the glass plates, sheets of "Melinex" (0.038 mm thick) were used to line the plates. The use of Melinex was found to give samples with less contamination and better surface finish than those prepared using mould release spray or mercury.

Specimens with varying thickness were made by adjusting the distance between the two sheets.

The liquid "degassed" resin was then poured slowly to avoid any air bubbles trapped within the casting. All the resin solutions were evacuated (degassed) by centrifuging and using a vacuum chamber prior to casting, so that the formation of voids was prevented. After the mould was filled, the whole assembly was placed with the glass plates of the mould in a horizontal position and firmly clamped, to ensure a tight seal, which prevents evaporation of styrene.

2.3.2 Laminates

A series of laminates was fabricated by the conventional hand-lay-up method. The laminates contained three layers of "E" glass mats and a gel coat tissue (fig. 14).

Since these laminates were used in contact with hot water, the chemical resistance layer of the laminate was fabricated as recommended by American Standard Test Method (C582 - 65T). Excess resin and bubbles were squeezed out of the laminate by rolling to give a consistent glass/resin composition.

The laminates were between 3 - 4 mm thick and the glass contents, determined by ignition, were found to be approximately 47% by weight for woven roving and 33% by weight for chopped strand laminates. The void content was determined by ASTM (D2734 - 70). Densities of laminates were measured by two different methods (D1505 - 68 and D792 - 66).

The curing cycle was as recommended by the manufacturers (table 3). Several precautions were taken to avoid poor castings and laminate construction. The materials for the process were packed and stored in the appropriate environment recommended by the manufacturers. The lamination was carried out by the same procedure each time. It was required that the cured specimens should have minimum residual stresses. One of the reasons for residual

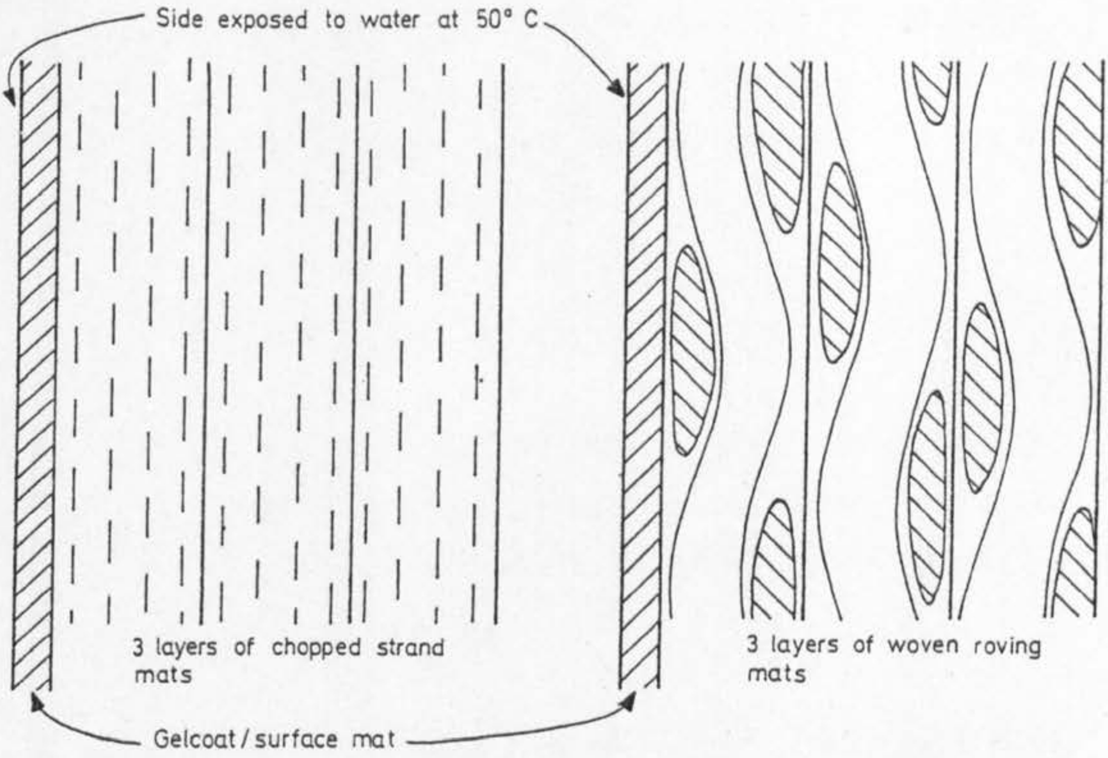


Fig. 14: Chopped Strand and Woven Roving Laminates (Cross-Sectional View)

stress is uneven cooling after curing. To prevent this, the specimens were cooled at a slow rate (about 40°C per hour). Though no special techniques were used to eliminate the voids in the laminates completely, they were kept to the minimum consistent with hand-lay-up. However, castings were made free of any visible voids.

Finished products were examined for defects and glass/resin ratios determined. To examine the effect of glass/resin ratio on permeation rate, laminates were prepared with varying glass content.

Laminates made from "heat cleaned" glass fibres were used to study the effect of debonding on the permeation rate. Cleaned glass fibres were obtained by heating the fibres up to 600°C.

2.4 METHOD OF DETERMINING PERMEABILITY

Permeation experiments were carried out with both unstrained and strained samples.

2.4.1 With Unstrained Samples

The apparatus consists of cells, each with two chambers, one "wet" and the other "dry" (fig. 15). These are separated by the test specimen. The upper chamber contained water at constant temperature, and the lower chamber contained a desiccant for measuring the weight of water which permeated through the specimen. Phosphorus pentoxide was used as the desiccant, and change in weight of phosphorus pentoxide due to absorption of water was measured periodically. Initially, the measurements were carried out every 24 hours, and after equilibrium stage, every four to five days. The whole assembly was securely clamped using rubber "O" rings and brackets. The joints were made leak proof using cold setting silicone rubber.

To determinethe reproducibility, a series of six tests was conducted with identical exposure conditions and different samples. It was found that the permeation rate measurements fall within 10% of the average value.

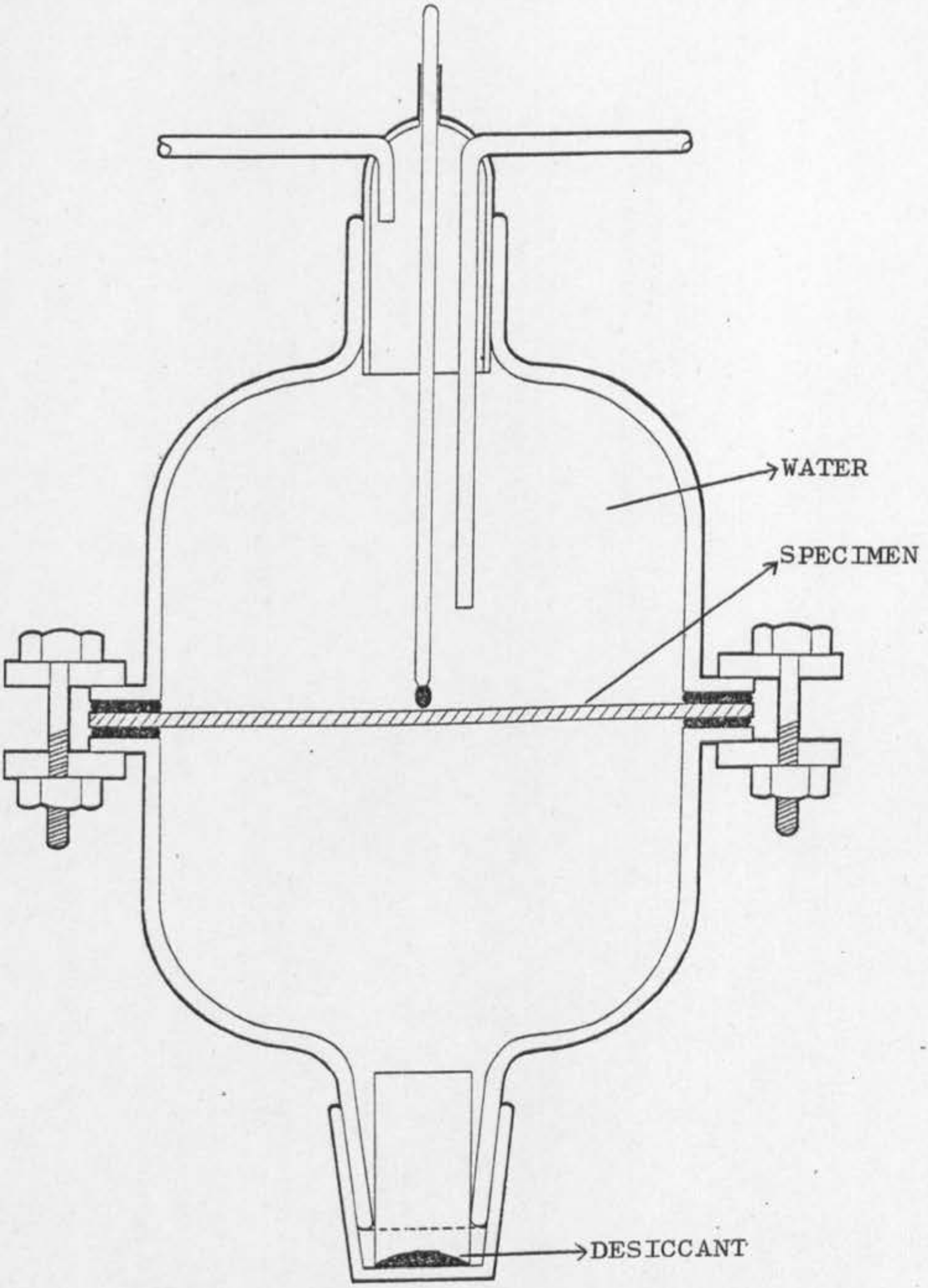


Fig. 15: Schematic View of the Apparatus for Measuring the Rate of Permeation of Liquid Water through a Flat Specimen into a Desiccant Chamber below

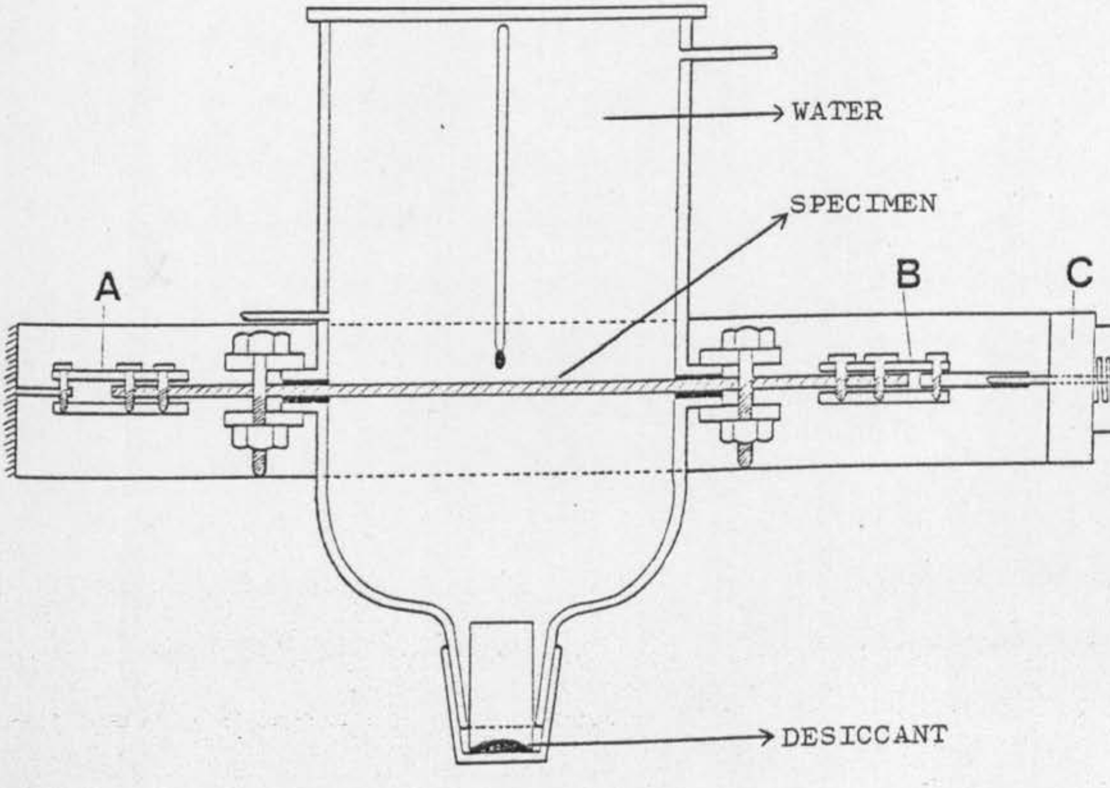


Fig. 16: Schematic View of the Apparatus for Measuring the Permeability of Resin Sheet Specimens, held between clamps A and B; Clamp B attached to Bar C and the Specimen loaded in Tension by Movement of Bolt D

2.4.2 With Strained Samples

Test rigs were designed and constructed for subjecting specimens to uniaxial tensile deformation along the length of the specimen. The samples (330 x 110 x 3.4 mm) were held between two detachable grips, each moveable, so that no torque is induced, and the strain applied is only along the long axis of the test piece. One set of the grips was attached to a fixed bar, while the other was connected to a screw assembly, as shown in fig. 16. The strain on the specimen was kept constant by adjusting the screw periodically. Fig. 17 shows a similar apparatus with a system of levers, through which the load is applied. In this case, the strain on the samples was held fixed by adjusting the level of fluid in the loading reservoir.

Strain was measured by mechanical strain gauges, and was monitored by an optical device. A Huggenberger tensometer type A was used in all the experiments.

In all the tests, the specimens were strained to a given extent and held at this constant elongation throughout the experiment.

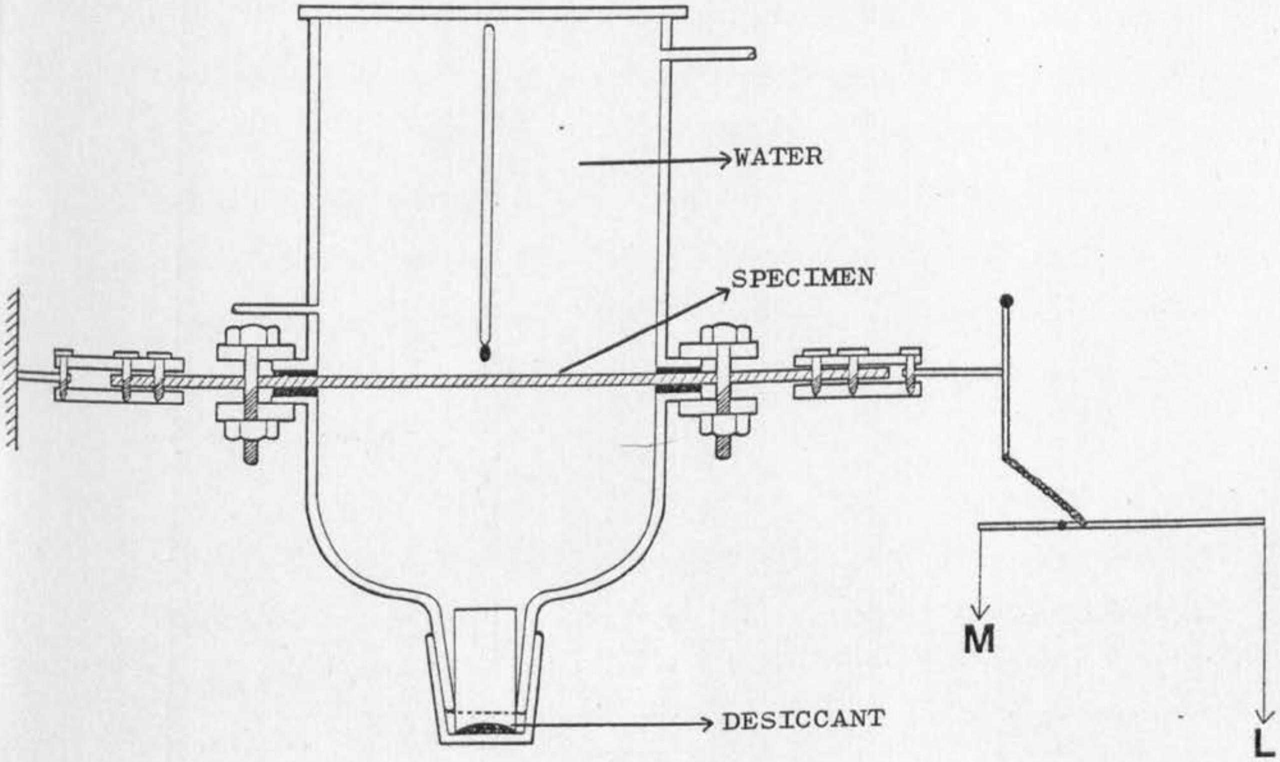


Fig. 17: Diagram of Lever-Operated Apparatus for Measuring the Rate of Permeation of Liquid Water through Specimens Subjected to Uniaxial Tensile Loading. Load Arm L against Balance Weight M to load Specimen

2.5 WATER ABSORPTION

In absorption measurements, the samples were immersed in stirred water baths. Temperature control was within ±1.0°C of the set temperature. Distilled water was used for the tests. The samples were weighed, dried and weighed again after predetermined periods of immersion in water at 50°C. The method of weighing wet samples was to take them out of the bath and place them in water at room temperature. After four or five minutes, these were taken out and excess water was removed by wiping. The weights were then measured at room temperature after three minutes. The samples were then heated to constant weight at 50°C.

Dimensional changes were measured by observing the distance between two marks on the specimen surface, using a travelling microscope.

The samples were prevented from drying by sandwiching them between two glass plates, entrapping a thin layer of water between the samples and the plates.

2.6 MICROSCOPIC EXAMINATION OF THE SAMPLES

Samples were examined periodically to study dimensional changes, and to observe any damage developing in the samples.

Three types of microscope were used for examining the damages developed in the specimens. An optical microscope was used for studying large dimensional changes, cracks and debonding. Because of the small depth of focus of optical systems at high magnifications, electron microscopes were used to study the microcracks present in the test samples.

Samples were observed using a Cambridge 600 Mark II scanning electron microscope and a Philips EM301 transmission microscope, operated at 80 KV with a 50 μm objective aperture.

There were, however, some problems in the use of these instruments, which proved troublesome. The intricate nature of the composite surface meant that, with some specimens, the coating would not penetrate to all the surface facets. This resulted in electrons accumulating on uncoated parts of the specimen and spoiling the view. During focusing the high concentration of the electrons sometimes causes local heating which results in the cracking of the gold coating.

The brittle nature of the sample made the preparation of section difficult.

However, despite these problems, the use of the electron microscope gave valuable information about the samples over that obtained with an optical microscope.

2.7 PHYSICAL AND CHEMICAL TESTS CARRIED OUT ON SPECIMENS

2.7.1 Density

A simple gravimetric method (ASTM D792-66) and a density gradient technique (ASTM D1505-68) were used to determine the apparent densities of the samples.

2.7.2 Glass Content

Composite samples were heated to 600°C in a muffle furnace until all the resin and binder was burnt off. The samples were then cooled to room temperature. The difference in original weights and the final weights of the samples gives the weight of glass fibres in the composites. This test was carried out according to the specification in ASTM D2583-66.

2.7.3 Void Content

The densities of the resins, the reinforcement and the composite were measured separately. The resin content was then measured, and a theoretical composite density was calculated. This was compared with the measured composite density. The difference in densities indicates the void content. For the correct determination of percentage voids, all tests were carried out at the same temperature. This method is in accordance with ASTM D2734-70.

2.7.4 Quantity of Leachable Materials

Powdered samples from each resin were extracted with

1. Water at 50°C
2. Deuterated water at 50°C and 100°C
3. Deuterochloroform

After evaporation of the filtered extract, in some cases the presence of a solid residue was observed. Addition of a small amount of solvent ($CDCl_3$) to the residue resulted in a solution concentrated enough to obtain conventional NMR spectra.

Extraction of powdered resin with H_2O or D_2O at 50°C produced a solution too dilute to be readily examined by NMR spectroscopy. It was, therefore, carried out at 100°C to accelerate the process. 10g of the material were refluxed with 5 mls of D_2O for 168 hours. The extract was evaporated to dryness under vacuum, using phosphorus pentoxide as a desiccant. The residue was dissolved in $CDCl_3$ and examined by HNMR spectroscopy using a 90 MHz instrument. In order to assess the importance of hydrolysis in this leaching process, the powdered resin was left to stand in a non-reactive solven, $CDCl_3$. The residue was examined by HNMR spectroscopy, as above.

CHAPTER THREE

RESULTS

Table 9: Assignment for the Labelled Protons for NMR

RESIN 1 :									
Assignment	(K)	(B)	(E)	(C) (F)	(D)	or (A^1) (A)	or (A^1) (A)	(J)	(G)
Chemical shift ppm downfield from TMS	1.58	1.89	3.15	4.02	4.26	5.50	6.09	6.74	7.07
RESIN 2 :									
Assignment	(6)	(10)	(7) (9)	(4)	(2)	(3)			
Chemical shift ppm downfield from TMS	1.38	3.80	4.40	6.84	8.16	8.63			
RESIN 3 :									
Assignment	(6)	(7)	(8)	(4)	(1)	(2)	(3)		
Chemical shift ppm downfield from TMS	1.36	4.34	5.35	6.84	7.50	8.17	8.64		
RESIN 4 :									
Assignment	(6)	(10)	(7) (9)	(8)	(5)	(4)	(1)	(2)	(3)
Chemical shift ppm downfield from TMS	1.30	3.80	4.40	5.30	6.23	6.82	7.48	8.14	8.61
RESIN 5 :									
Assignment	(6)	(7)	(8)	(4)	(1)	(2)	(3)		
Chemical shift ppm downfield from TMS	1.38	4.34	5.31	6.84	7.53	8.18	8.63		

Table 10: Data Obtained from NMR, Molar Ratios of Components Present

RESIN	IPA	FA	MA	PG	DEG	EXCESS GLYCOL %
2	1	0.92	≠	1.02	1.15	13.0
3	1	0.91	≠	2.36	-	23.6
4	1	0.47	≠	0.23	1.49	10.9
5	1	2.93	≠	4.53	-	15.3

≠ very small quantity present, not accurately measurable

Table 11: Number Average Molecular Weight by Vapour Pressure Osmometry

SAMPLE MOLARITY	BENZIL IN STYRENE		
	0.025	0.10	0.25
R	7.92	28.75	55.32
R	7.74	28.88	58.53
R	8.19	28.86	58.40
R	8.15	28.97	57.42
Average R	8.00	28.87	57.42

SAMPLE CONCENTRATION	RESIN 2 IN ACETONE		
	15 g/l	30 g/l	60 g/l
R	4.45	6.26	12.01
R	4.05	6.16	12.03
R	4.00	6.16	11.73
Average R	4.17	6.19	11.92
$\Delta R/C$	0.28	0.21	0.20

$\bar{M}n = 1126$

SAMPLE CONCENTRATION	RESIN 7 IN ACETONE		
	15 g/l	30 g/l	60 g/l
R	5.35	9.74	15.35
R	4.82	9.12	15.21
R	4.91	9.04	15.34
Average R	5.026	9.30	15.30
$\Delta R/C$	0.34	0.31	0.26

$\bar{M}n = 1110$

Table 11 (cont.)

SAMPLE CONCENTRATION	RESIN 8 IN ACETONE		
	15 g/l	30 g/l	60 g/l
R	4.15	8.41	13.91
R	4.74	8.91	13.50
R	4.61	8.78	14.85
Average R	4.5	8.7	14.1
Δ R/C	0.30	0.29	0.24

$\bar{M}n$ = 1003

SAMPLE CONCENTRATION	RESIN 9 IN ACETONE		
	15 g/l	30 g/l	60 g/l
R	3.95	8.1	12.09
R	4.20	7.5	11.63
R	4.00	7.8	12.1
Average R	4.05	7.8	11.94
Δ R/C	0.27	0.26	0.20

$\bar{M}n$ = 921

Table 12: Permeation Coefficients, Time Lag and Diffusion Coefficients of Water Through Castings

RESIN	WATER TEMPERATURE °C	PERMEATION COEFFICIENT Kg/m^{2}day/cm x 10^4	INTERCEPT ON X-AXIS HOURS	DIFFUSION COEFFICIENT cm^2/day x 10^3
1	50	5.87	76.8	6.06
2	50	4.76	168.0	3.22
3	50	5.61	127.2	2.77
4	50	12.74	79.2	5.60
5	50	8.95	48.0	8.86
6	50	7.39	52.8	11.11

Table 13: Permeation Coefficients, Time Lag and Diffusion Coefficients of Water Through Chopped Strand Laminates

RESIN	WATER TEMPERATURE °C	PERMEATION COEFFICIENT Kg/m^{2}day/cm x 10^4	INTERCEPT ON X-AXIS HOURS	DIFFUSION COEFFICIENT cm^2/day x 10^3
1	50	1.84	24	15.20
2	50	3.77	132	3.73
3	50	3.81	64.8	10.03
4	50	11.93	132	3.24
5	50	4.07	38.4	15.30
6	50	4.20	168	3.24

Table 14: Permeation Coefficients, Time Lag and Diffusion Coefficients of Water Through Woven Roving Laminates

RESIN	WATER TEMPERATURE °C	PERMEATION COEFFICIENT Kg/m^{2}day/ cm x 10^4	INTERCEPT ON X-AXIS HOURS	DIFFUSION COEFFICIENT cm^2/day x 10^3
1	50	0.58	72	9.61
2	50	1.33	144	4.05
3	50	1.76	72	10.81
4	50	4.50	168	2.34
5	50	1.80	72	4.99
6	50	-	-	-

Table 15: Effect of Glass Content and Arrangement on Permeability of Laminates to Water

RESIN	VOLUME FRACTION OF GLASS	GLASS ARRANGEMENT	P Kg/m^{2}day/cm x 10^4
1	0.0		5.87
	0.22	c.s.	1.85
	0.32	w.r.	0.58
2	0.0		4.76
	0.18	c.s.	3.77
	0.21	w.r.	2.29
	0.25	w.r.	1.33
3	0.0		5.61
	0.17	c.s.	3.81
	0.29	w.r.	1.76
4	0.0		12.74
	0.20	c.s.	11.93
	0.29	w.r.	4.50
5	0.0		8.95
	0.17	c.s.	4.07
	0.31	w.r.	1.80
6	0.0		7.39
	0.19	c.s.	4.20

c.s.: chopped strand
w.r.: woven roving

Table 16: Effect of Thickness of Polymer Film on its Water Transmission Rate

RESIN	FILM THICKNESS mm	WATER TRANSMISSION RATE Kg/m^{2}day at 50°C x 10^3	WATER TRANSMISSION RATE CONVERTED TO UNIT THICKNESS Kg/m^{2}day/cm x 10^4
1	1.18	4.45	5.25
	3.41	1.72	5.87
2	0.18	52.75	9.49
	0.24	26.20	6.29
	0.39	16.20	6.32
	0.49	13.30	6.52
	0.58	14.40	8.35
	1.15	7.07	8.13
	3.51	1.36	4.76
3	1.31	4.66	6.10
	2.97	1.89	5.61

Table 17: The Dependence of Permeability of Castings on Molecular Weight

$\bar{M}n$	PERMEABILITY COEFFICIENT kg/m^{2}day/cm x 10^4	INTERCEPT ON X-AXIS HOURS	DIFFUSION COEFFICIENT cm^2/day x 10^3
1126	4.76	168	3.22
1110	5.09	302	2.63
1003	6.81	271	1.59

Table 18: The Effect of Debonding on the Permeability

SAMPLE	GLASS CONTENT % BY WEIGHT	PERMEABILITY COEFFICIENT kg/m^{2}day/cm x 10^4	INTERCEPT ON X-AXIS HOURS	DIFFUSION COEFFICIENT cm^2/day x 10^3
chopped strand laminate	29.9	3.81	64.0	10.03
woven roving laminate	46.62	1.76	72.0	10.81
woven roving laminate - debonded	47.42	2.95	-	-

Table 19: Effect of Strain on the Permability of Cast Resins

RESIN	STRAIN %	WATER TEMPERATURE °C	PERMEABILITY COEFFICIENT Kg/m^{2}day/cm x 10^4
2	0	50°C	4.76
2	0.2	50°C	5.38
2	0.3	50°C	8.47

Table 20: Effect of Strain on the Permeability of Chopped Strand Laminates

RESIN	STRAIN %	WATER TEMPERATURE °C	GLASS CONTENT % BY WEIGHT	PERMEABILITY COEFFICIENT Kg/m^{2}day/ cm x 10^4
2	0	50°C	31	3.77
2	0.2	50°C	34	2.86
2	0.3	50°C	35	2.96
2	0.4	50°C	35	3.24
2	0.5	50°C	35	3.48
2	0.6	50°C	35	4.69

Table 21: Effect of Strain on the Permeability of Woven Roving Laminates

RESIN	STRAIN %	WATER TEMPERATURE °C	GLASS CONTENT % BY WEIGHT	PERMEABILITY COEFFICIENT $Kg/m^2day/cm \times 10^4$
2	0.0	50°C	35 (in phase)	2.29
2	0.0	50°C	42 (out of phase)	1.33
2	0.2	50°C	42 (in phase)	3.84
2	0.2	50°C	46 (out of phase)	1.44

Table 22: Change in Dimensions in Resins when Totally Exposed to Water at 50°C

TIME HOURS	% CHANGE IN DIMENSIONS IN RESIN 2	RESIN 3	RESIN 4	RESIN 5
168	+ 0.83	+ 0.30	+ 0.57	+ 0.68
336	+ 0.75	- 0.11	+ 1.06	+ 1.02
504	+ 0.80	- 0.11	+ 0.98	+ 0.47
672	+ 0.66	- 0.11	+ 0.58	+ 0.71
840	+ 1.05	- 0.11	+ 1.31	+ 0.68
1008	+ 0.95	- 0.11	+ 1.24	+ 1.01
1176	+ 1.29	- 0.11	+ 0.74	+ 1.12

Table 23: Change in Dimensions in Resins when Dried after Exposure to Water at 50°C

TIME HOURS	% CHANGE IN DIMENSIONS IN RESIN 2	RESIN 3	RESIN 4	RESIN 5
168	+ 0.07	0	- 0.65	- 0.14
336	+ 0.47	0	- 0.08	+ 0.25
504	+ 0.30	0	- 0.08	+ 0.21
672	- 0.08	0	- 0.70	+ 0.17
840	+ 0.08	0	- 0.24	- 0.05
1008	+ 0.25	0	- 0.16	0.00
1176	+ 0.03	0	- 0.66	+ 0.14

Table 24: Dependence of Heat Distortion Temperature on Acid Values

RESIN	ACID VALUE mg/KOH	H.D.T. °C
2	20	76°C
2	25	71.9°C
2	45	60.6°C
2	60	40.2°C

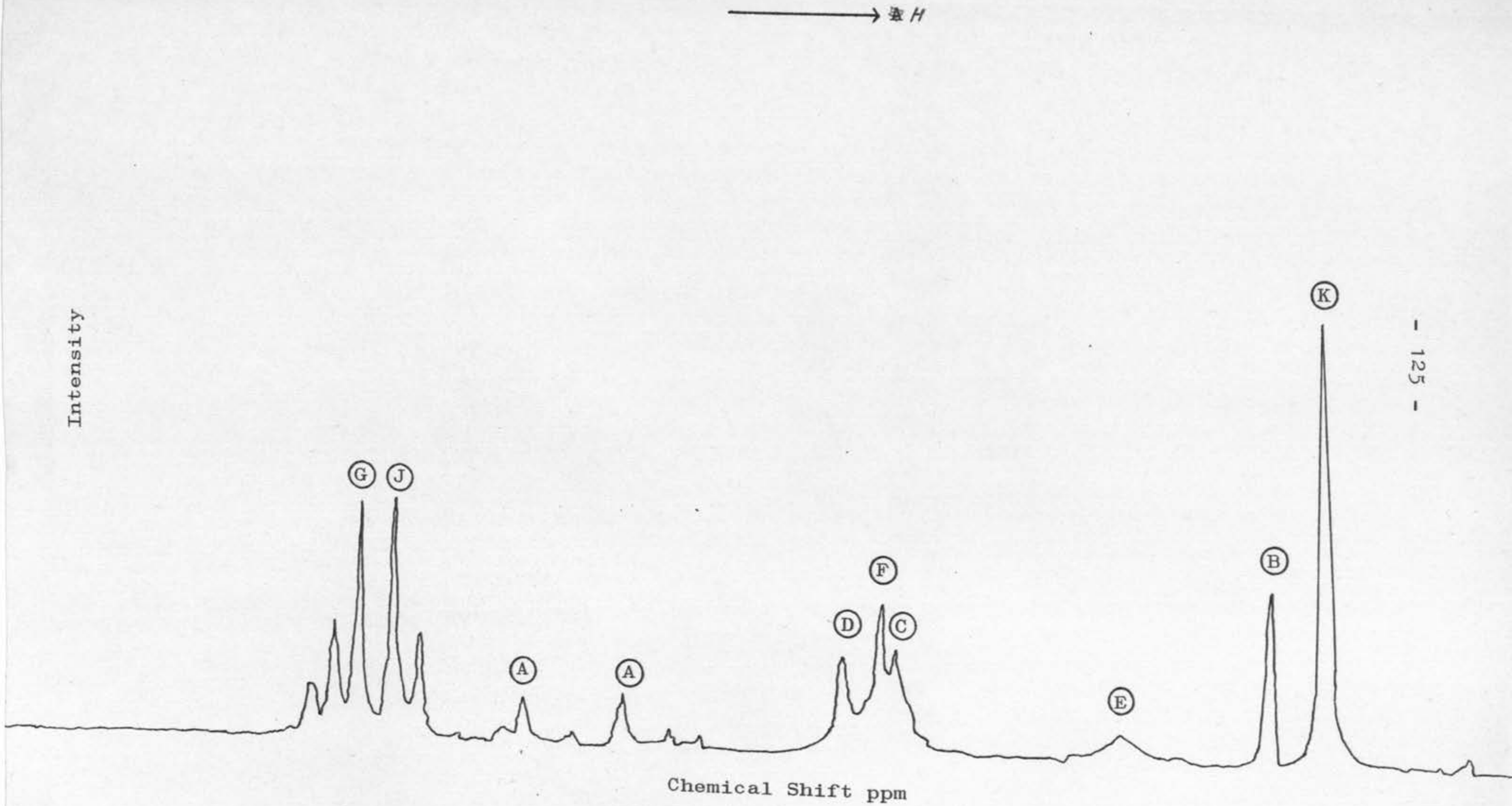


Fig. 18: NMR Spectroscopy of Resin 1

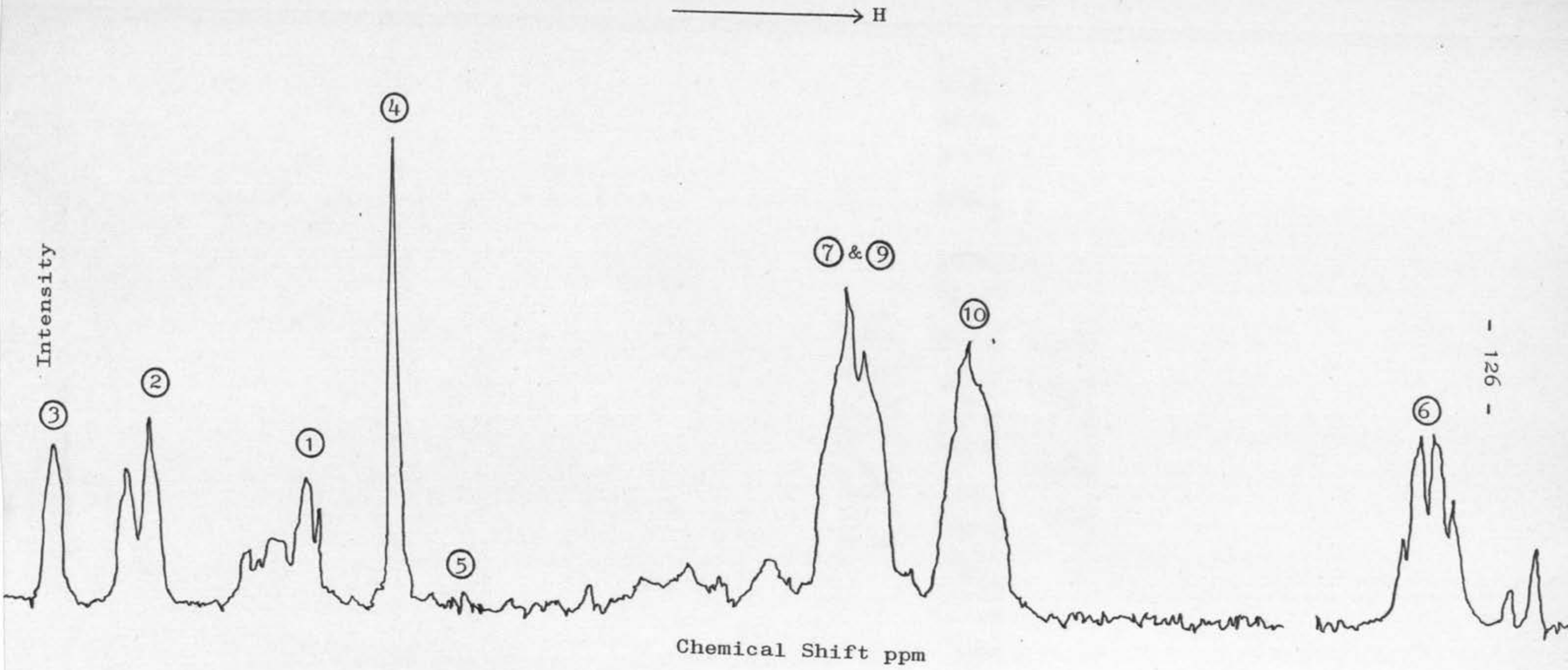


Fig. 19: NMR Spectroscopy of Resin 2

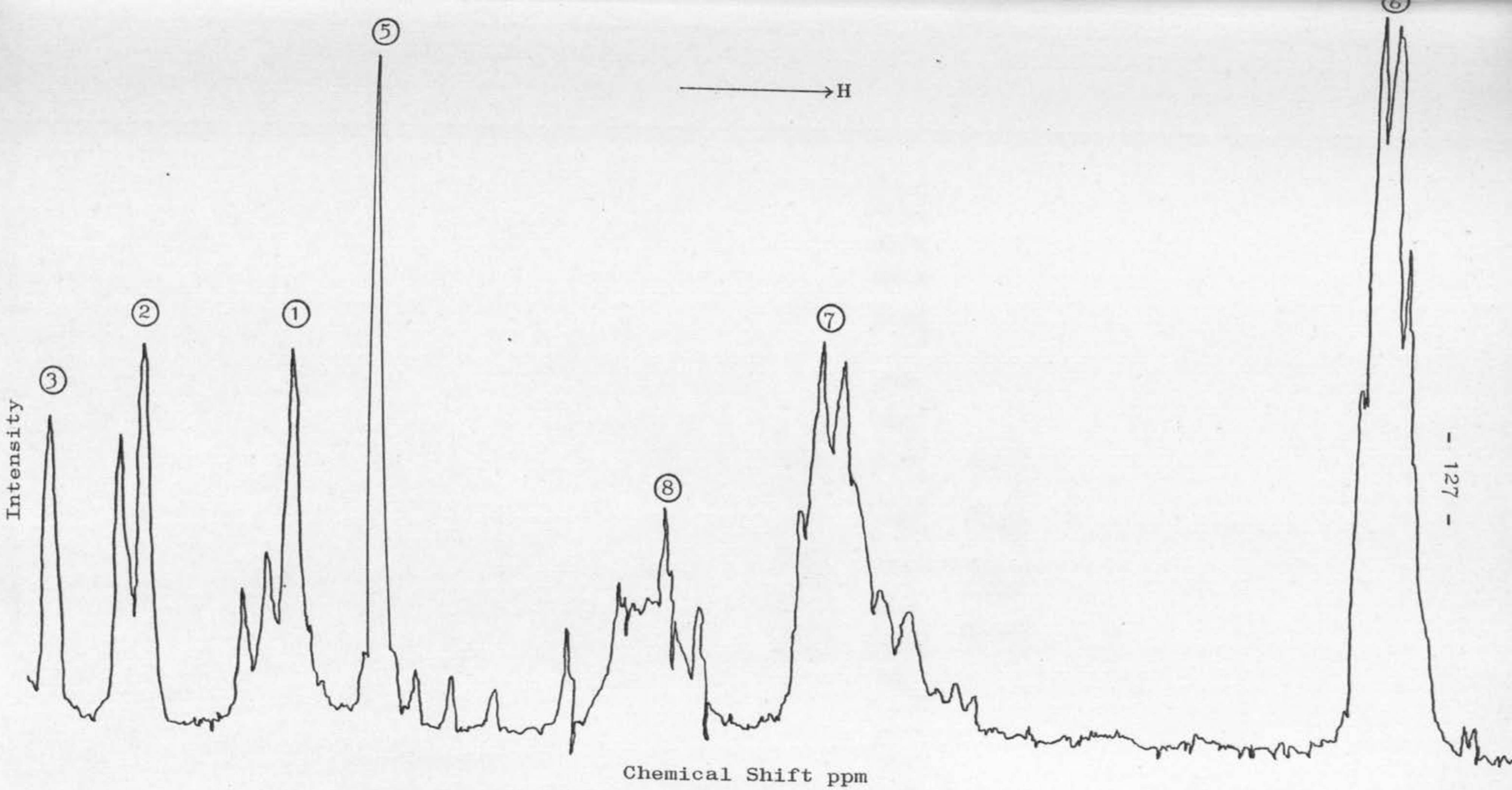


Fig. 20: NMR Spectroscopy of Resin 3

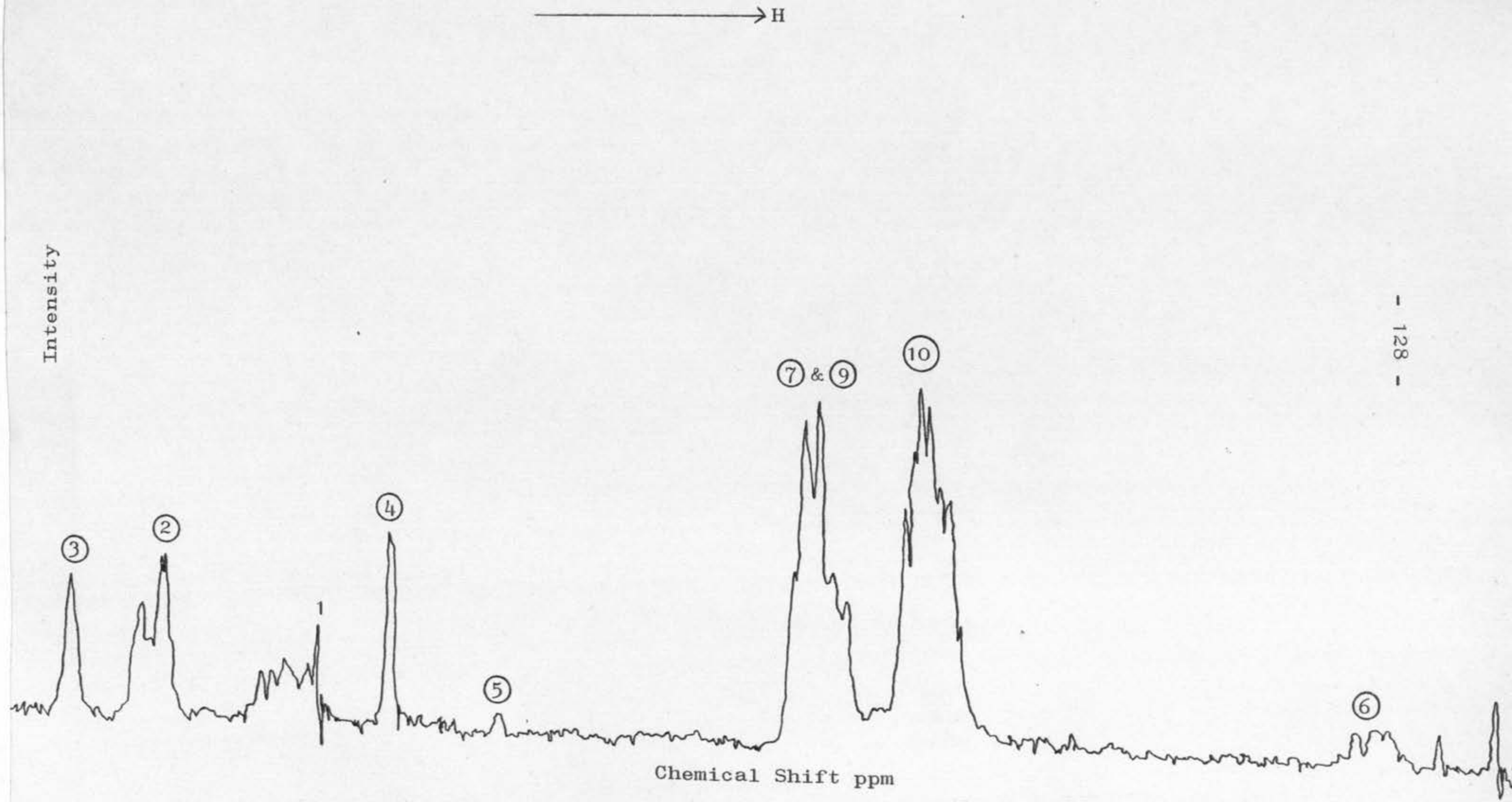


Fig. 21: NMR Spectroscopy of Resin 4

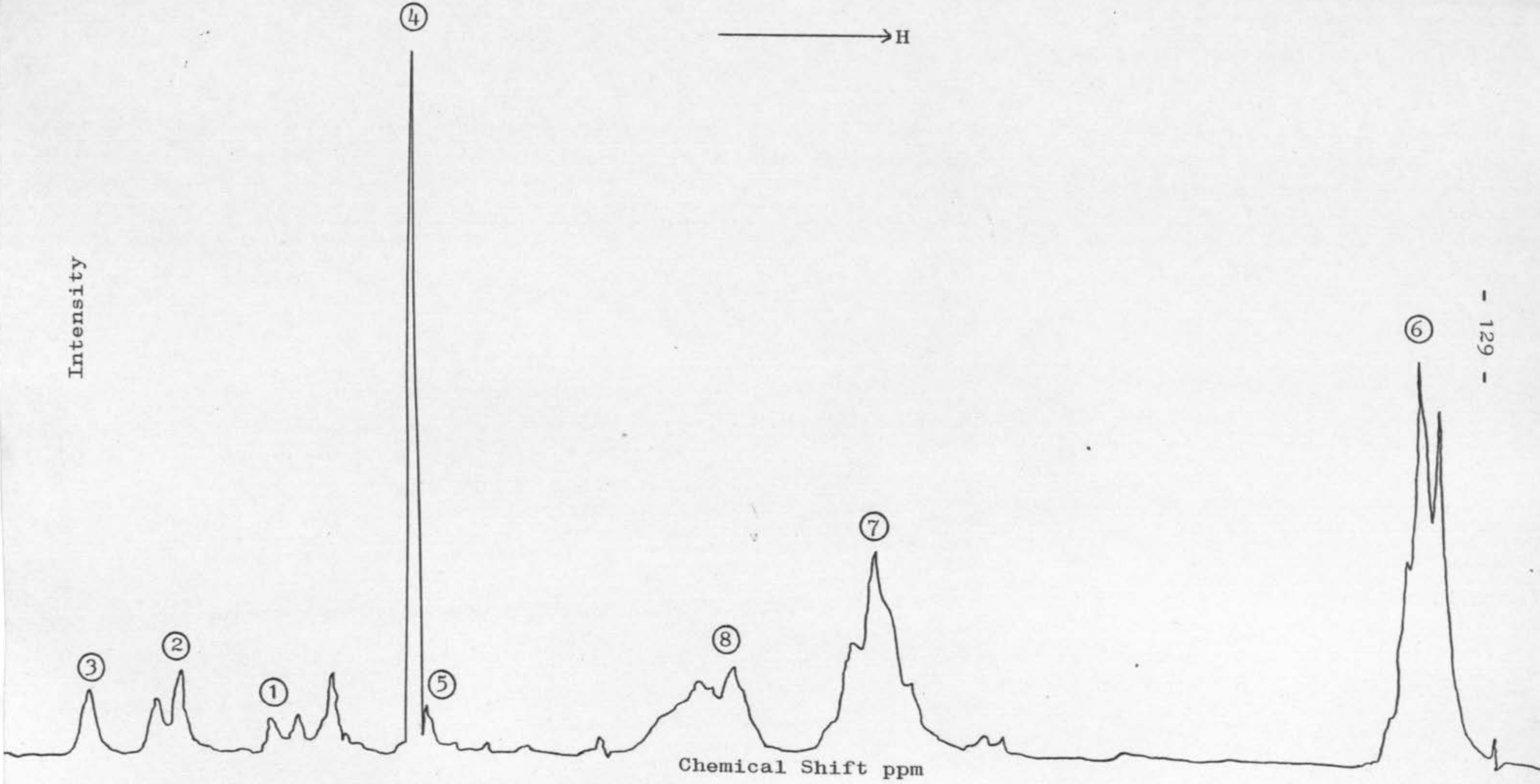


Fig. 22: NMR Spectroscopy of Resin 5

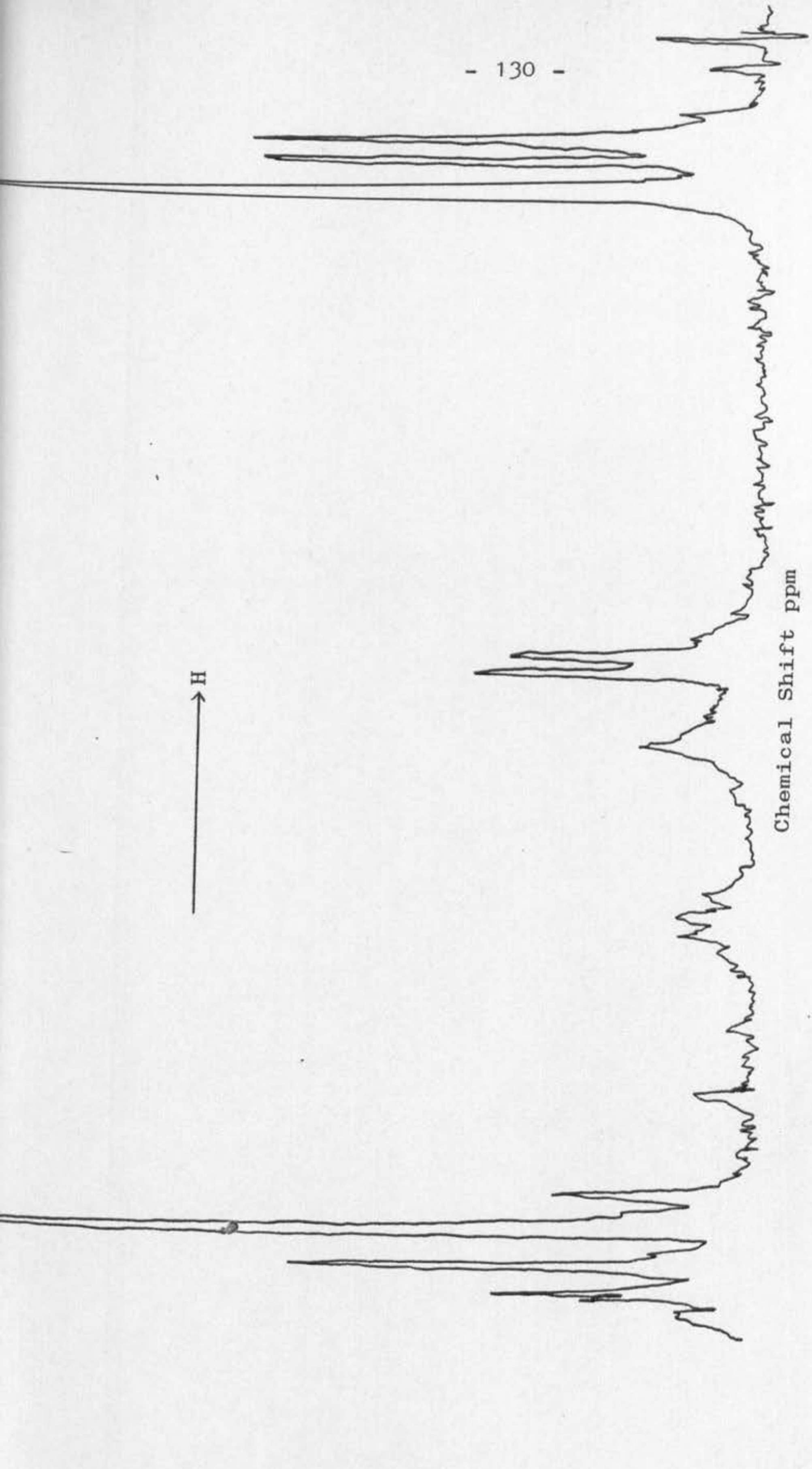
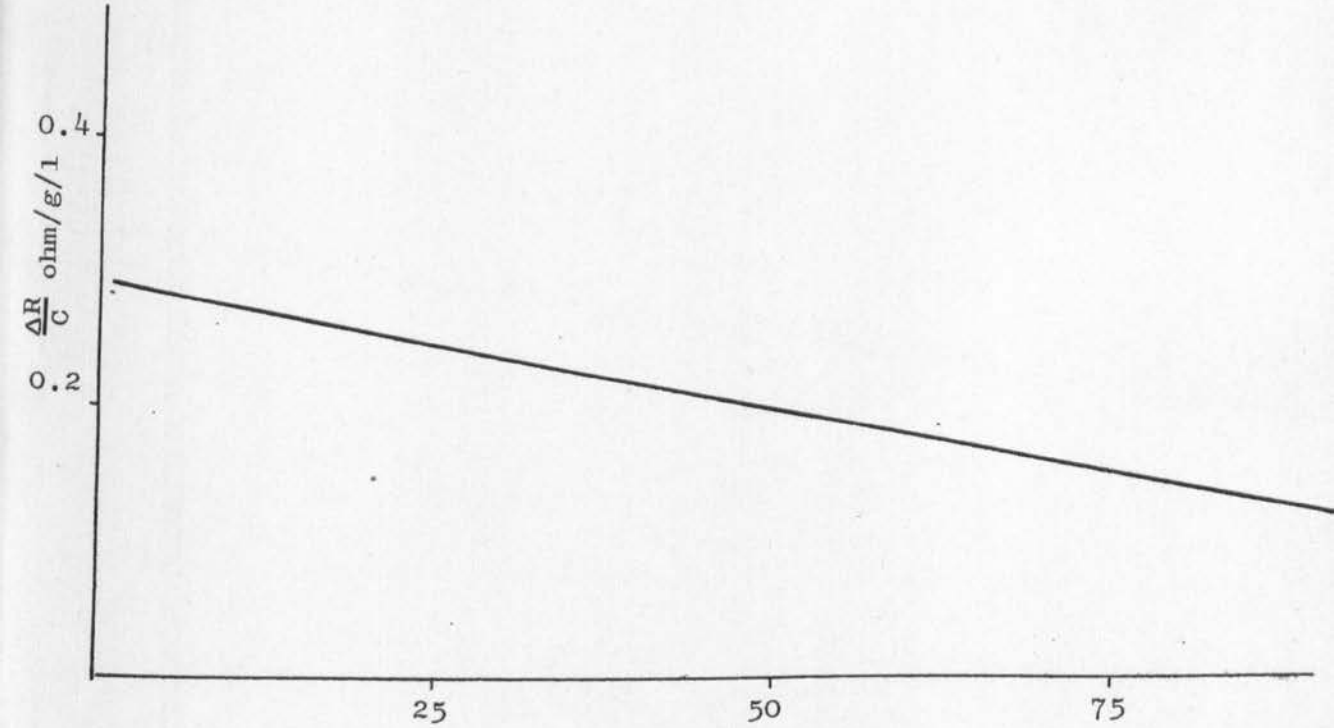
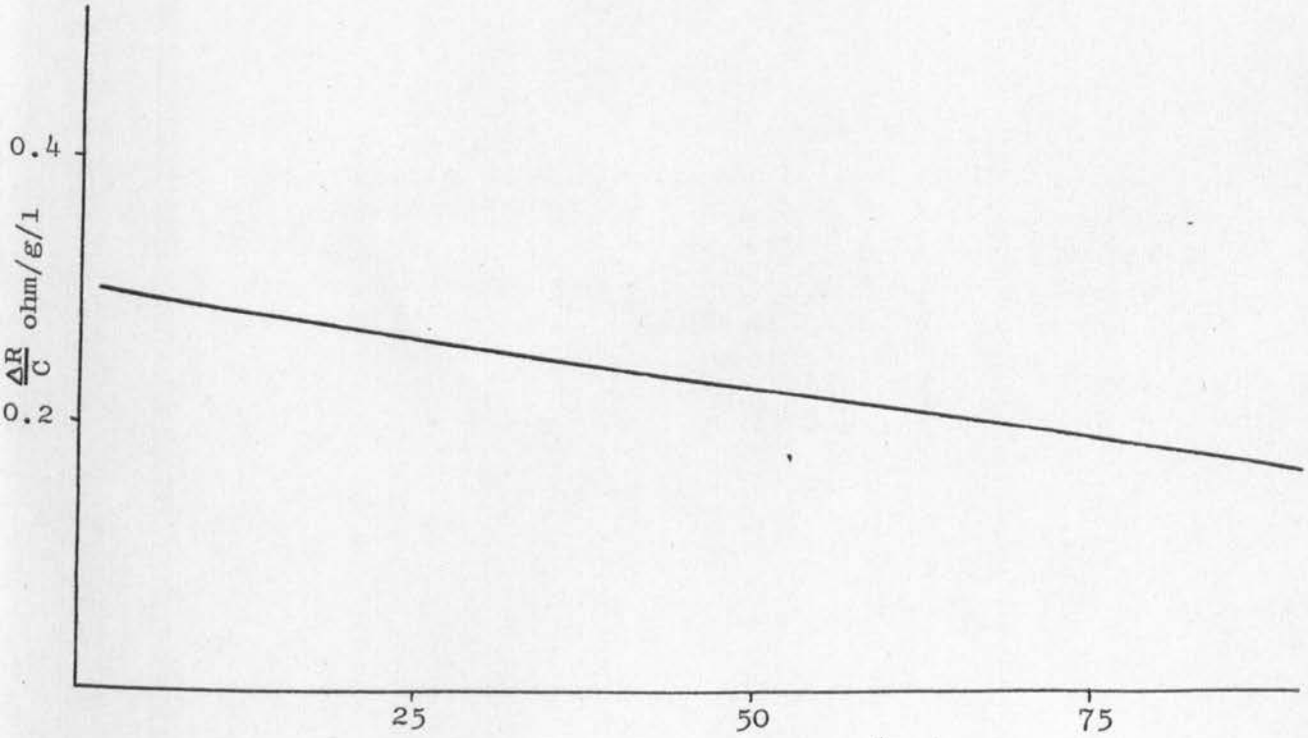


Fig. 23: NMR Spectroscopy of Resin 6



Concentration g/1

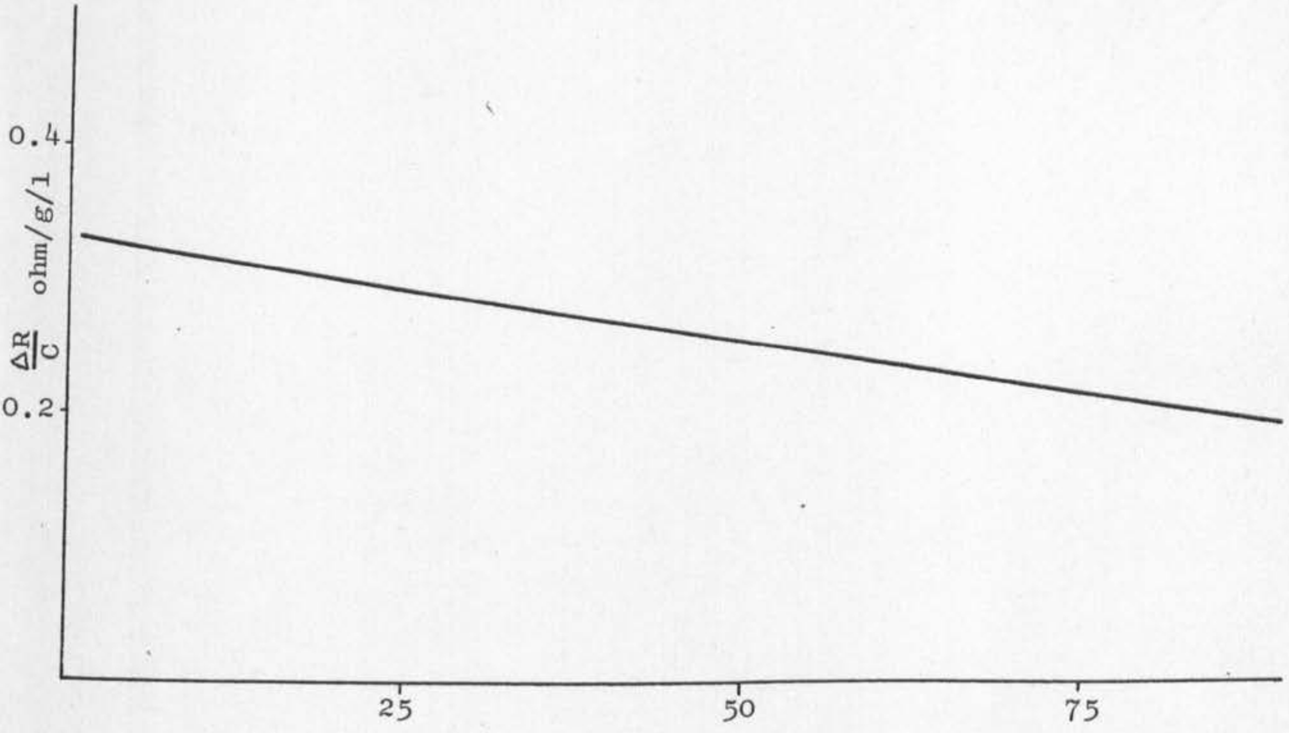
Calibration Curve for Resin 2



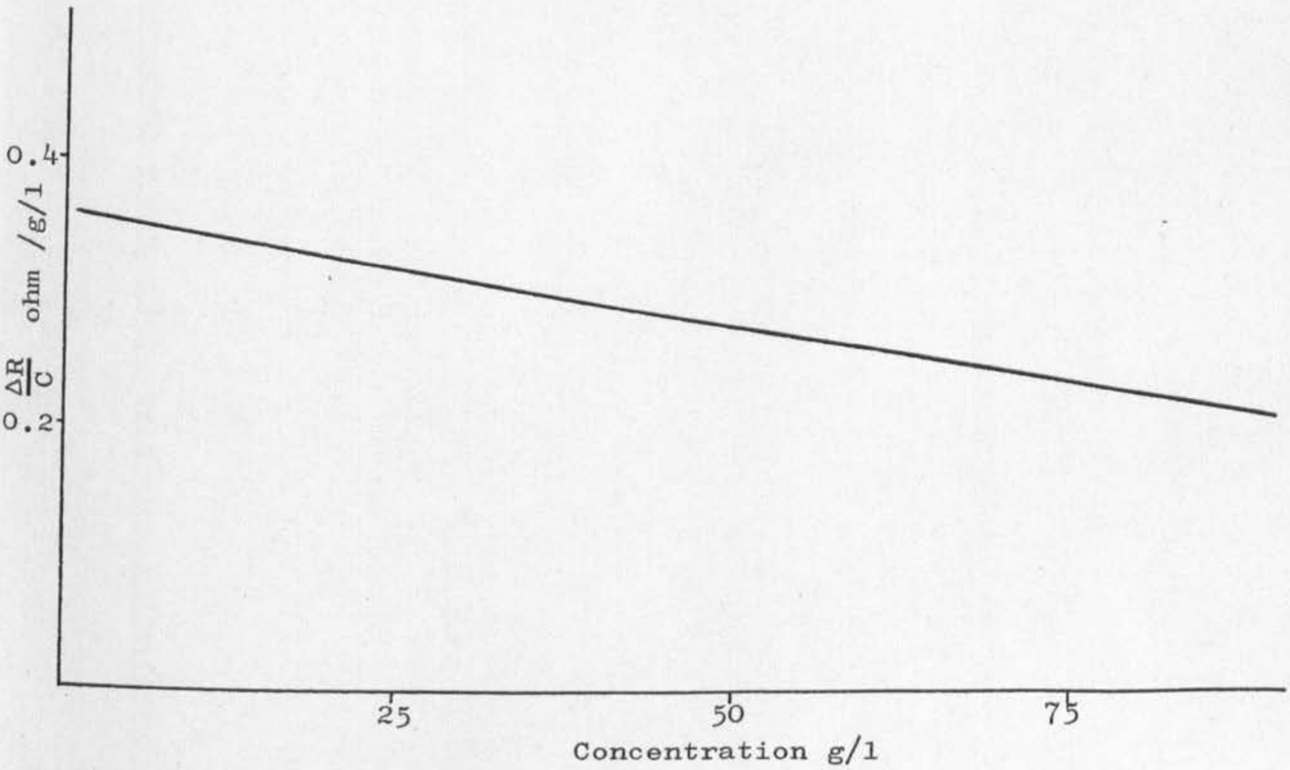
Concentration g/1

Calibration Curve for Resin 7

Fig. 24: $\bar{M}n$ by Vapour Pressure Osmometry



Calibration Curve for Resin 8



Calibration Curve for Resin 9

Fig. 25: $\bar{M}n$ by Vapour Pressure Osmometry

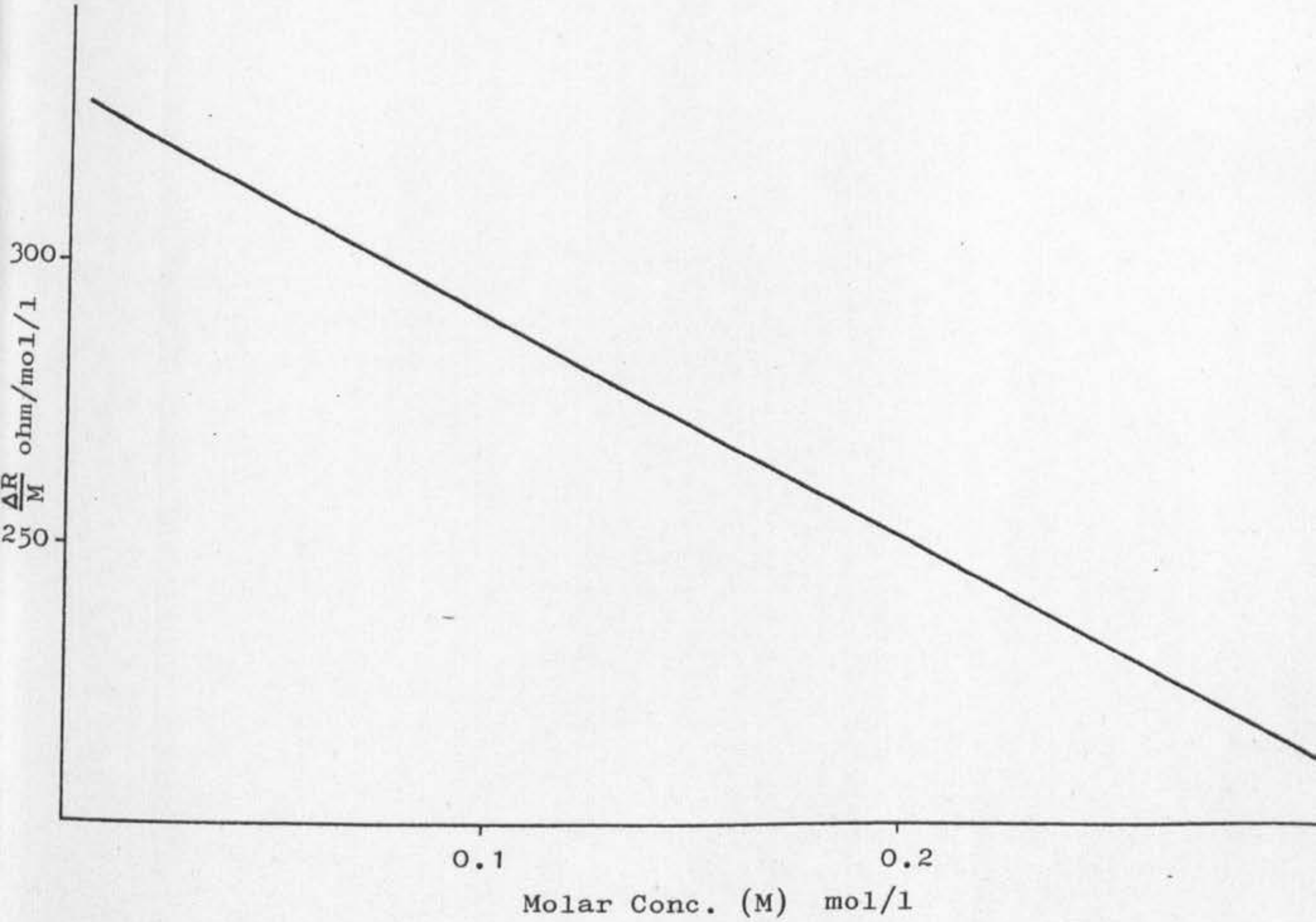


Fig. 26: Calibration Curve for Benzil ($\frac{\Delta R}{M}$ vs. M)

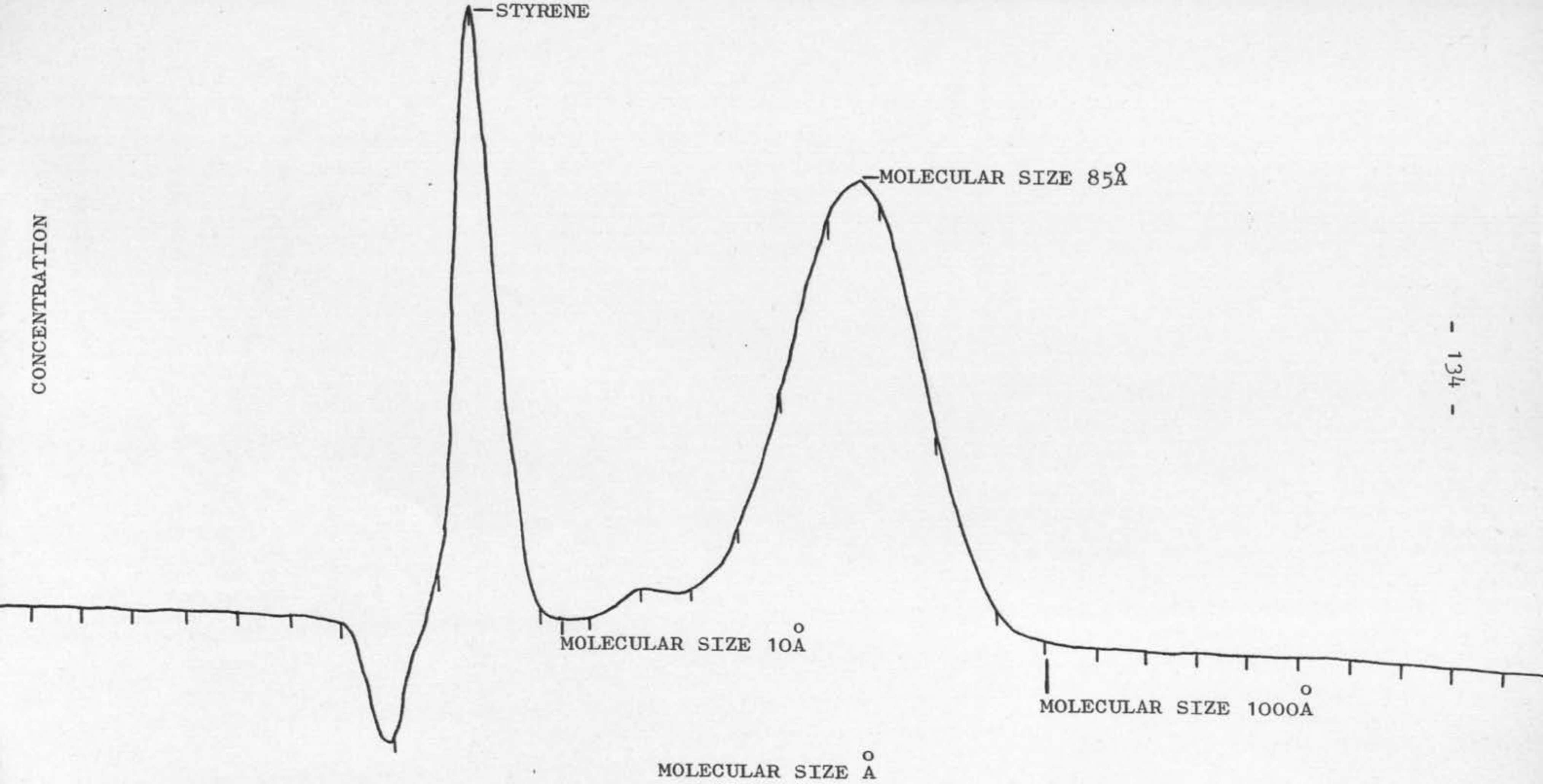


Fig. 27: Gel Permeation Chromatography for Resin 2, Batch 1

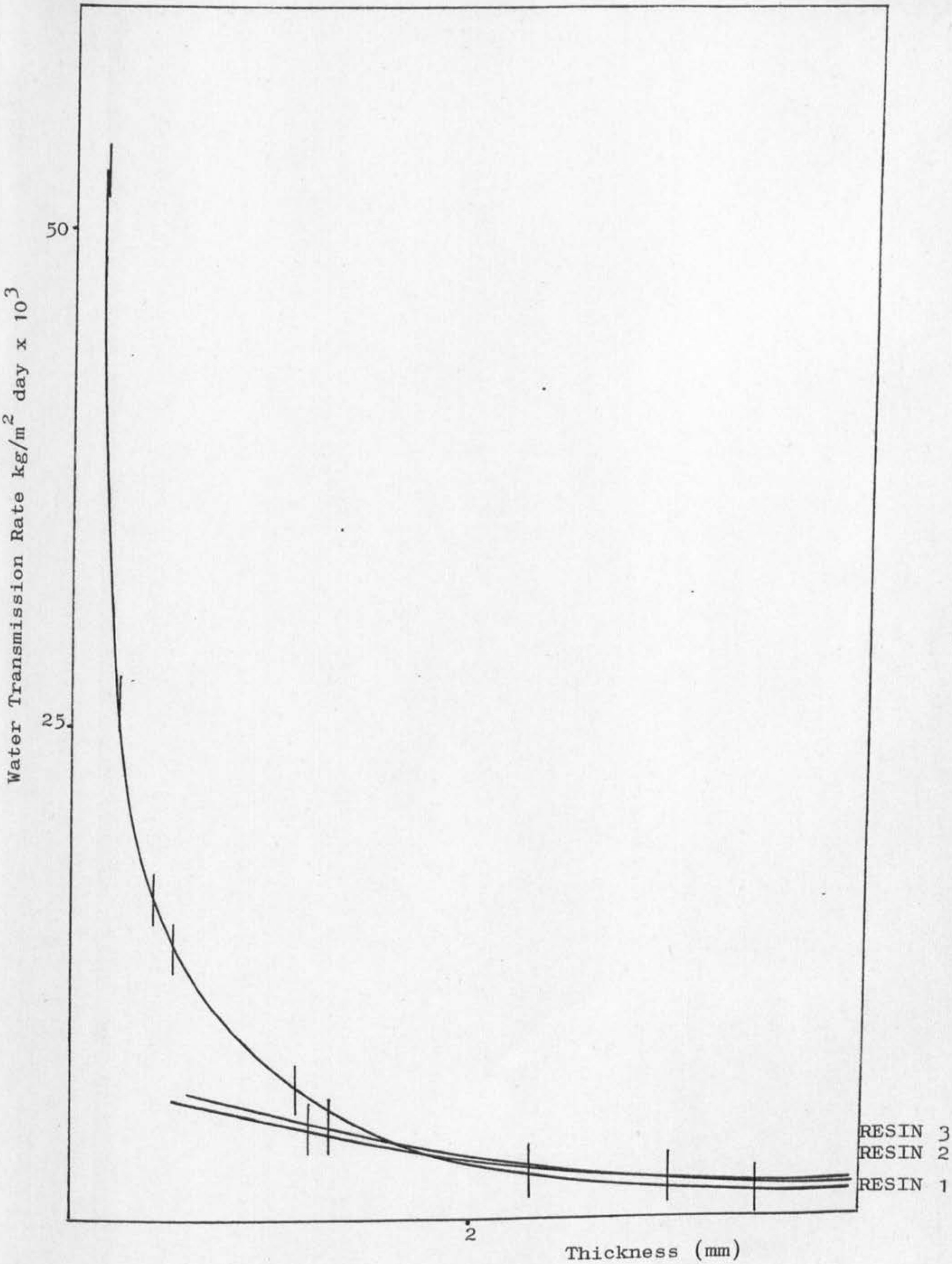


Fig. 28: Relationship Between Thickness and Water Transmission for Castings

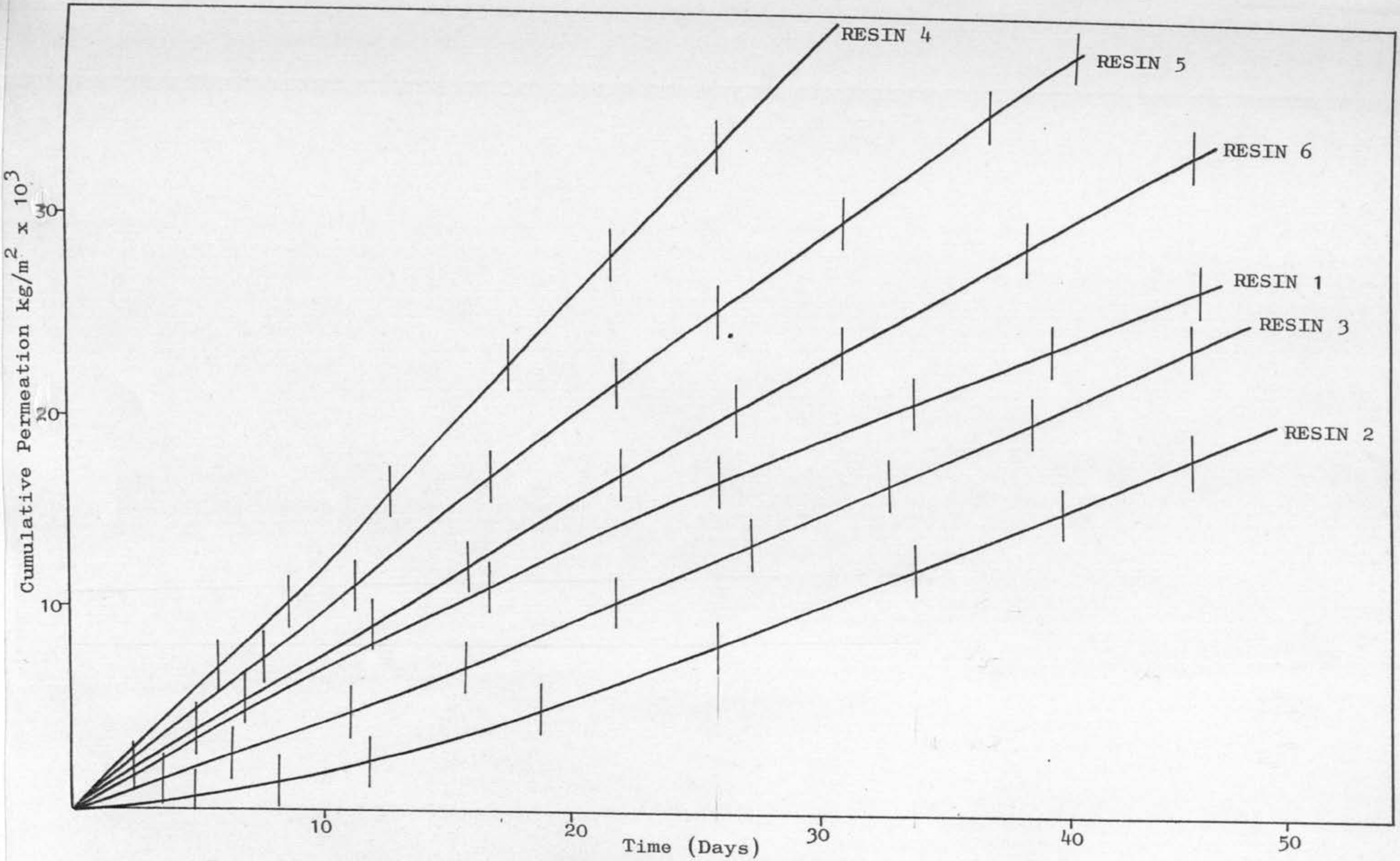


Fig. 29: Effect of Resin Composition on Transmission of Water Through Castings (corrected to 1 cm thickness)

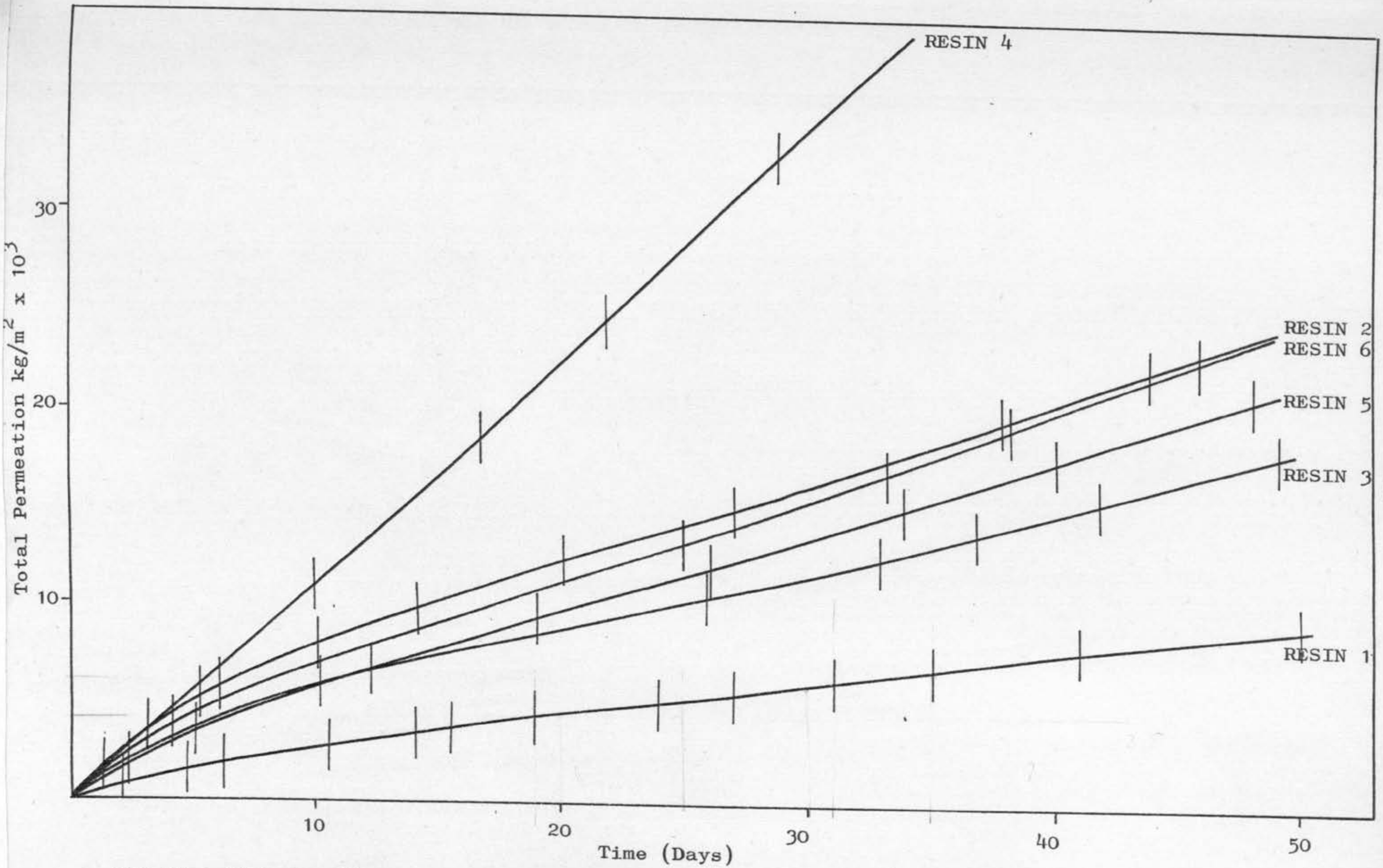


Fig. 30: Effect of Resin Composition on Transmission of Water Through Chopped Strand Laminates (corrected to 1 cm thickness)

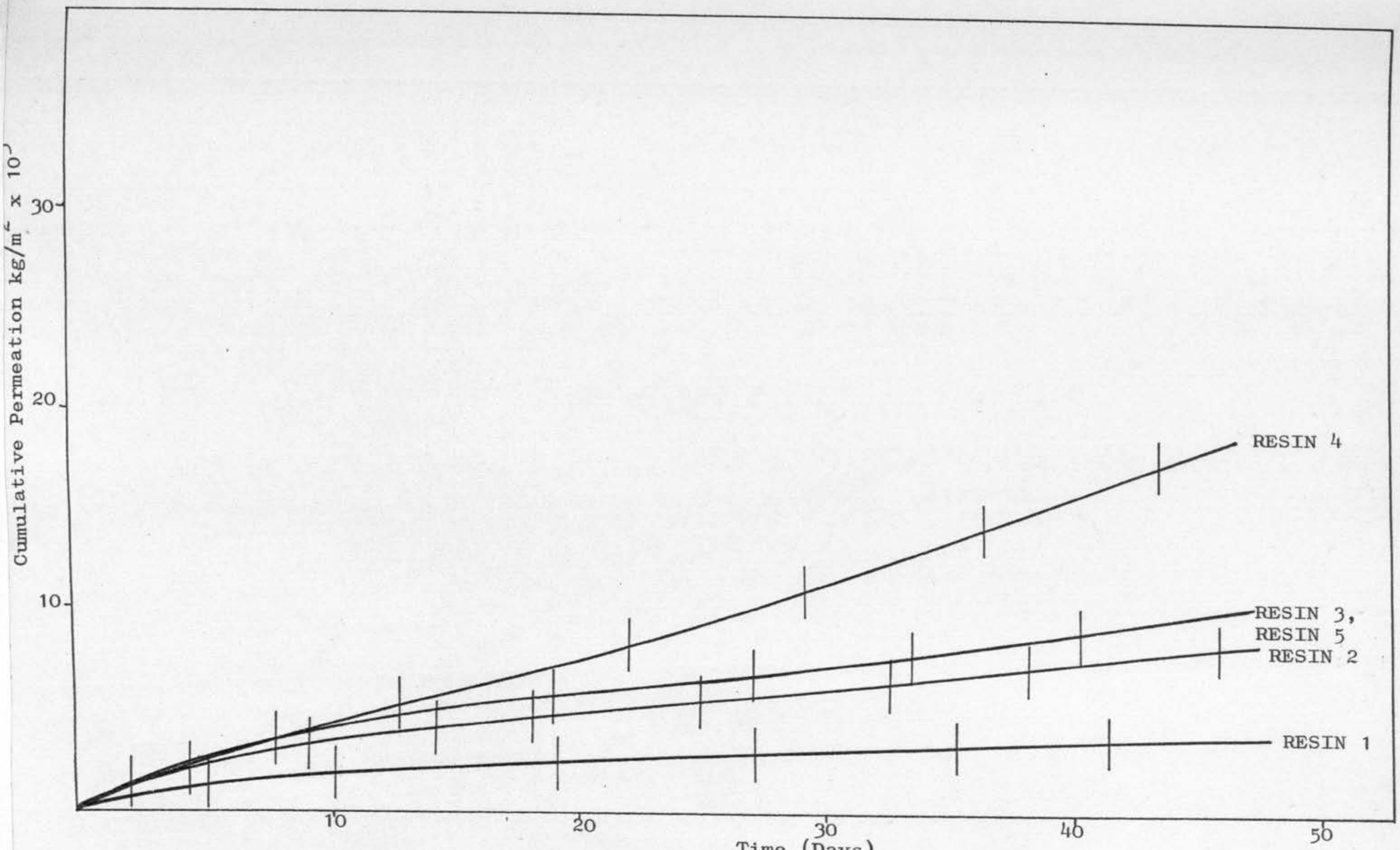


Fig. 31: Effect of Resin Composition on Transmission of Water Through Woven Roving Laminates (corrected to 1 cm)

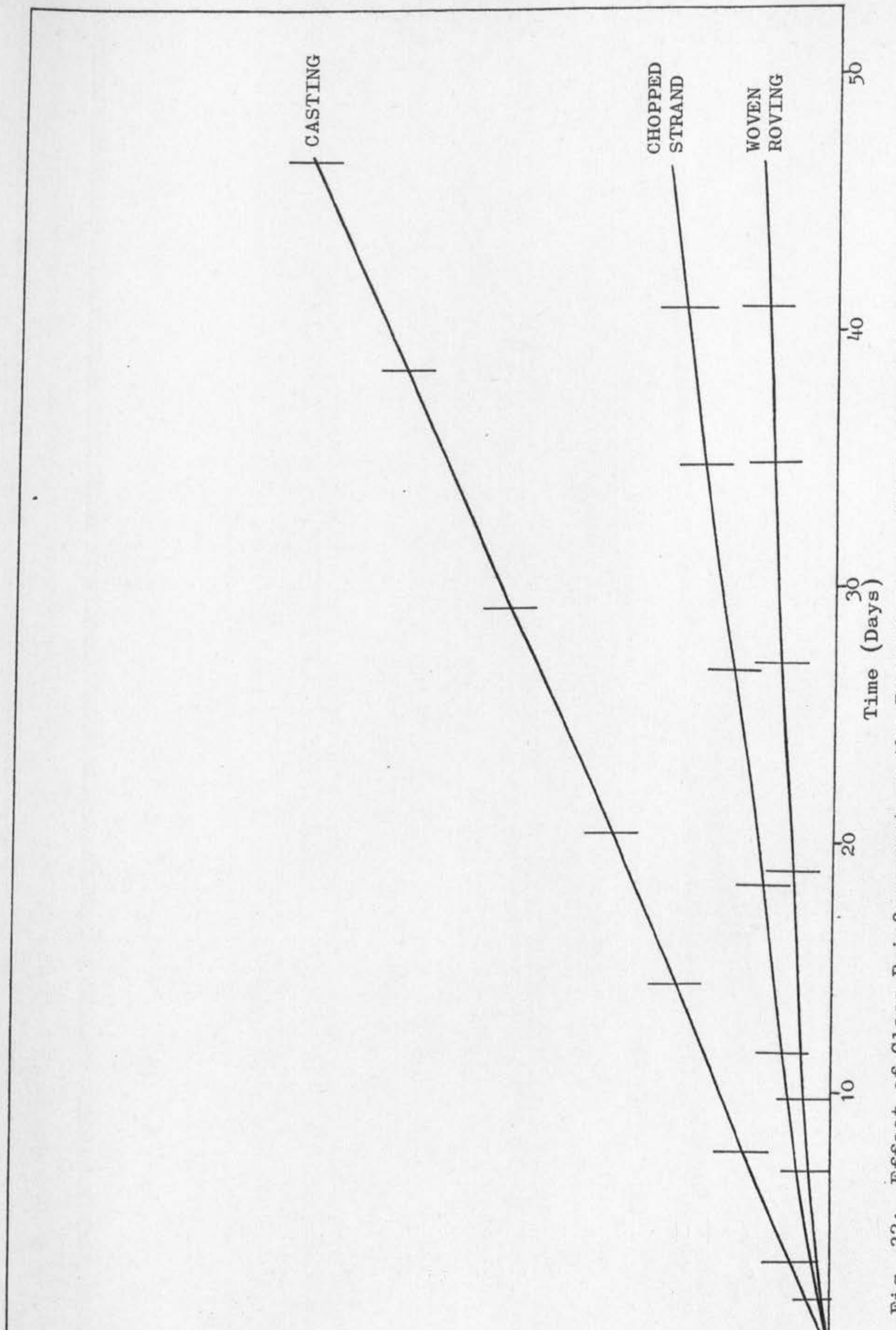


Fig. 32: Effect of Glass Reinforcement on the Transmission of Water Through Resin 1 (corrected to 1 cm)

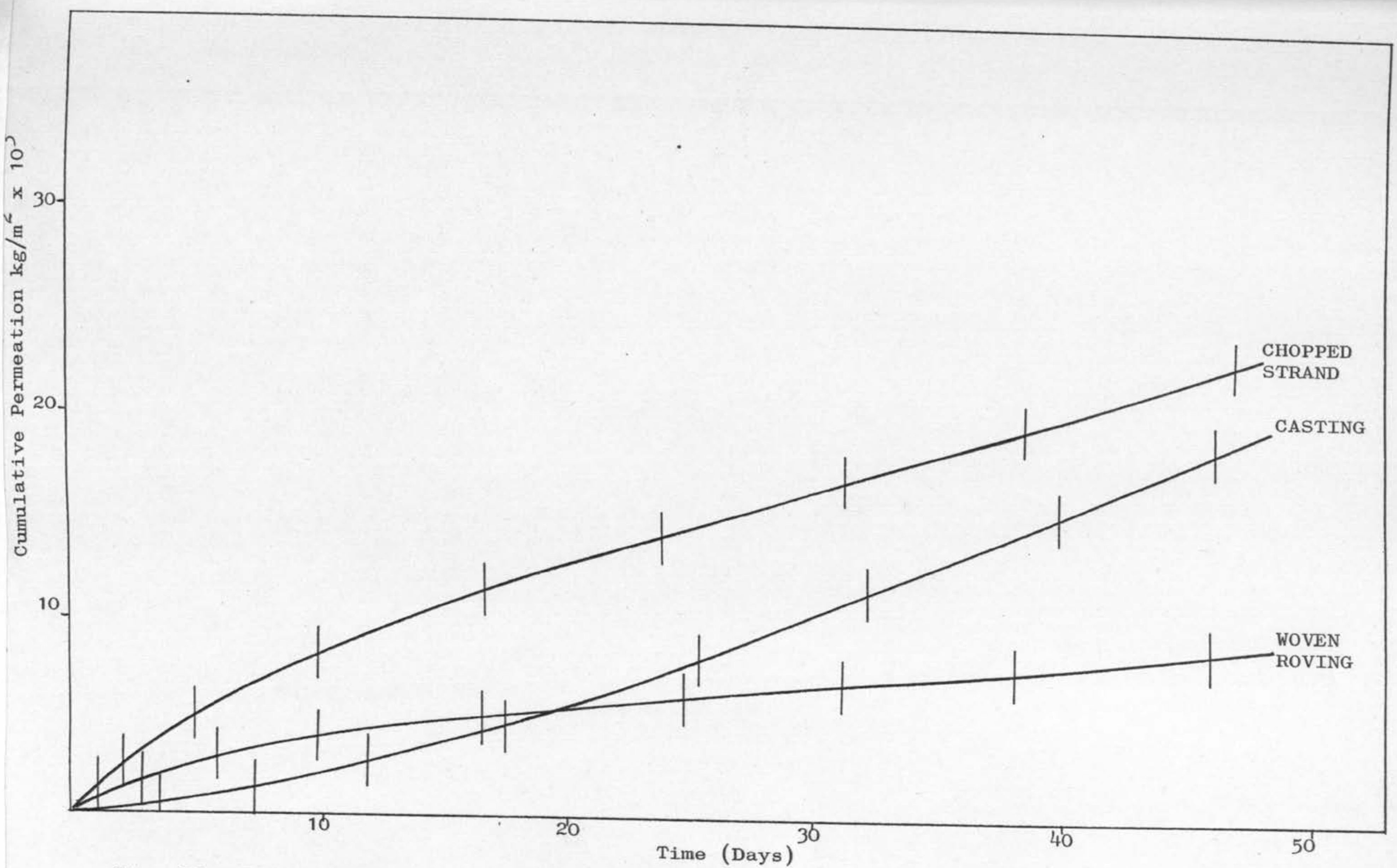


Fig. 33: Effect of Reinforcement on Transmission of Water Through Resin 2 (corrected to 1 cm)

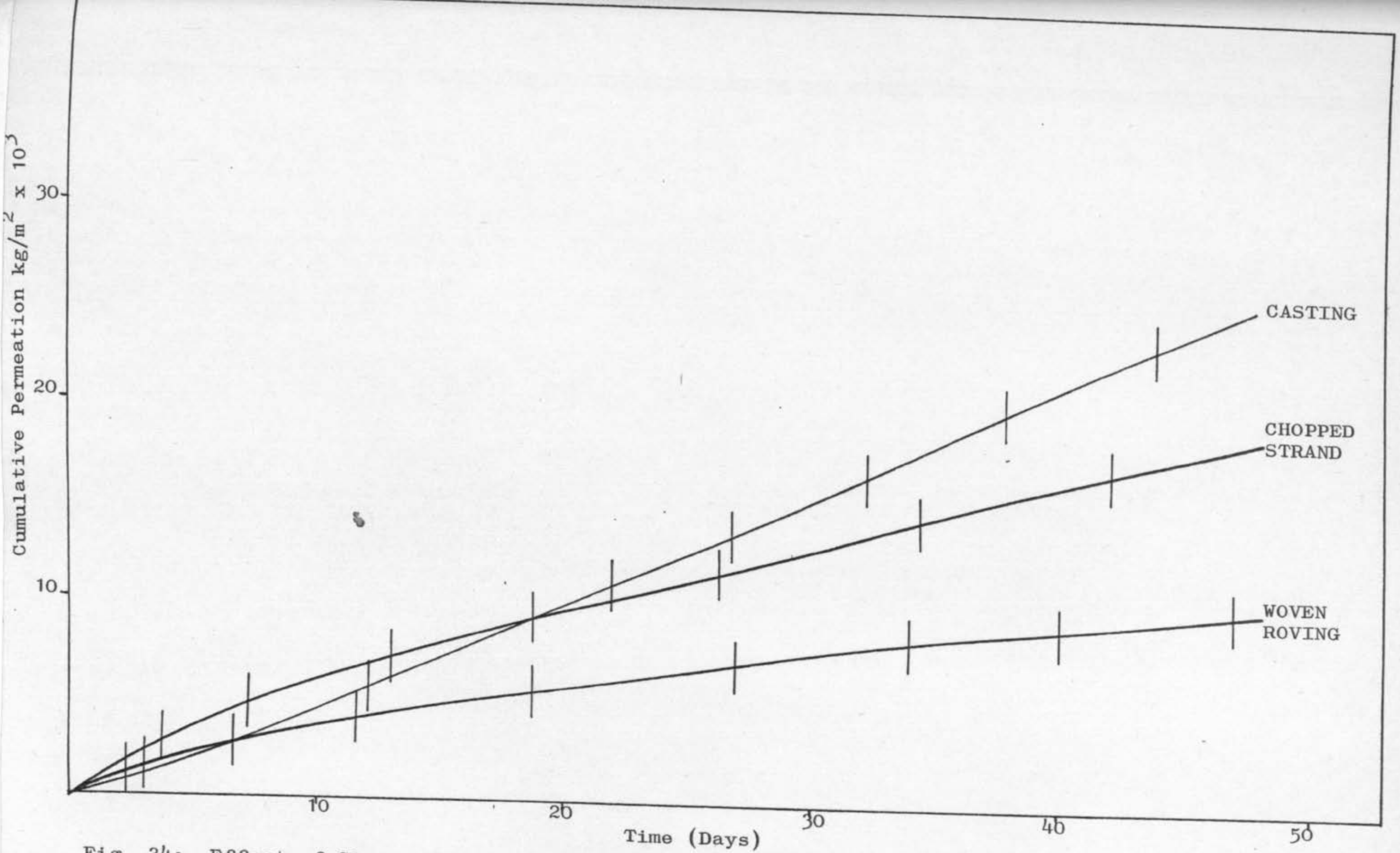


Fig. 34: Effect of Glass Reinforcement on the Transmission of Water Through Resin 3 (corrected to 1 cm)

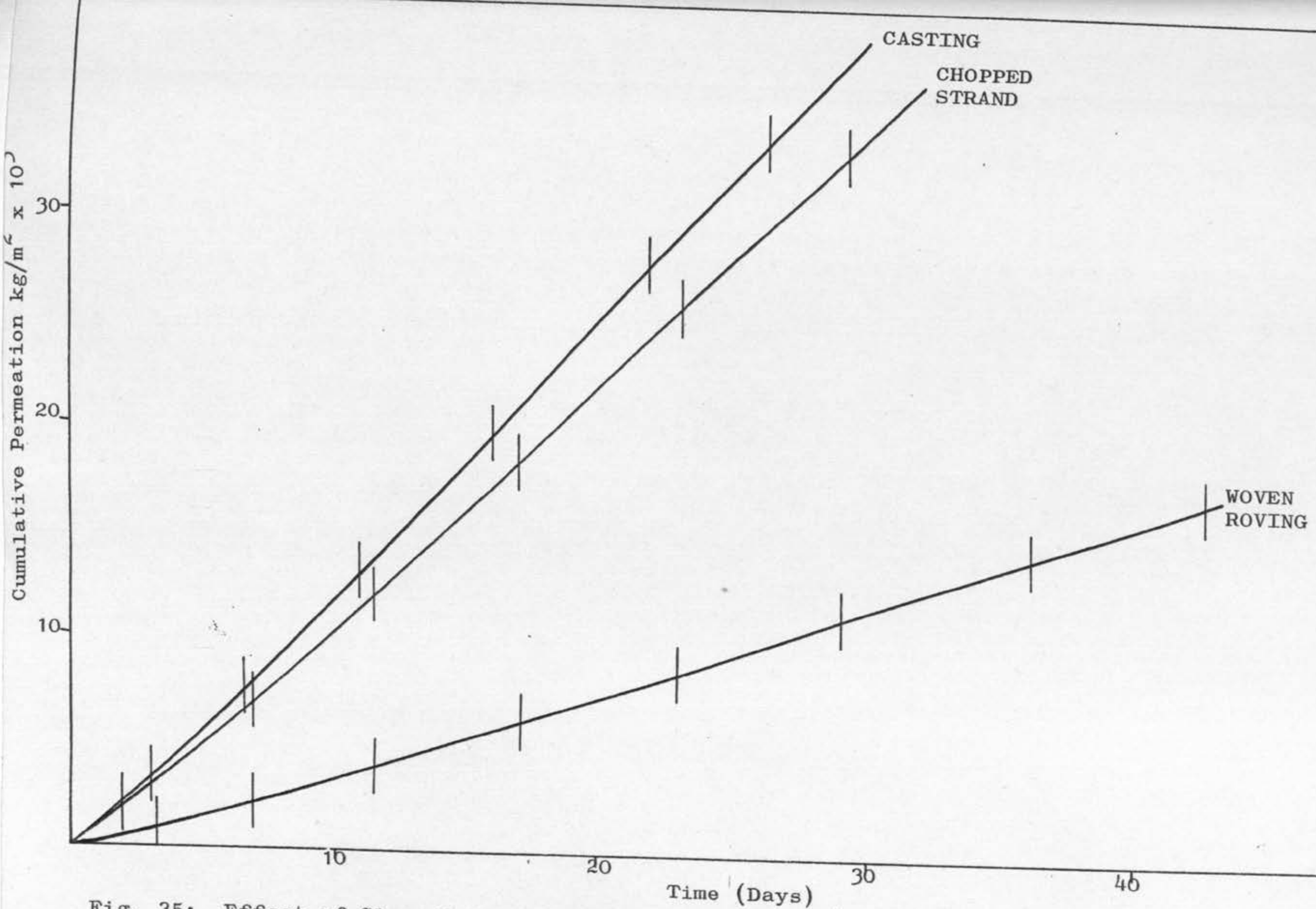


Fig. 35: Effect of Glass Reinforcement on Transmission of Water Through Resin 4 (corrected to 1 cm)

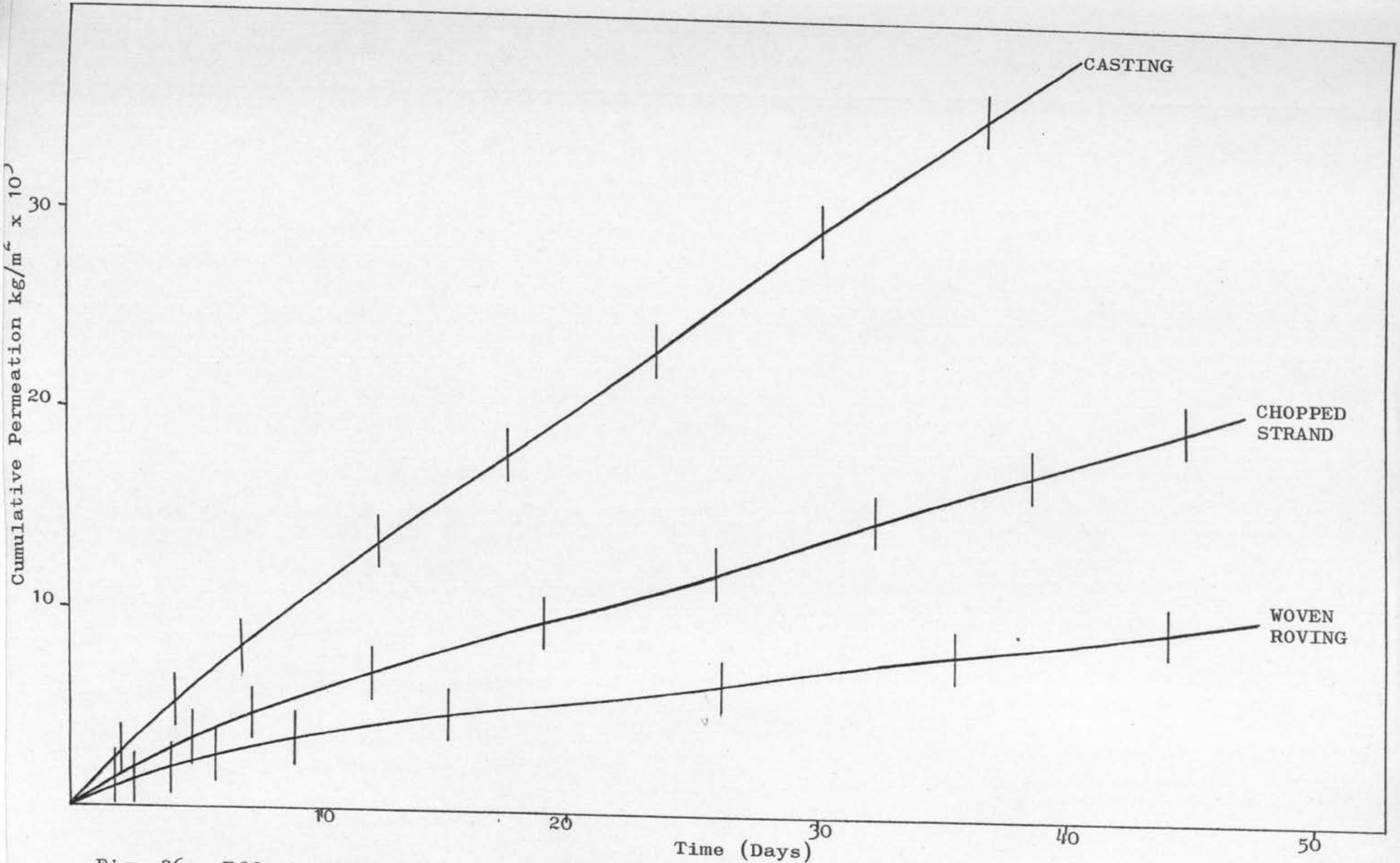


Fig. 36: Effect of Reinforcement on Transmission of Water Through Resin 5 (corrected to 1 cm)

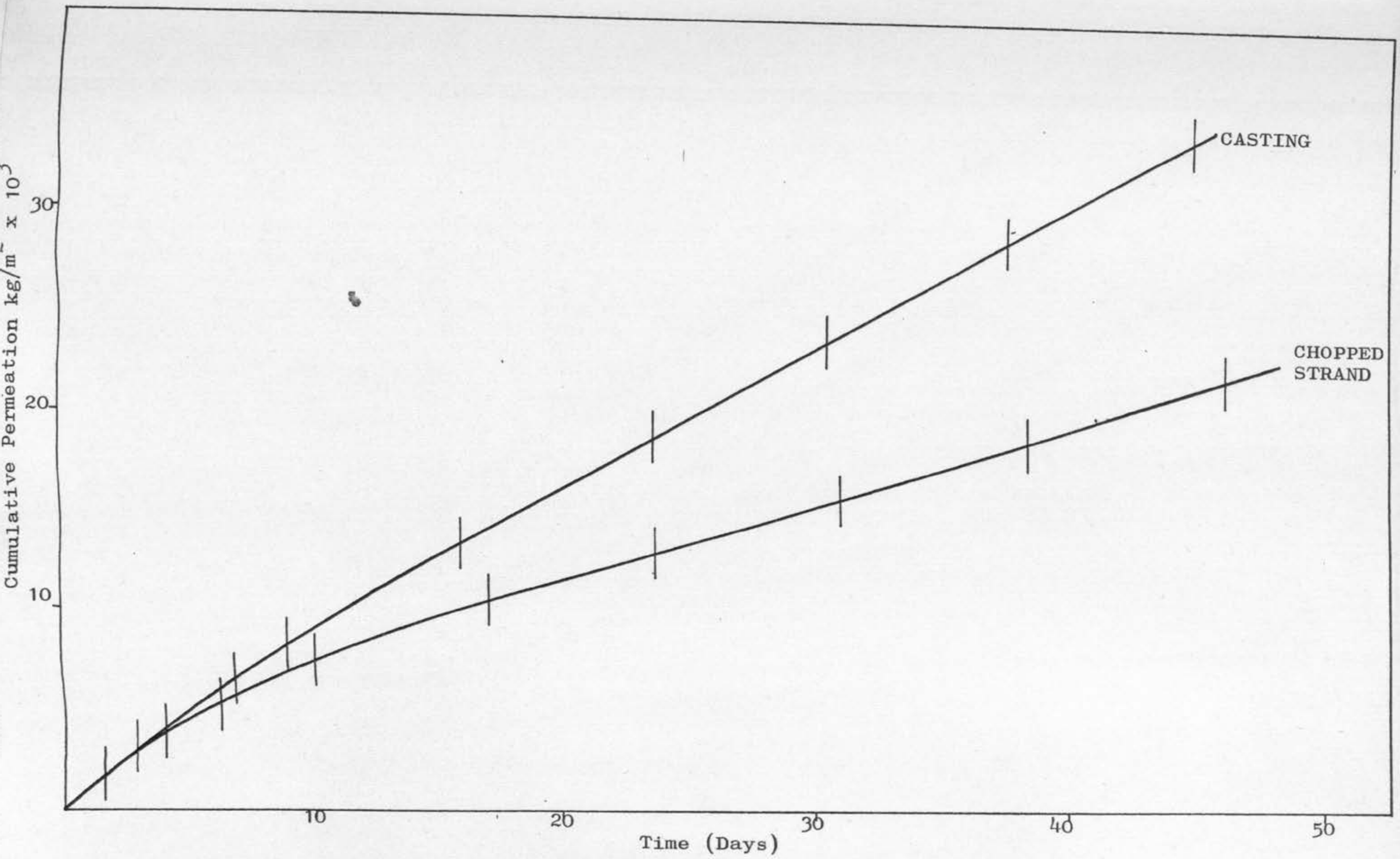


Fig. 37: Effect of Glass Reinforcement on Transmission of Water Through Resin 6 (corrected to 1 cm)

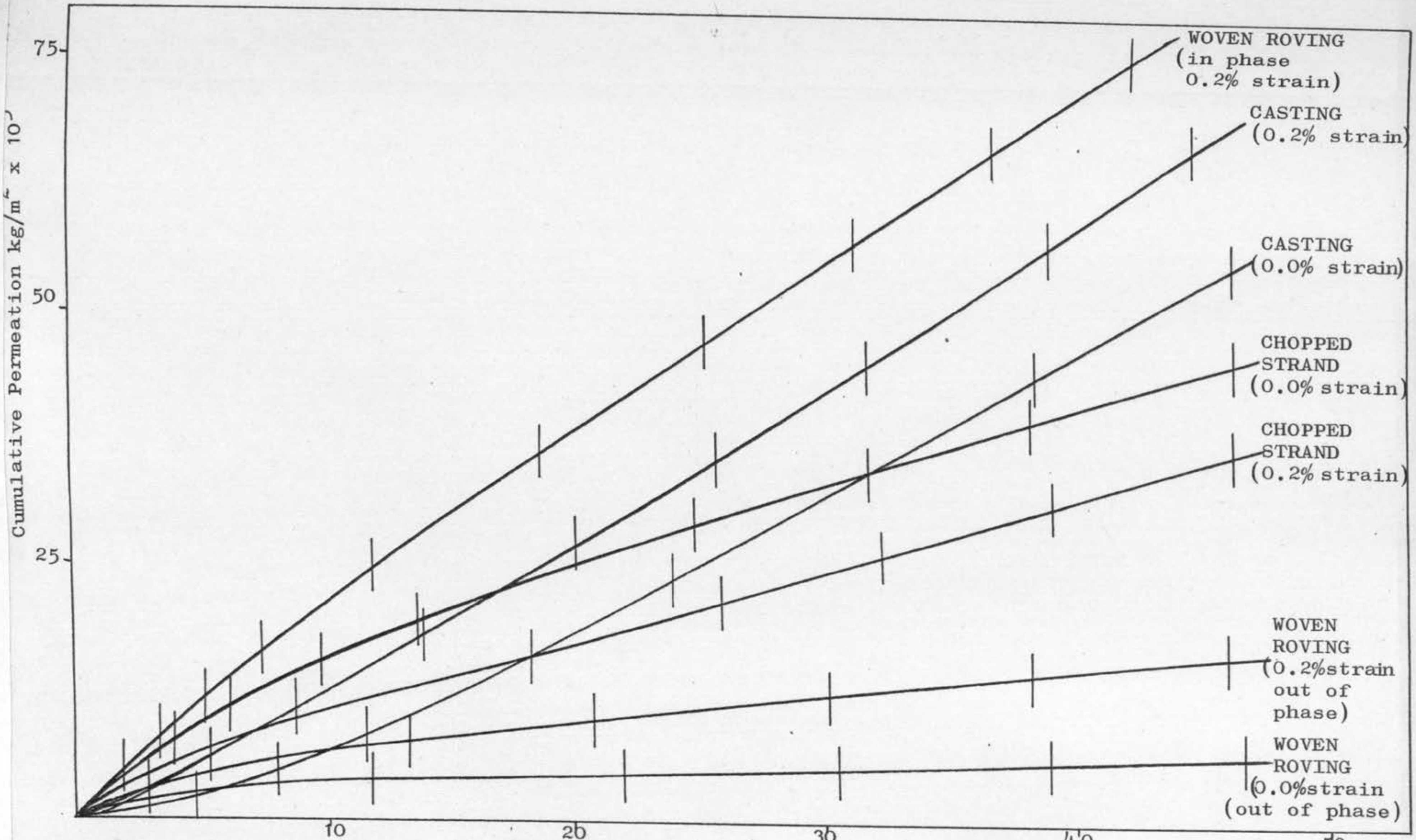


Fig. 38: Effect of Strain on Transmission of Water Through Castings and Laminates Made from Resin 2 (corrected to 1 cm)

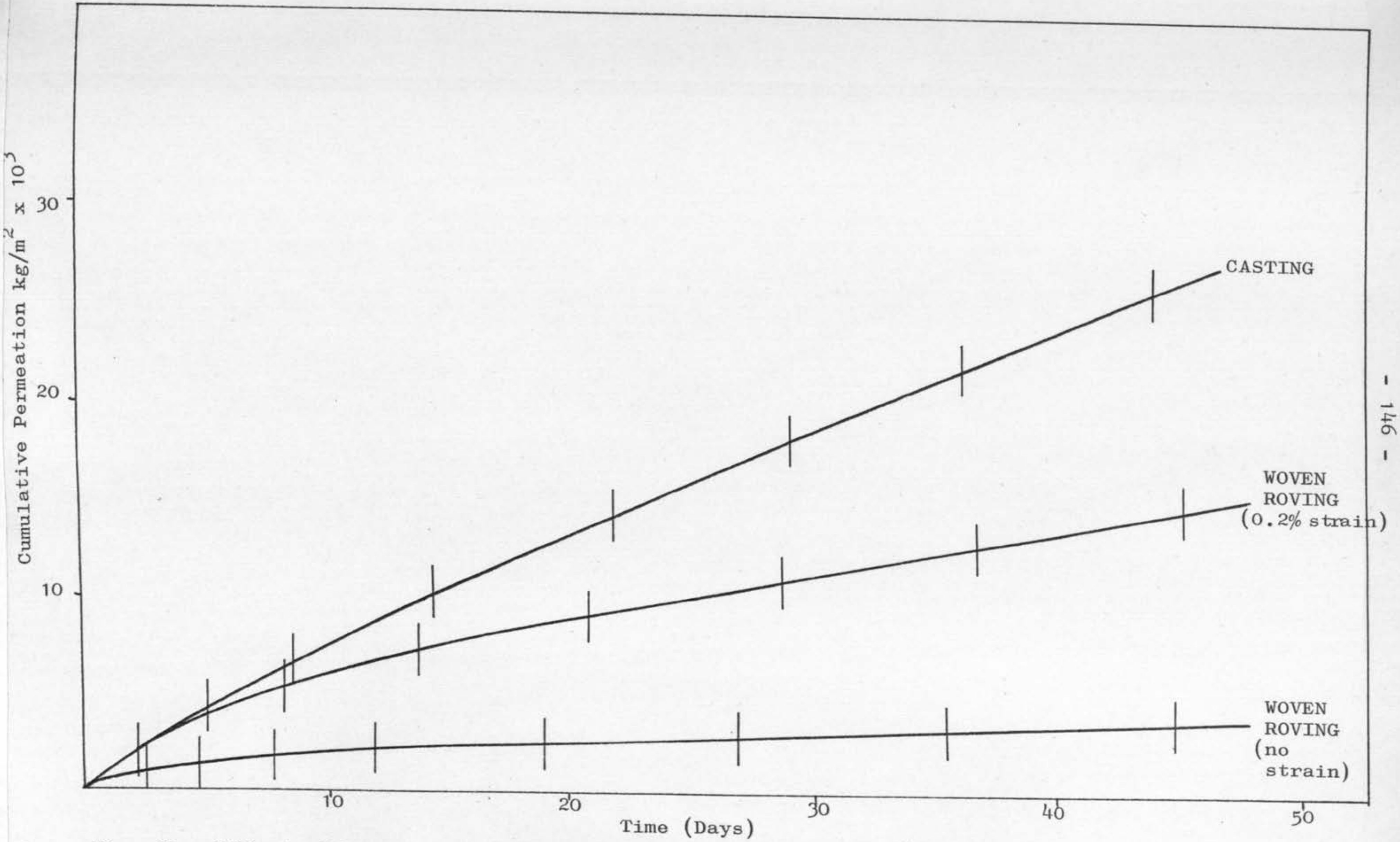


Fig. 39: Effect of Strain on Transmission of Water Through Castings and Laminates made from Resin 1 (corrected to 1 cm)

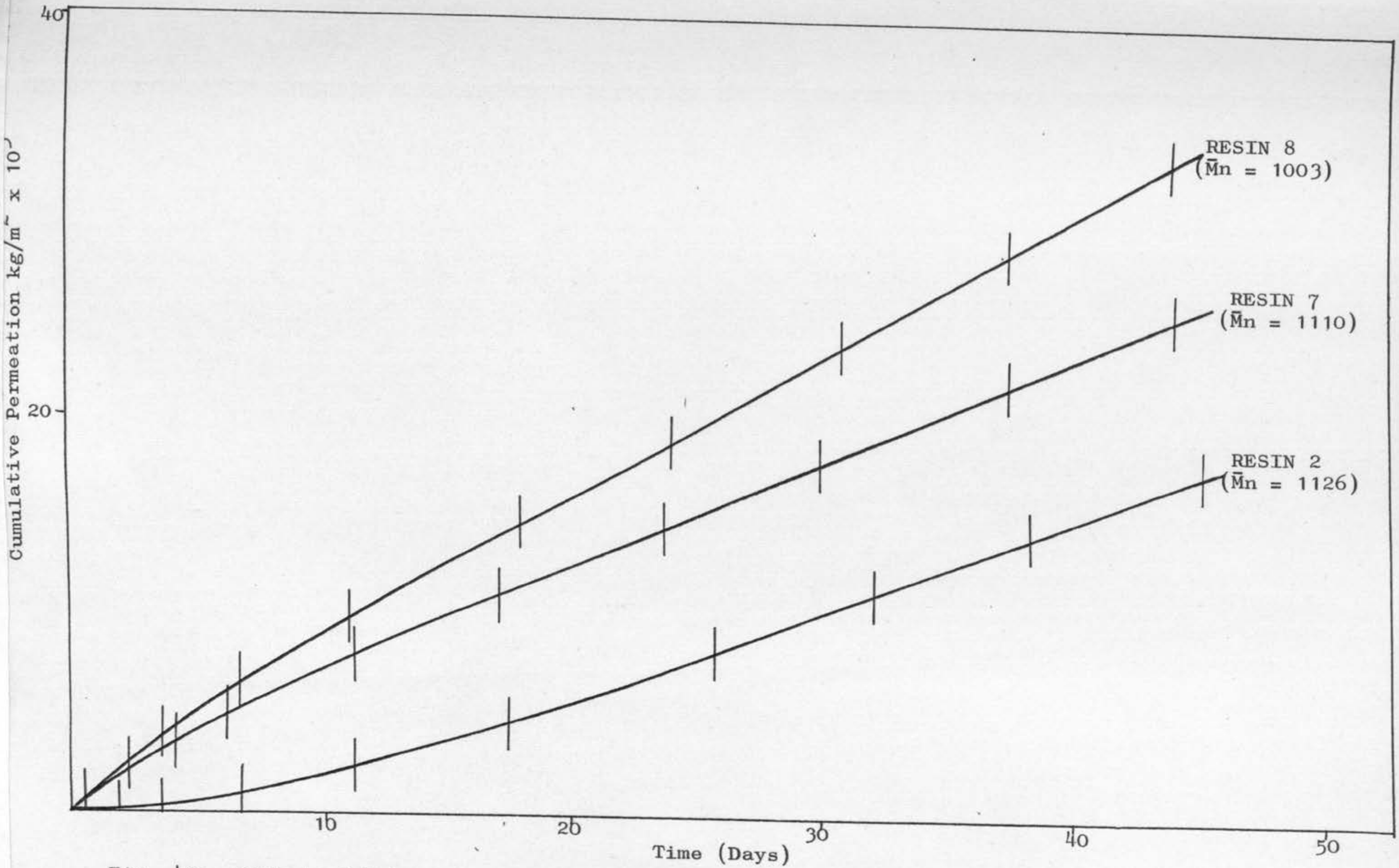


Fig. 40: Effect of Molecular Weight Distribution on Transmission of Water Through Castings (corrected to 1 cm)

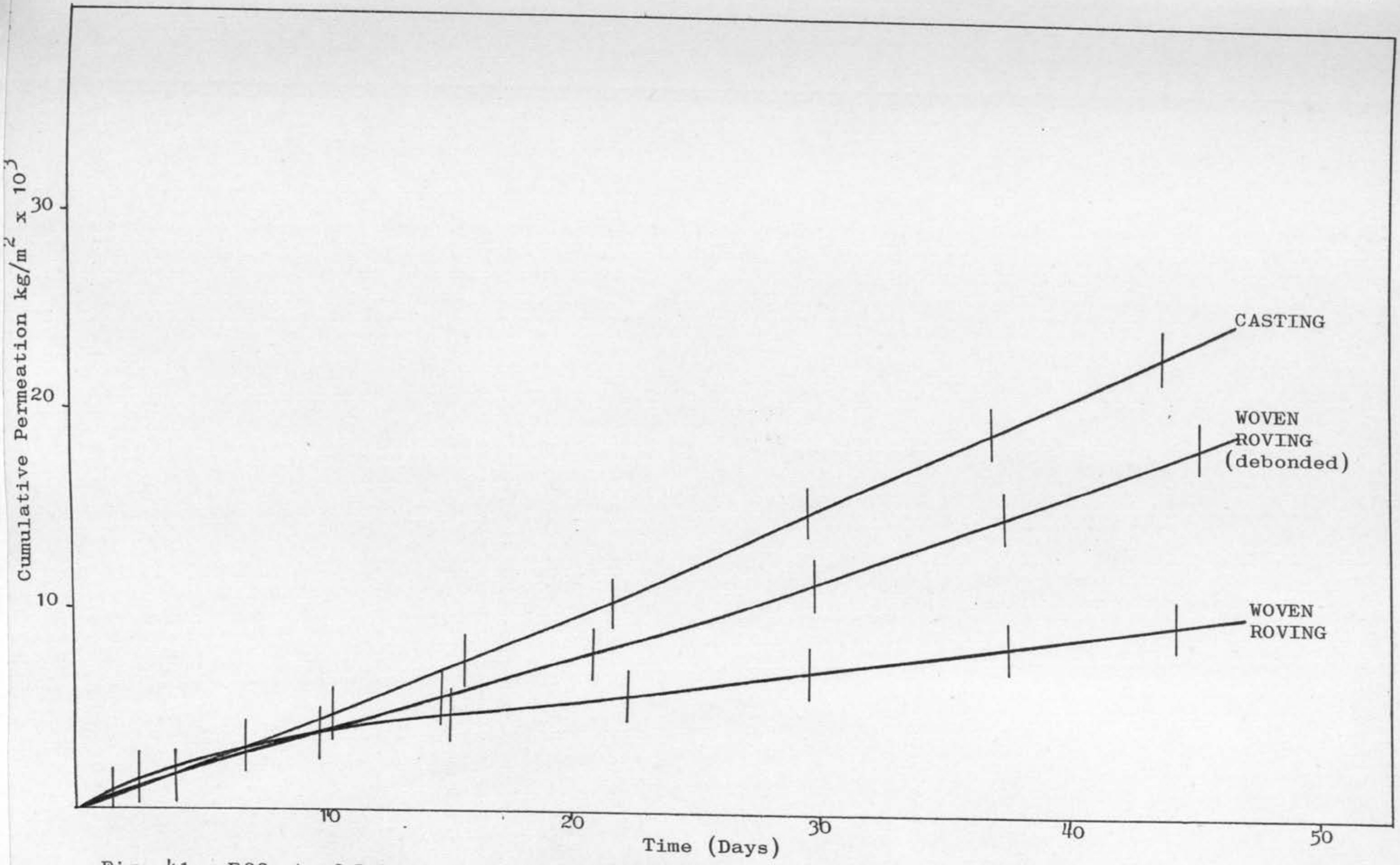


Fig. 41: Effect of Debonding on Transmission of Water Through Woven Roving Laminates made from Resin 3 (corrected to 1 cm)

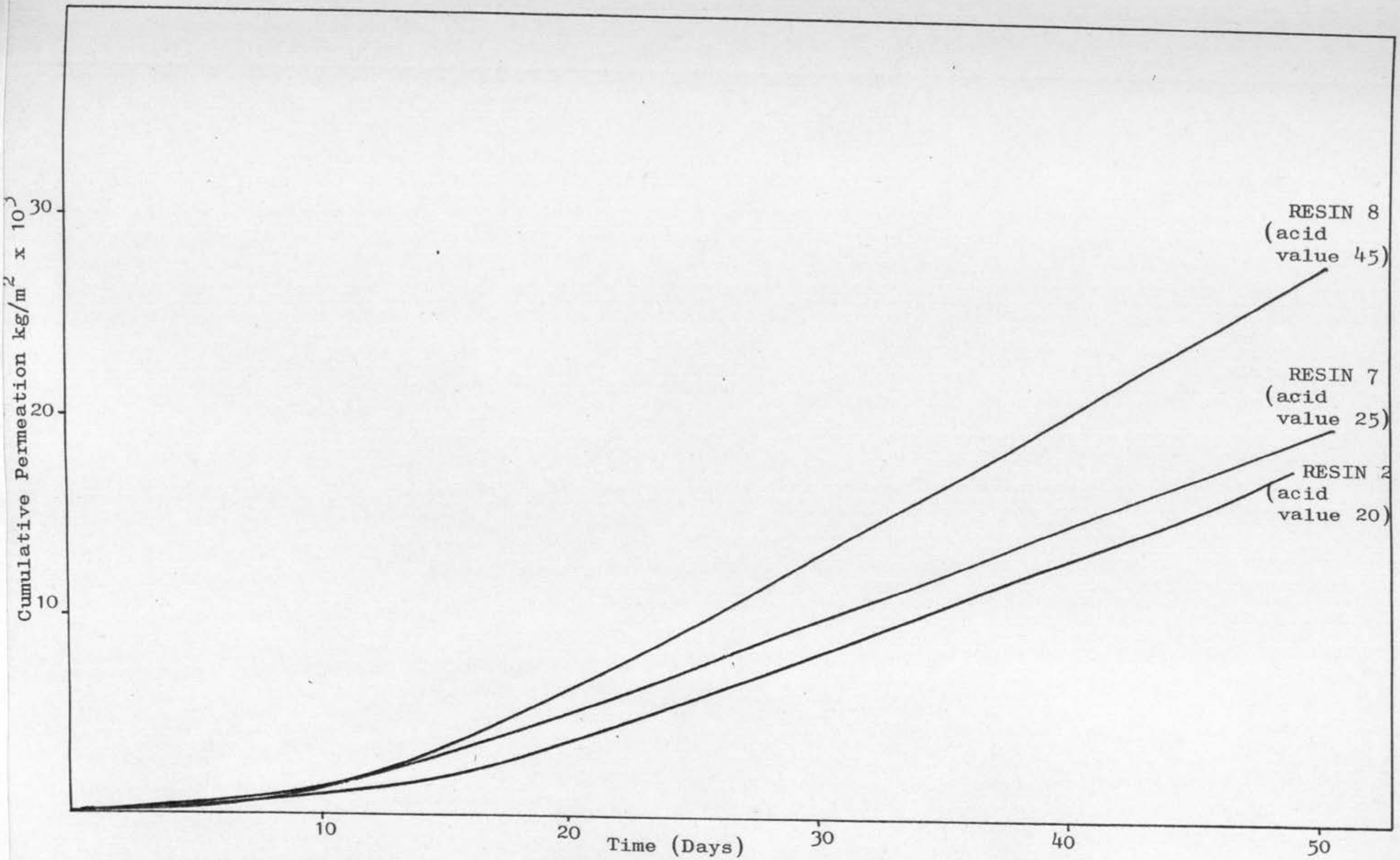


Fig. 42: Corrected Transmission of Water through Castings made from Resin with various Acid Values (corrected to 1 cm)

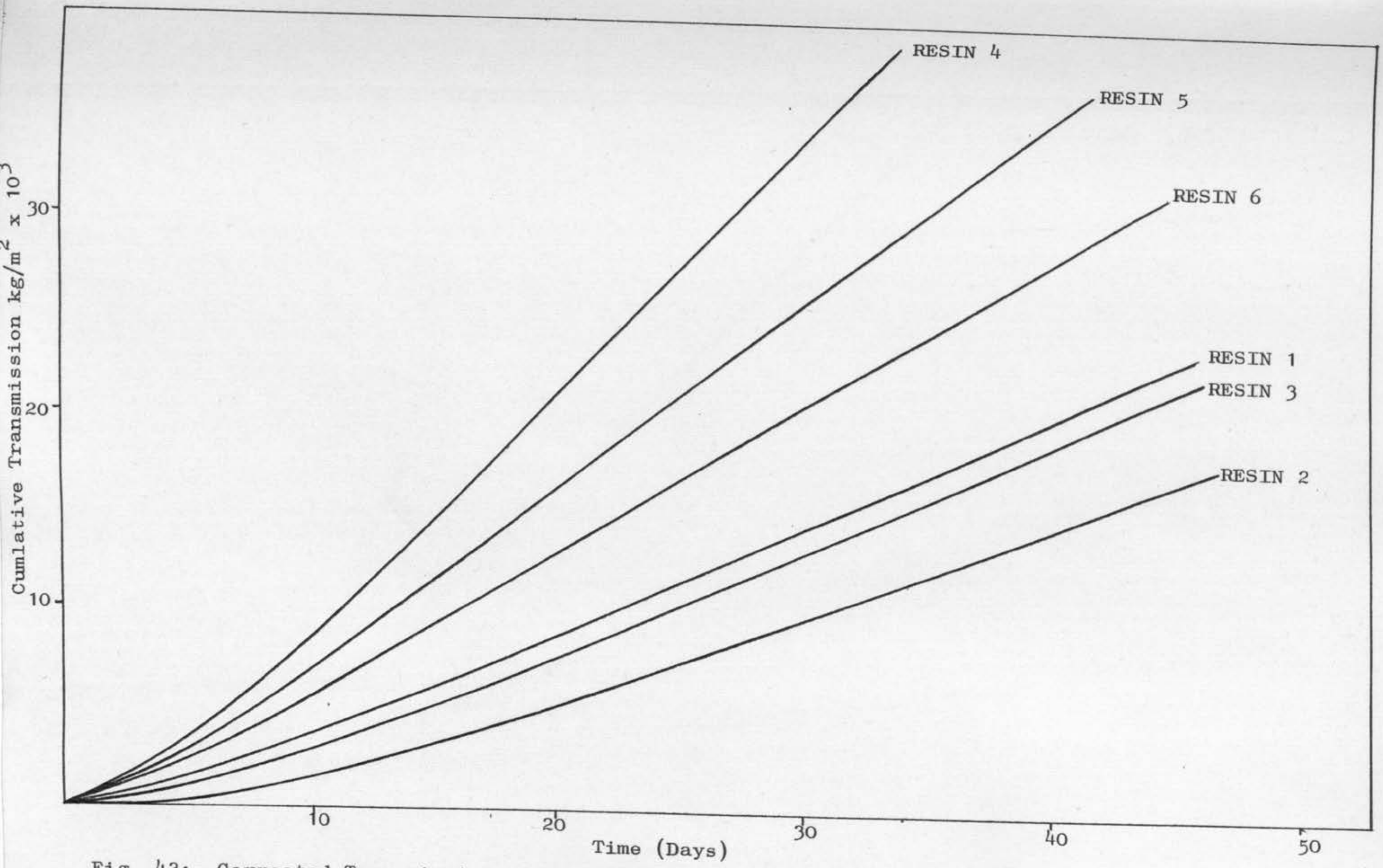


Fig. 43: Corrected Transmission of Water Through Castings made from Different Resins (corrected to 1 cm)

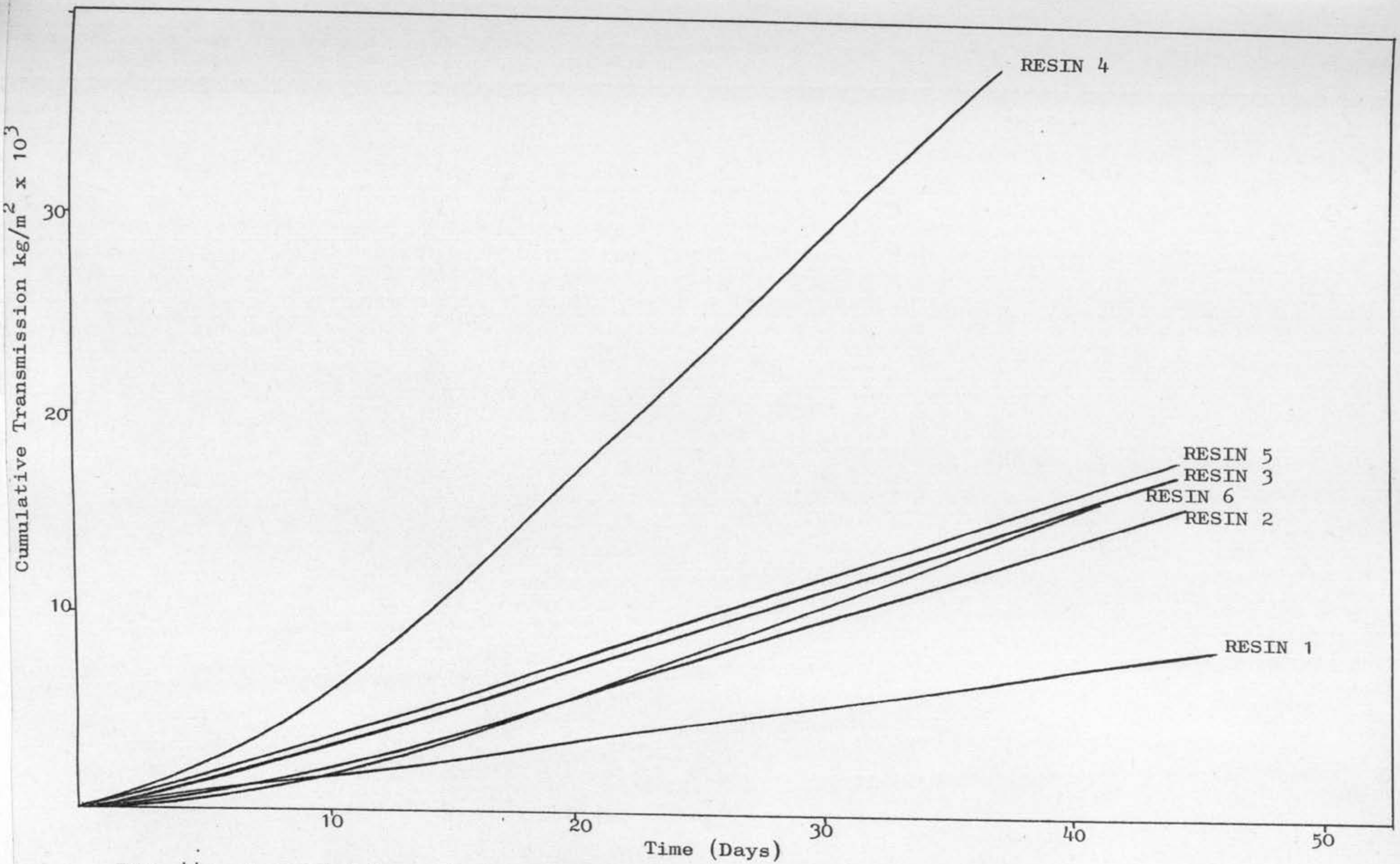


Fig. 44: Corrected Transmission of Water Through Chopped Strand Laminates made from Various Resins (corrected to 1 cm)

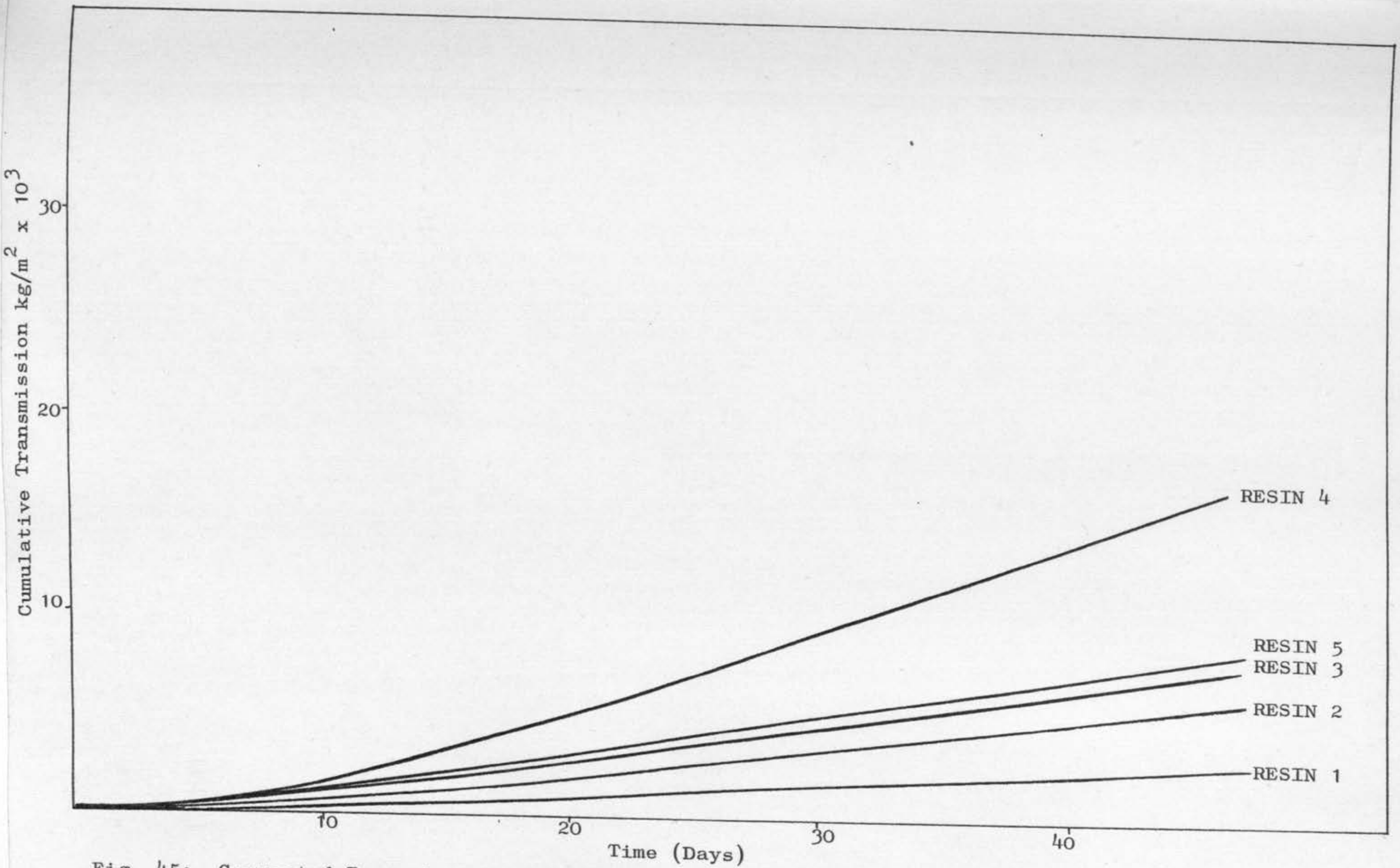


Fig. 45: Corrected Transmission of Water Through Woven Roving Laminates made from Different Resins (corrected to 1 cm)

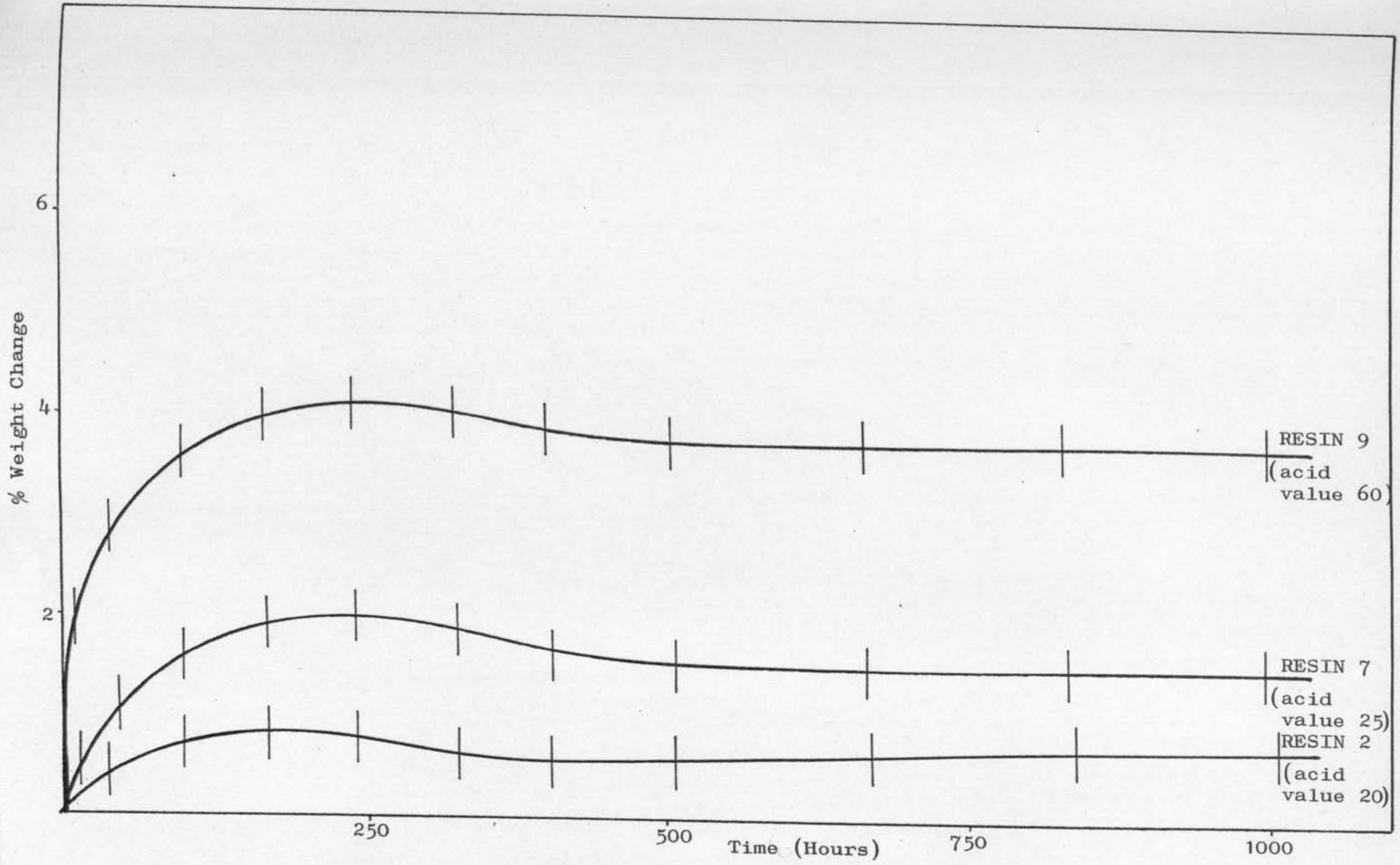


Fig. 46: Effect of Acid Value on the Weight Changes of Resins

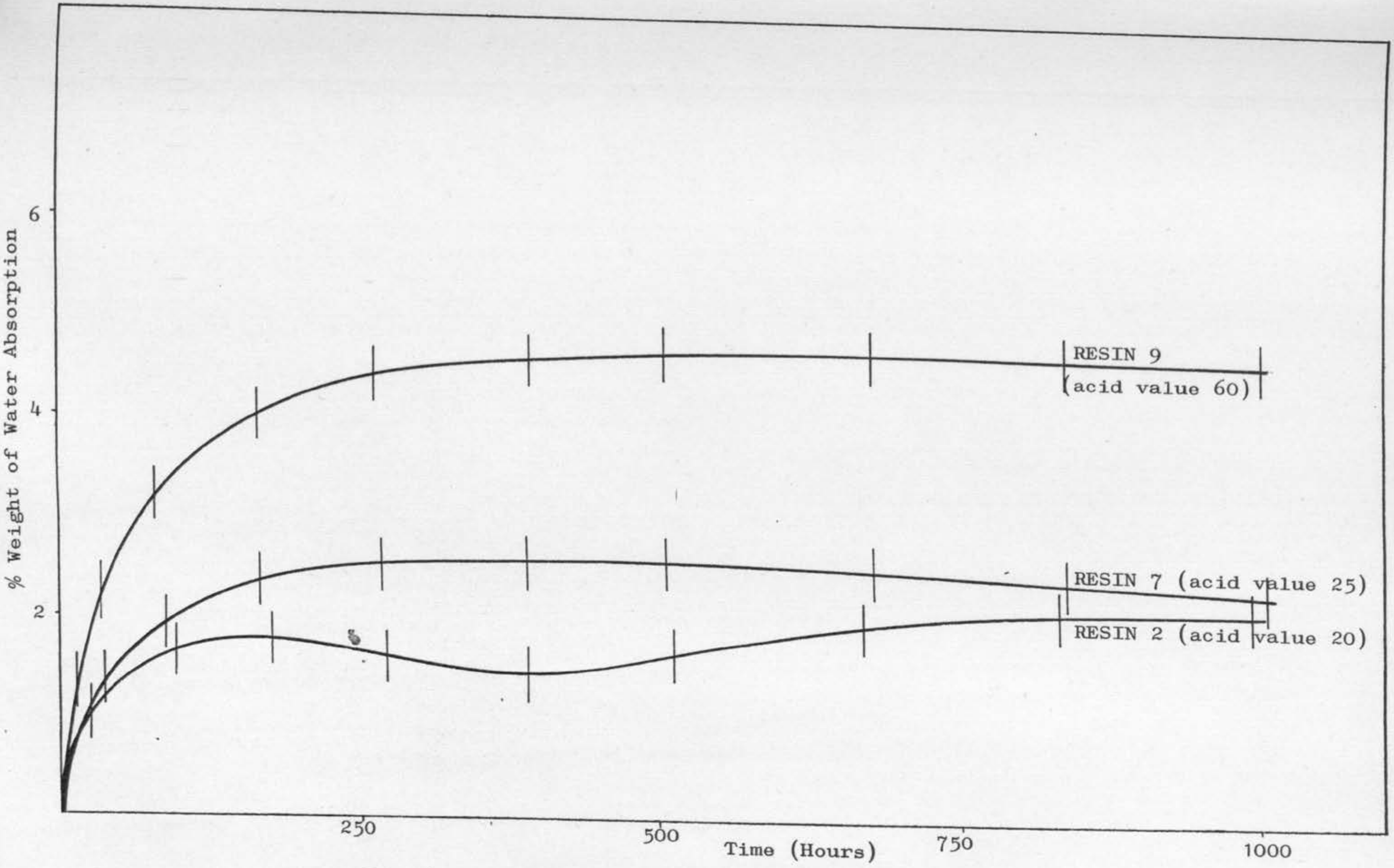


Fig. 47: Effect of Acid Value on Water Absorption of Resins

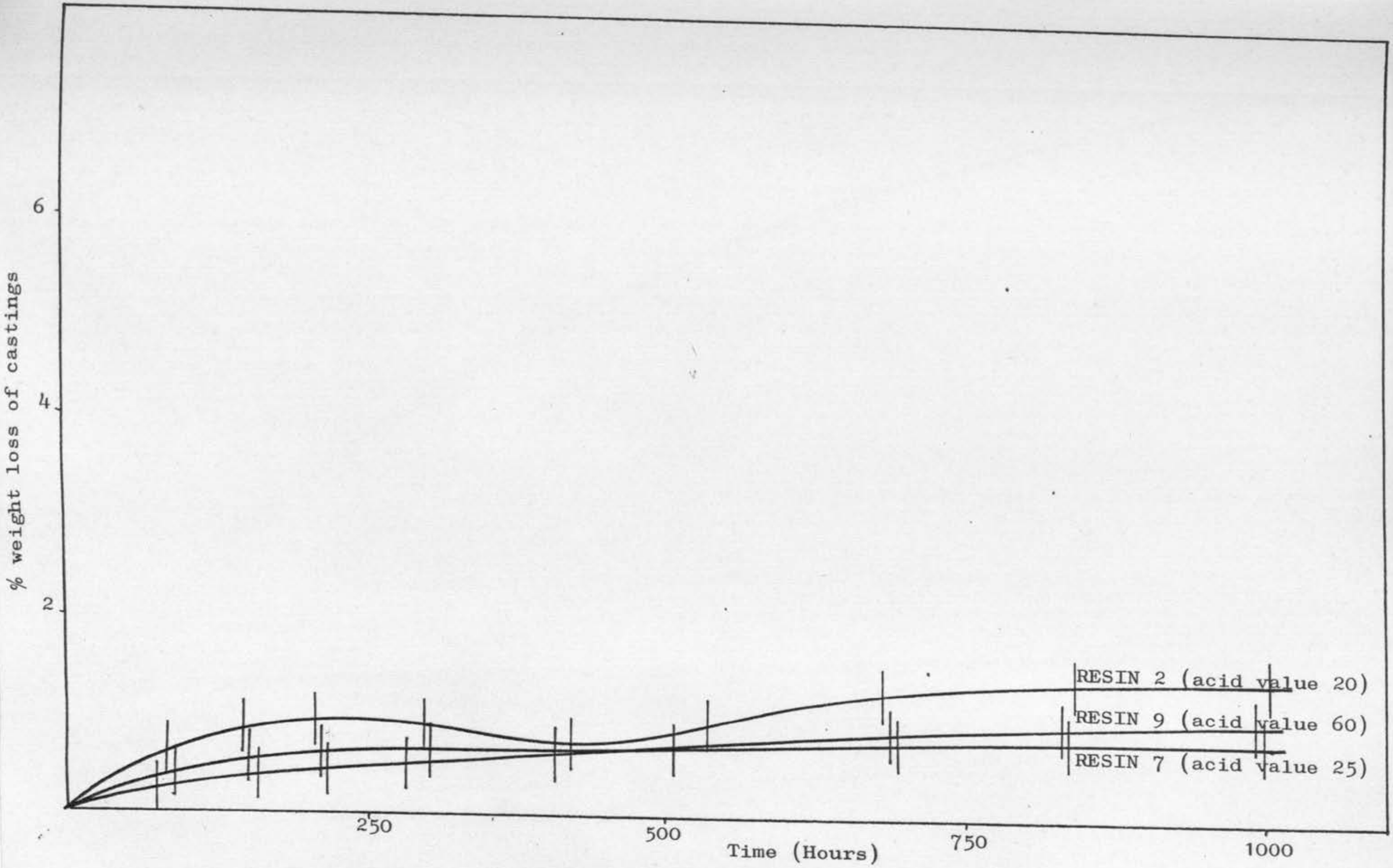


Fig. 48: Effect of Acid Values on Leaching of Materials

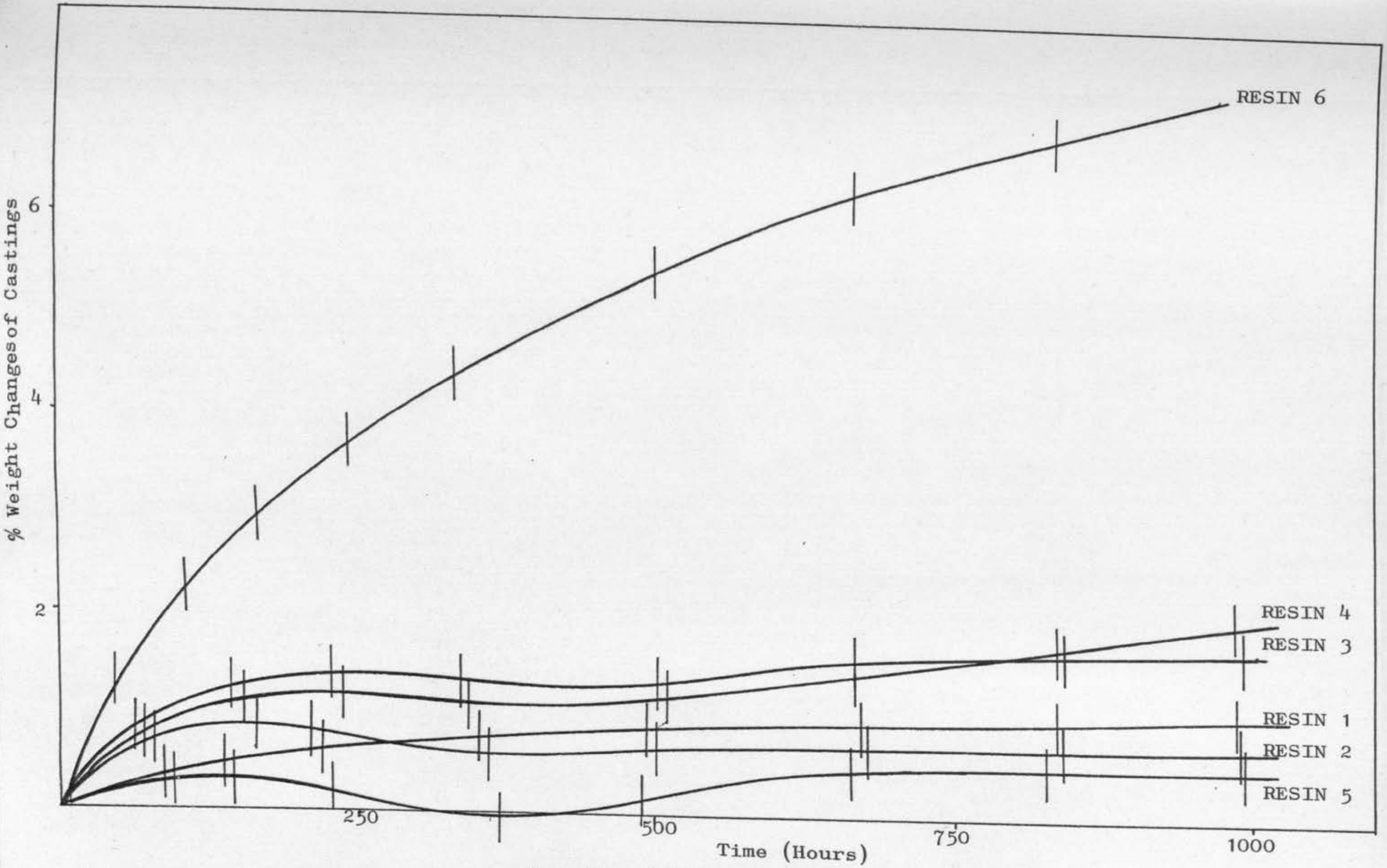
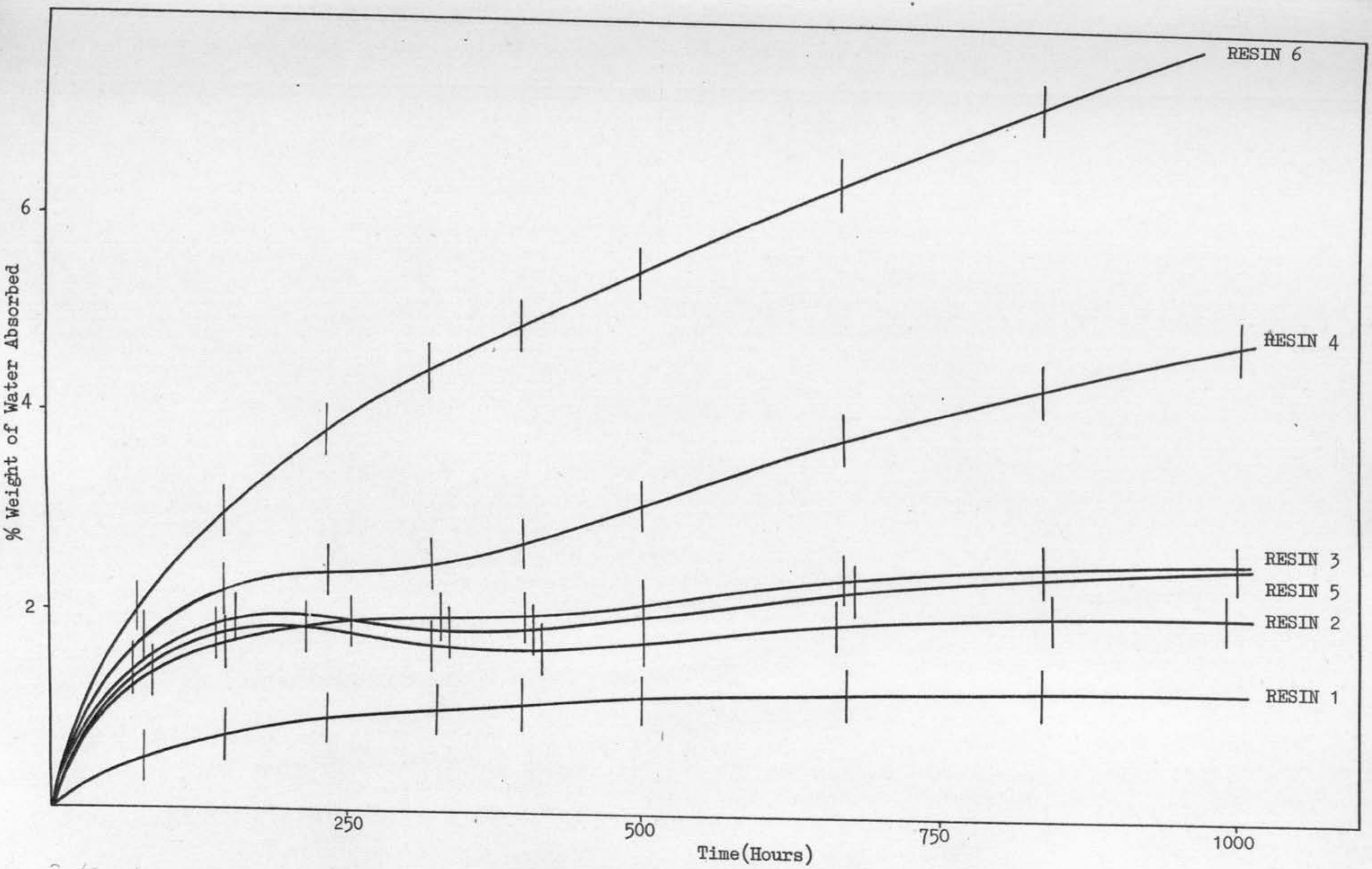


Fig. 49: Weight Changes of Castings

Temp. 50°C



? temp

Fig. 50: Dependence of Water Absorption in Castings on Resin Composition

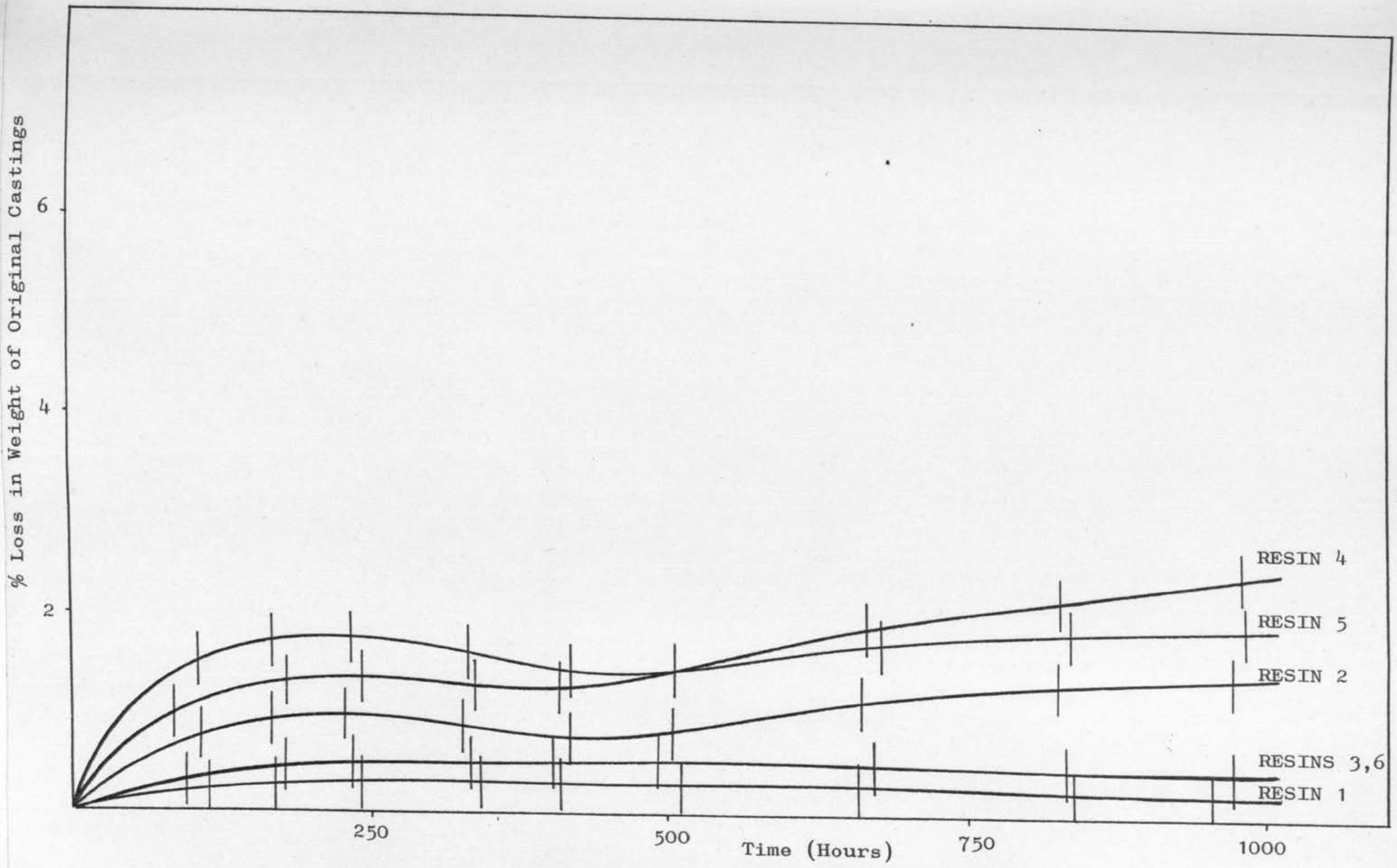


Fig. 51: Dependence of Weight Loss in Castings on Resin Composition

CHAPTER FOUR

DISCUSSION

4.1 REPRODUCIBILITY AND ACCURACY

4.1.1 Variability in the Properties of Resins

(i) Variation between Batches

Unsaturated polyester resins are generally made by a batch process. The acid value molecular weight distribution and styrene content of an uncured polyester resin can vary from batch to batch and may induce changes in the properties of castings and laminates made from different batches. Therefore, in the present investigation only one batch was used for each resin.

(ii) Storage Life of Resins

Unsaturated polyester resins have a limited life at room temperature, which is considerably reduced at temperatures greater than 25°C, or if the resin is exposed to the light. In order to maximise the storage life of the resins used in the present investigation, they were stored in lacquered cans at -10°C.

4.1.2 Specimen Fabrication Problems

(i) Castings

Void free castings without built-in stresses are difficult to prepare. Efforts were made, as described in the Experimental section, to obtain such castings. All resins were freed from dissolved air to reduce the formation of voids and bubbles.

Samples were prepared on the substrate, "melinex", i.e. polyester film, to avoid the possibilities of release agent having any influence on the water transmission measurements.

(ii) Laminates

It is difficult to make laminates without any voids or dry areas. The voids in the laminates were kept to a minimum (approx. 3% by volume). Laminate thicknesses were between 3 and 4.5 mm. Glass contents of chopped strand laminates were 18.2 ± 3% by volume. Woven roving laminates contained 25 to 32% by volume of glass fibres. Within a single laminate, specimens differed only by about 1%.

4.1.3 Sources of Error in the Measurement Techniques

(i) Possible Sources of Error

a) Entry of water vapour from the atmosphere into the desiccant chamber through the rubber seal.

b) Absorption of water vapour by the desiccant during removal for weighing.

c) Skin formation on desiccant after prolonged exposure.

d) Temperature fluctuations in the water.

e) Variations in thickness between samples.

f) Partial pressure created by unabsorbed vapour in the desiccant chamber.

(ii) Refinements to Minimise Errors

The procedures described in the Experimental section were adopted to correct for (a) and (b) above, and to minimise (c) and (d). It is reasonable to assume that (c) is of negligible importance because the desiccant was frequently changed.

Temperature fluctuation was kept to ± .5°C by the use of suitable thermostats.

(e) is a major factor which could cause error in the permeability calculations.

Fig. 28 shows the permeabilities of castings in the thickness range 0.18 mm to 3.75 mm. It is evident from the figure that transmission rate cannot be described in terms of the inverse law usually employed. However, transmission rate converted to unit thickness can be adopted, provided the thickness of the test films used lies within a close band. Hence, in the present investigation the thicknesses of all specimens made, castings as well as laminates, were kept between 3 and 4.5 mm.

Error (f) is minimal, provided that the rate of absorption of vapours by the desiccant is greater than the rate of permeation of water. This should be the case with a very powerful desiccant such as phosphorus pentoxide. When phosphorus pentoxide is used the equilibrium residual water vapour in dried air is 1 mg to 40,000 l air (51, 52).

(iii) Assumptions Made

After assessing the effect of these problems on the measurements, certain qualifications have to be made when calculating the transmission rate of water through castings and laminates.

1) The vapour pressure of water or any other monomer materials collected on the "dry side" of the cell is negligibly small.

2) The effect of voids in laminates can be neglected, provided that the total void content is less than 3% and no voids exist larger in diameter than 5% of the sheet thickness.

3) The transmission rate is inversely proportional to the thickness of the test specimen within the range of sample thickness employed in this investigation.

It was also assumed that the pressure, due to the head of liquid water above the specimen, was of negligible importance in the range 0.05 - 0.25 metres (this had been established previously by Taneja (40).

4.1.4 Comparisons with Other Published Data

The results obtained were compared to those of other workers using similar materials.

Table 25a shows, in order of magnitude of permeability, results similar to those obtained in the present work. However, table 25b illustrates the large variations in permeabilities caused by materials and exposure conditions.

Table 25a: Comparison of Results with other Published Data

TEMPERATURE	POLYMER*	REINFORCEMENT	THICKNESS	GLASS CONTENT % BY WEIGHT	EXPOSURE TIME	PERMEABILITY kg/m^{2}day/cm x 10^4	REFERENCE
50°C	isophthalic resin	castings	not known	-	3 weeks	10.4	40
60°C	isophthalic resin	castings	not known	-	3 weeks	13.0	40
70°C	isophthalic resin	castings	not known	-	3 weeks	19.3	40
80°C	isophthalic resin	castings	not known	-	3 weeks	38.4	40
30°C	isophthalic resin	chopped strand	not known	25	3 weeks	2.7	40
50°C	isophthalic resin	chopped strand	not known	25	3 weeks	6.3	40
70°C	isophthalic resin	chopped strand	not known	25	3 weeks	16.1	40
80°C	isophthalic resin	chopped strand	not known	25	3 weeks	34.1	40
80°C	bisphenol-A fumarate	chopped strand	1 cm	not given (but estimated to be 27)	12 weeks	24.0	39

*polyester - unless otherwise stated

Table 25a (cont.)

TEMPERATURE	POLYMER*	REINFORCEMENT	THICKNESS	GLASS CONTENT % BY WEIGHT	EXPOSURE TIME	PERMEABILITY kg/m^{2}day/cm x 10^4	REFERENCE
100°C	bisphenol-A fumarate	woven roving	1 cm	48	12 weeks	6.0	39
50°C	resin 1	castings	3.4 cm	-	5 weeks	5.9	present work
50°C	resin 2	castings	3.5 cm	-	5 weeks	4.8	present work
50°C	resin 3	castings	3.0 cm	-	5 weeks	5.6	present work
50°C	resin 4	castings	3.3 cm	-	5 weeks	12.7	present work
50°C	resin 5	castings	3.3 cm	-	5 weeks	9.0	present work
50°C	resin 6	castings	3.8 cm	-	5 weeks	7.4	present work
50°C	resin 1	chopped strand	3.0 cm	38.9	5 weeks	1.9	present work
50°C	resin 2	chopped strand	3.5 cm	31.4	5 weeks	3.8	present work

*polyester - unless otherwise stated

Table 25a (cont.)

TEMPERATURE	POLYMER*	REINFORCEMENT	THICKNESS	GLASS CONTENT % BY WEIGHT	EXPOSURE TIME	PERMEABILITY kg/m^{2}day/cm x 10^4	REFERENCE
50°C	resin 3	chopped strand	4.0 cm		5 weeks	3.8	present work
50°C	resin 4	chopped strand	3.3 cm	35.1	5 weeks	11.9	present work
50°C	resin 5	chopped strand	3.8 cm	30.7	5 weeks	4.0	present work
50°C	resin 6	chopped strand	3.7 cm	33.9	5 weeks	4.2	present work
50°C	resin 1	woven roving	4.1 cm	51.8	5 weeks	0.6	present work
50°C	resin 2	woven roving	3.8 cm	41.5	5 weeks	1.3	present work
50°C	resin 3	woven roving	3.4 cm	46.6	5 weeks	1.8	present work
50°C	resin 4	woven roving	3.4 cm	47.9	5 weeks	4.5	present work
50°C	resin 5	woven roving	3.0 cm		5 weeks	1.8	present work

*polyester - unless otherwise stated

Table 25b: Comparison of Results with other Published Data

TEMP.	POLYMER*	REINFORCMENT	THICKNESS	GLASS CONTENT % BY WEIGHT	EXPOSURE TIME	PERMEABILITY $kg/m^2 day/cm$	REFERENCE
100°C	general purpose	chopped strand laminate	1 cm	not given(but estimated to be 27)	1 week	192.0×10^{-3}	39
100°C	low acid isophthalic	chopped strand laminate	1 cm	not given(but estimated to be 27)	1 week	30.4×10^{-3}	39
100°C	bisphenol-A fumarate	chopped strand laminate	1 cm	not given(but estimated to be 27)	1 week	3.6×10^{-3}	39
100°C	bisphenol-A fumarate	casting	1 cm	-	12 weeks	8.6×10^{-3}	39
100°C	bisphenol-A fumarate	surface mat	1 cm	10	12 weeks	7.4×10^{-3}	39
100°C	bisphenol-A fumarate	chopped strand	1 cm	27	12 weeks	5.9×10^{-3}	39
100°C at 20 atm	bisphenol-A fumarate	chopped strand	1 cm	not given(but estimated to be 27)	3 days	42.9×10^{-4}	85
50°C	epoxy resin	casting	0.0635 cm	-	-	1.5×10^{-6}	108
50°C	epoxy resin	glass beads filled	0.0635 cm	vol. fraction 0.1	-	1.2×10^{-6}	108
20°C	alkyd resin	film	not known	-	-	6.72×10^{-6}	89
20°C	epoxy resin	film	not known	-	-	2.9×10^{-6}	89
20°C	chlorinated rubber	film	not known	-	-	2.3×10^{-6}	89
20°C	chlorinated rubber with plasticizer	film	not known	-	-	0.6×10^{-6}	89

*polyester - unless otherwise stated

4.2 DEPENDENCE OF PERMEABILITY ON DIFFUSION AND SOLUBILITY

When studying the permeability of liquid water through castings and laminates it is important to note that the permeability of a resin or a laminate is not a fundamental property, but a composite quantity governed by both the diffusion coefficient and the solubility of the water in the polymers.

If the diffusion coefficient is independent of concentration and Henry's Law holds, it can be deduced from Fick's Law that:

$$P = DS \quad \ldots\ldots\ldots\ldots\ldots\quad [16]$$

where P is the permeability coefficient, D the diffusion coefficient and S the solubility coefficient.

It has already been demonstrated that this equation is valid only if there is no interaction between the polyester film and the penetrant is absent (30 - 32). Present investigation shows that equation [16] does not apply to the systems employed here.

Table 26: Dependence of P, D and S on the Resin Composition

RESIN	PERMEABILITY COEFFICIENT (P) kg/m^{2}day/cm x 10^4	DIFFUSION COEFFICIENT (D) cm^2/day x 10^3	SOLUBILITY COEFFICIENT (S) g/cm^3 x 10^3	DS kg/m^{2}day/cm x 10^4
Resin 1	5.87	6.06	14.77	8.95
Resin 2	4.76	3.22	24.20	7.79
Resin 3	5.61	2.77	30.00	8.31
Resin 4	12.74	5.60	61.20	34.42
Resin 5	8.95	8.86	30.00	26.58
Resin 6	7.39	11.11	101.20	112.43

It is obvious that each water-polymer system has its own permeability characteristic. Among the water-polymer systems given in table 26, the diffusion coefficient either increased or decreased with solubility without any obvious trend.

In hydrophilic polymers, such as polyester resins, the diffusion coefficient and the solubility vary with the affinity of the material for water. For polyester resins, it appears reasonable to distinguish between two forms of water, which may be regarded as 'mobile' (or free) and 'immobile' (or bound) fractions. It is assumed that at all times local equilibrium exist throughout the membrane between these two forms.

If other factors are the same, the more hydrophilic the resin, the higher the number of water molecules sorbed. If diffusion coefficient is concentration dependent, it will vary with varying concentration of free water molecules (15, 80). The more hydrophilic the resin, the higher the number of bound water molecules and lower the number of free water molecules. This should result in a decrease in the diffusion coefficient with increasing concentration of water in the polymer.

However, the calculated values of D and S clearly show that this is not the case (table 27).

Table 27: Chemical Constituents of Resins and their D and S

RESIN	ESTER GROUPS /100 ATOMS	ETHER GROUPS /100 ATOMS	PENDANT OH GROUPS /100 ATOMS	AROMATIC GROUPS /100 ATOMS	PENDANT CH_3 GROUPS /100 ATOMS	ATOMS BET. CROSS-LINKS	DIFF. COEFF. (D) IN cm^2/DAY x 10^3	SOL. COEFF. (S) IN g/cm^3 $x10^3$
Resin 1	3.85	11.54	7.69	11.54	15.39	52	6.06	14.77
Resin 2	19.05	4.76	-	4.76	4.76	21	3.22	24.20
Resin 3	22.22	-	-	5.56	11.11	18	2.77	30.00
Resin 4	16.67	8.33	-	5.56	-	36	5.60	61.20
Resin 5	24.24	-	-	3.03	12.12	11	8.86	30.00
Resin 6	-	-	-	-	-	-	11.11	101.20

There are three important variables which may interfere with the study of the relationship between D and S. They are:

1. The percentage free volume
2. Physical defects, such as voids and cracks
3. Percentage weight of leachable material

To eliminate these three considerations, a particular resin (resin 2), which shows no physical damage by water, was investigated in order to determine the relationship between diffusion coefficient and solubility coefficient. The resin was modified by the addition of low molecular weight material (propylene glycol/maleate) in quantities up to 15% w/w. As the proportion of low molecular weight substance increases, the concentration of water in the polymer increases. At the same time the diffusion coefficient decreases (table 28).

Table 28: Effect of Adding Low Molecular Weight Materials ON P, D AND S

QUANTITY OF LOW MOLECULAR WEIGHT RESIN ADDED % w/w	P kg/m^2 day/cm×10^4	D cm^2/day×10^3	S g/cm^3×10^3
0	4.76	3.22	24.2
2	5.09	2.63	26.62
15	6.81	1.59	45.32

The addition of low molecular weight substance alters the number of end groups and the concentration of hydrophilic groups present within the material. Therefore, the introduction of more polar groups increases the proportion of bound water present, hence reducing D.

4.3 THE OBSERVED EFFECT OF RESIN COMPOSITION ON THE PERMEABILITY IN THE FIRST 100 HOURS

4.3.1 Effect of Saturated/Unsaturated Acid Ratio

Any change in the size or the number of groups along the polyester chain would influence the path of water to the hydrophilic sites. For example, the use of saturated acid in increasing quantities has decreased the permeation rate of water by up to nearly 38% (table 29).

Table 29: Comparison of Resin 3 and Resin 5

RESIN	MOLAR % OF COMPONENT PRESENT			PERMEATION RATE $kg/m^2day/cm \times 10^4$	ABSORPTION % w/w
	IPA	MA	PG		
Resin 3	25	25	50	5.61	2.5
Resin 5	12.5	37.5	50	8.95	2.5

One of the reasons for this is that a cast resin with a higher degree of crosslinking exhibits higher water sorption because of lack of hydrophobic aromatic ring, which contributes towards steric hindrance to water transmission.

4.3.2 Effect of Glycols

Boenig (1) observed that the chain length of the glycol affects the water absorption in both rigid and flexible castings. In a series of tests conducted with a casting containing a constant saturated/unsaturated acid ratio of unity and a styrene content of 33% by weight, he noted that substitution of propylene glycol by diethylene glycol caused an increase in water absorption from 0.8 to 2.6%. This was attributed to the increased flexibility of the casting caused by the ether linkage in the glycol and the increased hydrophilicity due to the polarity of the ether oxygen. A similar behaviour was reported by Parker and Moffett (5) from their study of water absorption by polyesters.

The results obtained in the present study for water permeation show that the permeation rate of water through castings made from resin 2, which contain propylene glycol and diethylene glycol in equal molar proportions, is less than that observed for resin 3, which has propylene glycol only. A similar pattern was observed in the sorption of water in these resins (table 30). The reason for this is not immediately clear, but may lie in either the weight of leachable uncrosslinked material present in the casting and/or in microvoids caused by water sorption and leaching. This will be discussed in subsequent sections.

Table 30: Comparison of Resin 2 and Resin 3

RESIN	MOLAR % OF COMPONENT PRESENT				PERMEATION RATE kg/m^{2}day/cm $\times 10^4$	ABSORPTION % w/w
	IPA	MA	PG	DEG		
Resin 2	25	25	25	25	4.76	2.0
Resin 3	25	25	50		5.61	2.5

4.3.3 The Extent of Crosslinking

The extent of crosslinking of a polyester resin is, in practice, incomplete because some reactive groups will still be present in the resin. Other reactive groups, with which these might form crosslinks, are unable to react because of steric effects. Mohr and Oleesley (6) reported experimental evidence regarding the amount of residual unsaturation present at various stages of curing polyester resins. They reported that what may be considered, in practice, as an optimum cure (i.e. with maximum development of a range of physical properties) occurs when 92 - 95% of the unsaturation has been converted. They found that neither extra catalyst nor post-curing would produce further reaction.

Boenig in his conclusion agrees with Mohr and Oleesley in saying that under normal curing conditions general purpose polyester, that contains about two moles of styrene monomer per mole of fumarate unsaturation, has 95% of all the unsaturation, both styrene and fumarate reacted.

When water molecules first diffuse into the polyester castings, leaching of monomers starts almost simultaneously. Initially, the leaching process is diffusion rate controlled and it is likely that during this initial period, the majority of the low molecular weight materials is removed.

Both these processes would facilitate movement of polymer chains and affect crosslinking of unreacted active sites. This may result in further crosslinking, which may cause the polymer network to become more compact. This could lead to some of the unbound species and the sorbed water molecules being eliminated from the matrix. This would result in a change in rate of water transmission through the castings and laminates.

The final crosslinking probably restricts the movement of leachable materials in the network, thereby temporarily reducing the rate of removal of monomers by leaching.

These two processes, taking place in the initial stage of permeation, probably explain the characteristic "humps" observed in water permeation and absorption curves shown in figs. 29 and 50.

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4.3.4 Effect of Resin Composition on Hydrolysis

In the presence of water at temperatures higher than ambient, scission of polyester chains can occur by hydrolysis (reverse esterification), thus producing leachable low molecular weight chains.

It has been suggested (58) that, when a casting becomes saturated with boiling water, a hydrolysis reaction begins, so producing low molecular weight breakdown products. This is not detectable in the present investigation, where samples are exposed to water at 50°C. If water degrades cured polyester resins by hydrolysis at this temperature, then the total weight of leached products will increase with time. The results obtained in the present study, however, show that the weight of leached materials from a resin matrix remains constant within the limits of experimental error (fig. 51). The results of an analysis of the extracts of powdered castings with D_2O and $CDCl_3$ are given in table 31.

Table 31: Analysis of the Extracts of Powdered Castings with D_2O and $CDCl_3$

RESIN	MOLAR WEIGHT RATIOS OF COMPONENTS PRESENT IN THE EXTRACT		
	EXTRACT WITH WATER	EXTRACT WITH D_2O	EXTRACT WITH $CDCl_3$
2	Too dilute to measure	IPA : MA : BPG :BDEG:UBPG:UBDEG 1.85:0.65:1.80:1.80:1.67: 1.36	IPA :MA: BPG :BDEG:UBPG:UBDEG 1.77:00:1.30:1.75:1.15: 1.15
3	Too dilute to measure	IPA : MA : BPG :UPBG 2.20:0.25:4.50:5.00	IPA : MA : BPG :UBPG 2.17:0.75:4.10:4.30
4	IPA : MA :BDEG:UBDEG: PG 4.33:0.40:0.95: 3.99 :3.10	IPA : MA :BDEG:UBDEG: PG 1.00:0.00:0.97: 0.90 :0.15	IPA :MA:BDEG:UBDEG: PG 0.50:00:0.10: 0.00 :0.00
5	Too dilute to measure	IPA : MA : BPG :UBPG 1.60:2.40:4.20:7.30	IPA : MA : BPG :UBPG 1.70:1.60:3.60:1.00

IPA = isophthalic acid; MA = maleic anhydride; BPG = bound propylene glycol;

BDEG = bound diethylene glycol; PG = propylene glycol; DEG = diethylene glycol

Analysis of the extracts of powdered castings with D_2O and $CDCl_3$ show that there are products due to hydrolysis present in the extract with D_2O. This suggests that hydrolysis does take place in the polymer network in the presence of water. However, the extent to which the hydrolysis reaction occurs at 50°C may be very small, so as not to make any significant change in the water transmission rate.

4.3.5 Influence of Unreacted Low Molecular Weight Materials

Before crosslinking, the polyester has a distribution of molecular weights and contains low molecular weight fraction. Many of these molecules are saturated, and hence do not become part of the crosslinked network, formed by subsequent reaction with styrene.

The data for water absorption and leaching of low molecular weight substances for various resins are given in table 32.

When samples of cast resins were exposed to water at 50°C, absorption into the casting and leaching of monomers from the polymer took place simultaneously.

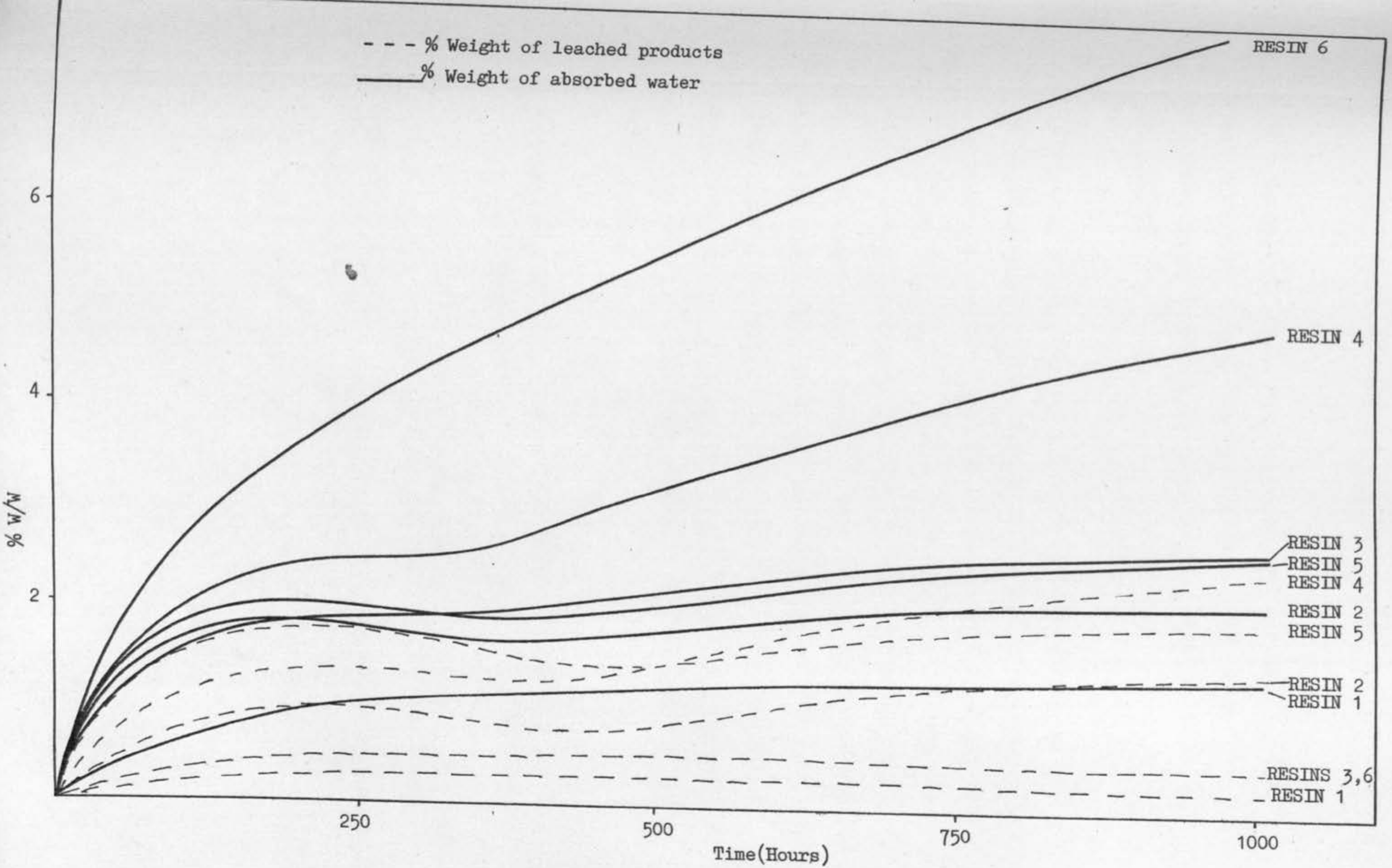
Table 32: Percentage Weight of Water Absorbed and Leached Materials by Castings after Equilibrium during Immersion at 50°C

RESIN	MOLAR % OF COMPONENT PRESENT				ABSORPTION % w/w	LEACHING % w/w
Resin 1	vinylester				1.3	0.3
	IPA	: MA	: PG	: DEG		
Resin 2	25	25	25	25	2.0	1.6
Resin 3	25	25	50	0	2.5	0.6
Resin 4	33.3	16.7	0	50	5.1	2.7
Resin 5	12.5	37.5	50	0	2.5	2.1
Resin 6	bisphenol				8.8	0.5

Experiments have shown that the weight of water absorbed by a cast resin is proportional to the weight of leached materials from the resin (fig. overleaf).

The percentage weight of leachable material present in a cast resin is one of the factors determining the weight of water sorbed by the resin at equilibrium sorption and hence the permeability, because the water molecules occupy the sapce left by the unreacted materials.

The exceptions to this general behaviour were found to be in two cases (e.g. resins 4 and 6). Here, the castings developed extensive damage, which resulted in large proportions of water being absorbed. The damage observed in resin 6 was on the surface of the casting, The surface was probably under cured, and the semi cured surface layers would consist



Comparison of water absorption and leaching for resins of a large percentage of hydroxyl and carbonyl groups and more free volume than the bulk of the material. This in turn would accommodate a high percentage of water molecules.

In view of this, the effect of molecular weight distribution on permeability of castings to water was determined. Resin 2 was modified by the addition of low molecular weight material (propylene glycol/maleate) in quantities up to 25% w/w. As can be seen from table 33, the castings based on polyester with the lowest proportion of the low molecular weight resin have the lowest permeability and absorption. With increasing proportion of lower molecular weight resins, the permeability of the castings increases steadily. Absorption of water into the polymer follows a similar pattern (table 33).

Table 33: Effect of Low Molecular Weight Resin on Permeability, Water Absorption and Leaching of Low Molecular Weight Materials

QUANTITY OF LOW MOLECULAR WEIGHT RESIN ADDED % w/w	PERMEABILITY kg/m^{2}day/cm x 10^4	ABSORPTION % w/w	LEACHING % w/w
0	4.76	2.0	1.5
2	5.10	2.2	0.9
15	6.81	3.6	0.8
25	-	4.4	0.7

On the other hand, the percentage weight of leachable materials decreases with increasing proportion of the low molecular weight resin. This indicates that the percentage weight of unreacted materials, though contributing to water permeation and absorption, is not the major contributory factor. Other factors, such as the number of polar groups present, % free volume and the number and distribution of voids and cracks within the matrix, also influence water transmission.

4.4 LONG TERM EFFECTS

4.4.1 Observed Long Term Permeation Rates

As described in the earlier section, permeability of a polymer to water depends on the chemical components which make up the polymer chains and the crosslink density of the polymer network. The presence of water in the material in turn affects the physical and chemical nature of the resin matrix by causing hydrolysis, leaching of the polymer chains, swelling and cracking of the resin. Therefore, the percentage of water present in a cast resin depends not only on the various chemical components in the casting, but also on the physical and chemical changes which are induced by water.

Hence, the dependence of the permeability of a cured resin cannot be discussed in terms of either the chemical components in the resin or the physical state of the material alone, but in relation to each other.

4.4.2 Comparison of Resin Characteristics

The permeabilities of castings, chopped strand and woven roving laminates have been denoted by symbols P_c, P_s and P_w. The number in the subscript corresponds to the resin number.

i) Resins 2 and 3

If P_{c2} and P_{c3} were to be compared, we would expect $P_{c2} > P_{c3}$. This is because the glycol used in resin 2 increases the water absorption from 0.25% to 2.6%. However, experimental results showed that $P_{c3} > P_{c2}$ (table 26).

Visual examination by transmission and electron microscope revealed that castings made from resin 3 showed void-like cavities extending from the surface into the bulk material after exposure to water (plates 1 and 2, table 34). On the other hand, castings made from resin 2 contain no cracks at all, even after 2000 hours of exposure.

Table 34: Permeabilities and Damage Observed in Resins when Exposed to Water at 50°C

RESIN	MOLAR % OF COMPONENTS PRESENT IPA : FA : PG : DEG	PERMEATION RATE kg/m^{2}day/cm x10^4	DAMAGE OBSERVED
2	25 25 25 25	4.76	None
3	25 25 50	5.61	Surface Damage

Electron micrograph

PLATE 1
Exposed Surface of Resin 3 after 7 Days, x 100

PLATE 2
Exposed Surface of Resin 2 after 12 Weeks, x 100

Absorption tests showed that the percentage weight of water absorbed by resin 3 was greater than that for resin 2 (table 35). Furthermore, the percentage weight of materials leached out from resin 3 was much less than that observed for resin 2. These results, together with the microscopic evidence, suggest that the main factor contributing to the high value of permeability for resin 3 is the development of microvoids.

ii) Resin 3 and 5

Comparing the crosslink densities of resins 3 and 5, resin 5 has a higher ratio of unsaturated to saturated acid than resin 3. Thus, it was expected that absorption of water, and therefore the permeability of castings made from resin 5 to water, would be greater than that of castings made from resin 3 (1, 5). Results obtained showed that $P_{c5} > P_{c3}$ (table 29).

iii) Effect of Acid Values

Assessing the effect of low molecular weight polymer additive on the permeability of resin 2, it was found that an increase in the acid value of the resin increased the permeability and the water absorption (table 33 and fig. 48).

However, the quantity of leachable material decreased. There may be two possible reasons for this:

1. The low molecular weight unsaturated additive added might have reacted with the low molcular weight fraction in the original resin, thus reducing the proportion of leachable low molecular weight substance present.

2. Because of the addition of low molecular substance, there is a large number of hydroxyl groups present. The bound water in the polymer may have reduced the quantity of materials leached out.

4.4.3 Microscopic Examination of Specimens

Visual examination of a large number of specimens of various cast resins showed that damage caused by water can be classified into two kinds:

1. Internal cracking, which may take the form of isolated disc-shaped cracks or, in cases of more advanced damage, intersecting internal crack configurations.

2. The development of opacity during exposure to water.

1. Disc Cracking

Considering the first mode of cracking, these cracks were found only in castings made from resin 4. The cracks were randomly orientated and there were no examples where they had a preferred orientation parallel to the specimen's plate surface (plate 3). This suggests that mechanisms must exist whereby diffused water can generate pockets of pressure within the resin. Such a theory is further substantiated by the fact that, in advanced cases, internal cracks close to, and parallel to, the external surface had produced blisters on the surface (plate 4). After an extensive investigation, Ashbee et al. (58) concluded that disc cracking was initiated at sites of soluble inclusions in the resin, and that the

Optical Microscope

PLATE 3
Exposed Casting of Resin 4, x 100

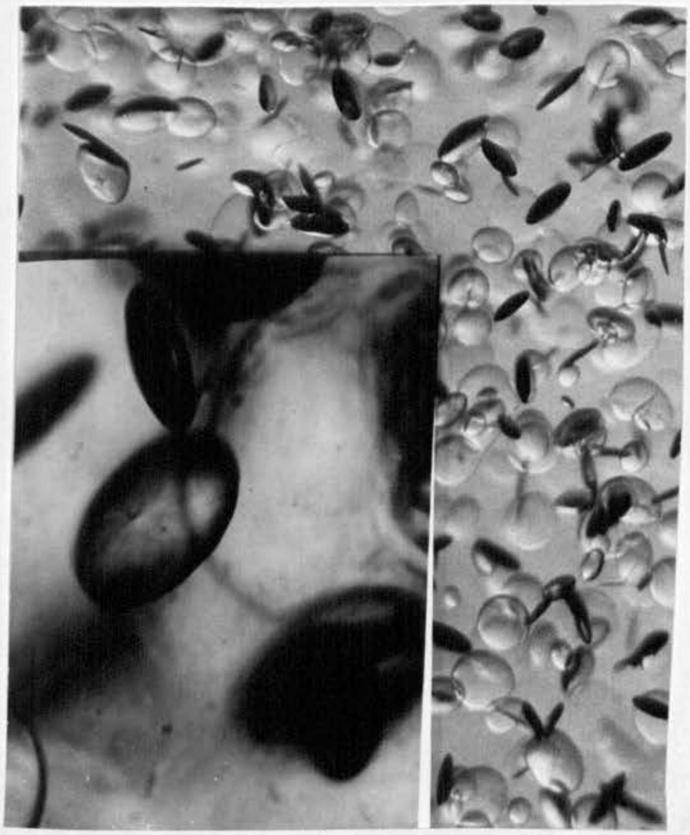


PLATE 4
Exposed Surface of Resin 4, x 1000

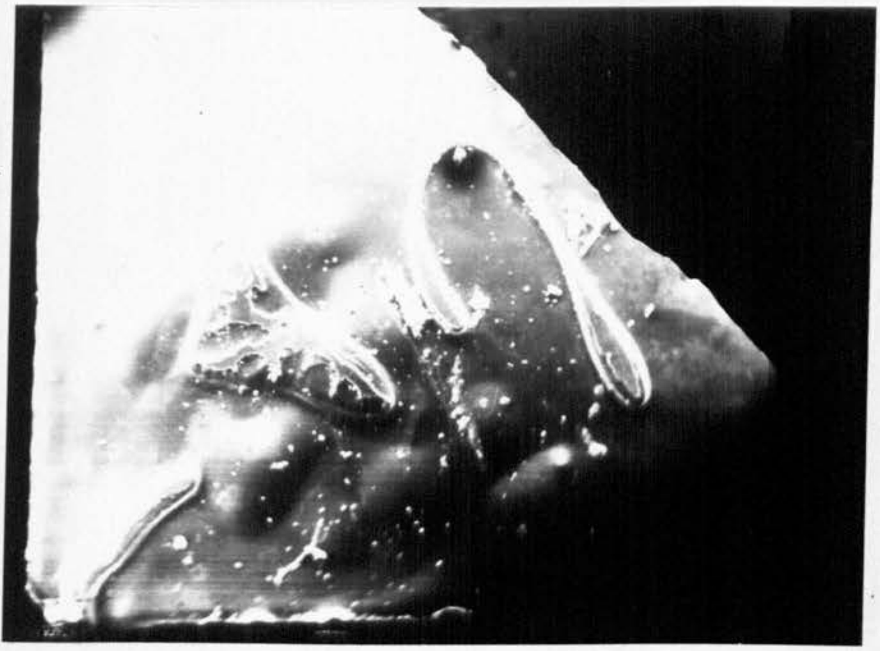


PLATE 5
Disc Crack in Resin 4, x 1000

cracks were formed by osmotic pressure created by the solution of these impurities.

110 120

Steel (ref. 113, 114) also noted the onset of small disc cracks in polyester resins when exposed to water at temperatures above 40°C. He related this phenomenon to localised swelling, glass transition temperature, degree of cure and a critical level of water absorption. He noted that the activation energy of the process (100 kJ/mole) was similar to that required for hydrolysis of the ester linkage.

The findings from the present study show that, when specimens are exposed to water at 50°C, the following facts emerge:

i) Disc cracking occurs only in cured resins with a very low degree of crosslinking (e.g. resin 4). However, when samples of other resins were exposed to water at higher temperatures, onset of disc cracking was observed at 70°C for resin 2, 80°C for resin 5 and at 100°C for resin 1.

This seems to follow the theory put forward by Steel that disc cracking is associated with some peak level of water absorption. If the equilibrium value of water absorption exceeds the critical level of water absorption for a particular resin, the formation of disc cracks occurs.

ii) During the drying out process, after exposure to water, some of the internal disc cracks slowly fade, until finally no traces can be seen by the optical microscope.

However, in the advanced stage, disc cracks will not fade away as easily as in the early stages of disc cracking, but remain in that form, even after prolonged periods of drying. This suggests that, once the advanced stage of cracking has been reached, at best only part of the damage is reversible and the rest is permanent.

iii) In the final stages of the drying out process, examination of the cracks under an electron microscope shows little sign of any deposit left behind on the crack site (plate 5). However, the number of samples examined under the electron microscope were limited because of the difficulty in sample preparation. Further examination is needed to confirm any impurities present.

2. Surface Damage

Some of the castings used in the absorption tests, developed an opacity on being exposed to water. The rate of development of the opacity was rapid for those resins with a high degree of air inhibition on the surface. In extreme cases the opacity took the form of a gelatinous layer on the outer surface of the castings. Plates 6 - 10 show the opaque white surface layers on castings made from different resins.

When samples were immersed in water the opacity on the surfaces of the castings made from resins 3, 5 and 6 can be observed after 100 - 150 hours of exposure; while castings made from resins 1 and 2 showed little sign of opacity, even after 2000 hours in water. On drying, however, these opaque layers slowly disappear.

In the case of extensive opacity, the layers remain unaltered, even after prolonged drying.

Plates 11 - 15 show photographs of the opaque layer of resin 5 while examining under transmission microscope. The structure of the surface layer resembles that of a foam rubber with numerous interconnecting holes. It is a very much more open structure at the surface (with very large void-like cavities) than in the interior of the layer.

PLATE 6
Exposed Surface of Resin 2 after 12 Weeks, x 1000

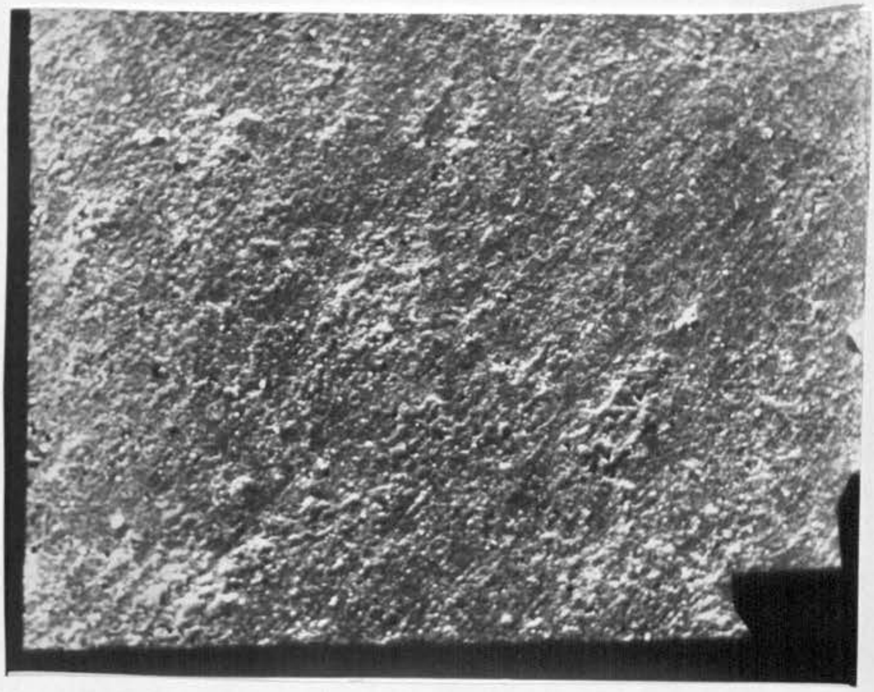


PLATE 7
Exposed Surface of Resin 3 after 12 Weeks, x 1000

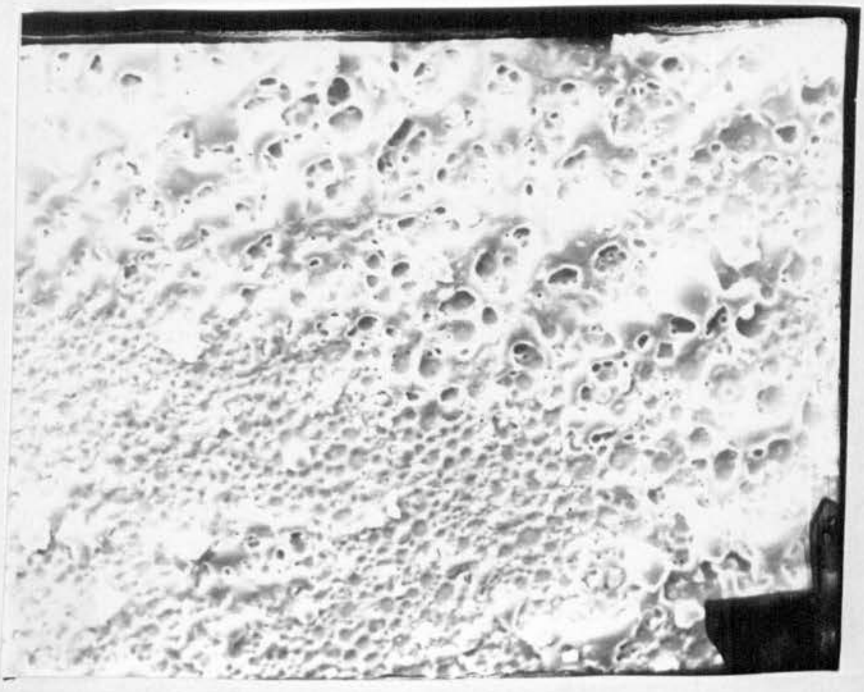


PLATE 8
Exposed Surface of Resin 4 after 12 Weeks, x 1000

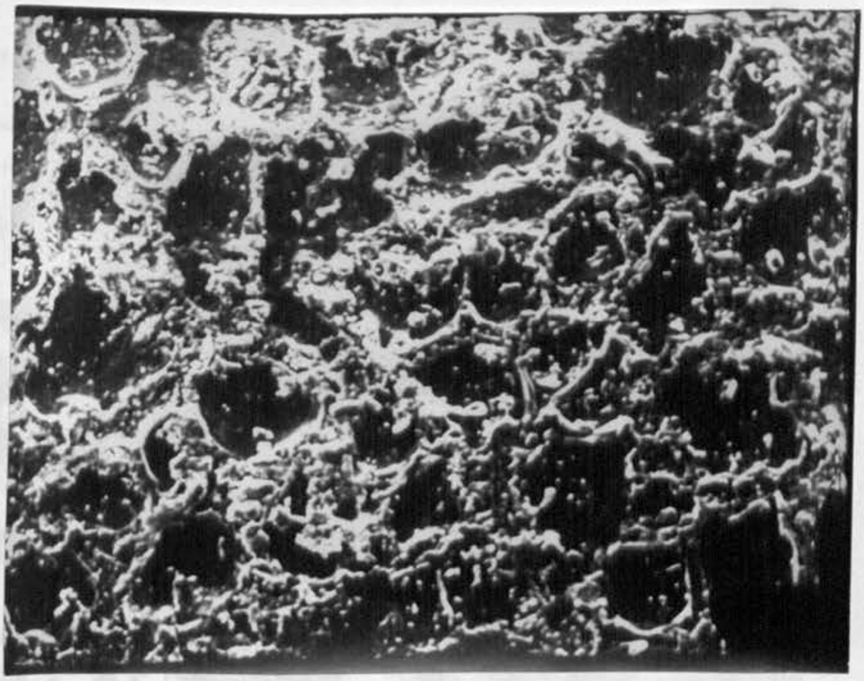


PLATE 9
Exposed Surface of Resin 5 after 12 Weeks, x 1000

PLATE 10
Exposed Surface of Resin 6 after 12 Weeks, x 1000

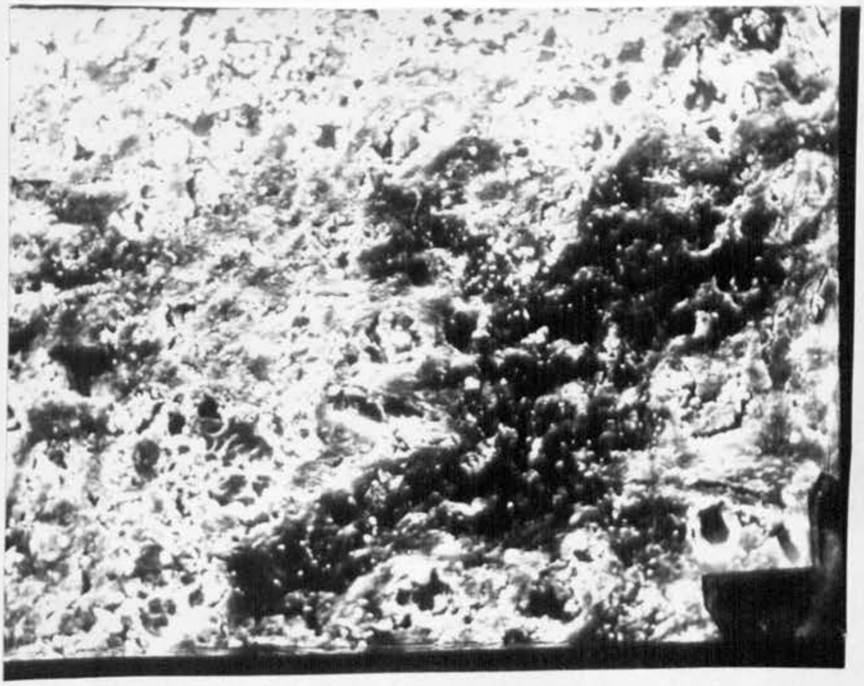


PLATE 11
Unexposed Samples of Resin 5
1.9K, x 5,700

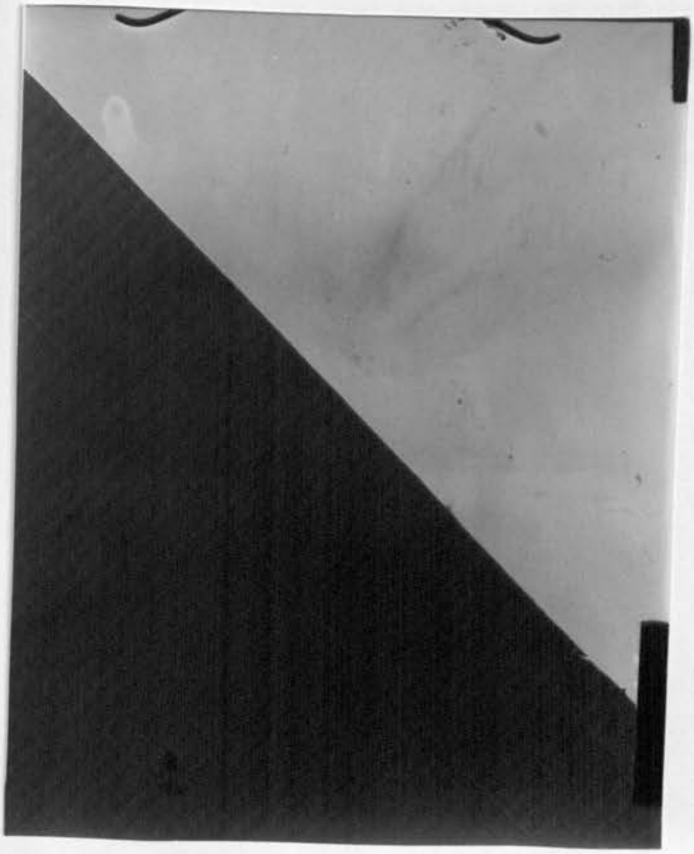


PLATE 12
Sample of Resin 5 Exposed to
Water for 10 Days
1.9K. x 5,700

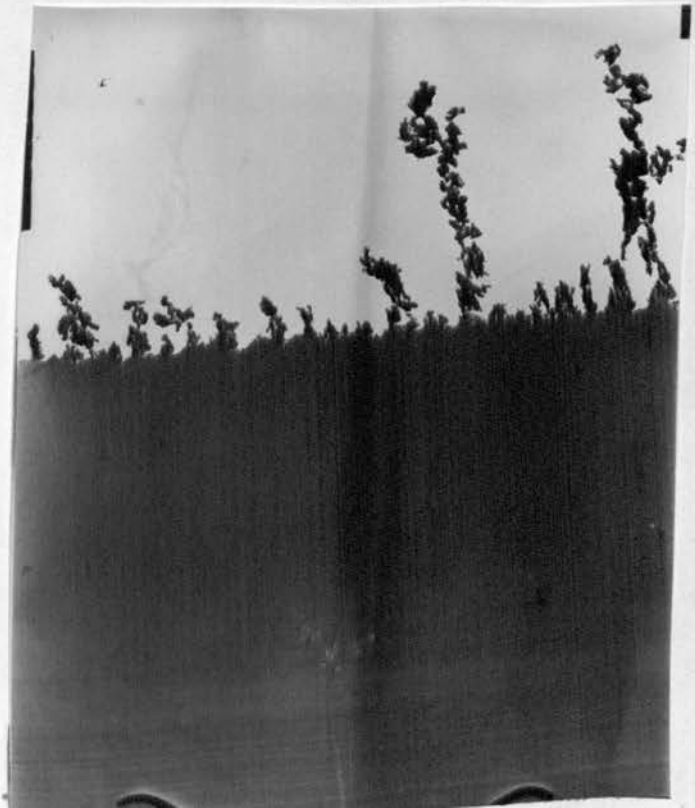


PLATE 13
Sample of Resin 5 Exposed to
Water for 10 Days
1.9K, x 17,100

PLATE 14
Sample of Resin 5 Exposed to
Water for 10 Days
19K, x 57,000

PLATE 15
Sample of Resin 5 Exposed to
Water for 10 Days
19K, x 51,000

The damage from the surface layer extends into the resin bulk to a depth of about 10 - 100 micro metres.

This type of opacity was observed by Rosen (72) and Pantony (81). Pantony observed the opaque layer in laminates immersed in water, and suggested that this was due to hydrolysis and leaching of polymer molecules from the surface. Rosen, on the other hand (72), attributed the opacity to microfracture formation in the resin, and clustering of water molecules about polar sites in polymers, in voids or cracks in the resins.

Polyester resins contain polar groups, so there is the possibility of water clustering occurring about sites such as hydroxyl and carbonyl groups. Also, undercured surface layers would contain a large percentage of these groups and more free volume than the bulk of the material to accommodate high proportion of water molecules. If the opacity is due to water molecules present on the casting surface and causing light scattering, on drying, the opacity should be reversible.

This is so for castings made from resins 3 and 5 exposed up to 170 hours. However, castings exposed to longer periods retained their opacity, even after prolonged drying.

This suggests that the opacity found in castings exposed to water may be due to two factors:

1. The large number of water molecules sorbed in the undercured layer reflect and scatter the light entering the samples.
2. In severe cases, the undercured surfaces may contain not only numerous water molecules, but also voids and holes, therefore leaving a permanent opacity on the surface.

4.4.4 Immersion of Resin in Water

i) Weight Changes

Table 35 and fig. 49 show the change in weight observed when cast resin films were totally immersed in water at 50°C. These results show the net change in weight of the specimens due to the combined effect of water sorption and leaching of unreacted low molecular weight materials from the films.

It is usual to associate change in weight of the specimens with water absorption by the material. This was found not to be true for all the resins studied in the present investigation. This is because there is a certain loss of leachable materials from all resins. The higher the proportion of leachable material present, the higher the degree of error in estimating the weight of water aborbed (table 35).

Table 35: Dependence of Change in Weight of Resins on Absorption and Leaching when Samples were Immersed in Water at 50°C

RESIN	CHANGE IN WEIGHT % w/w	ABSORPTION % w/w	LEACHING % w/w
Resin 1	1.10	1.3	0.30
Resin 2	0.60	2.0	1.60
Resin 3	2.00	2.5	0.60
Resin 4	2.50	5.1	2.70
Resin 5	0.30	2.5	2.10
Resin 6	8.25	8.75	0.50

ii) Water Absorbed

The percentage weights of water sorbed by castings made from six different resins when they were totally exposed to water at 50°C are given in table 35 and table 49 fig 50. These results indicate that there is an initial increase in weight in all polyester resins. The extent of water absorption is governed by:

a) The chemical constituents present in the original resin
b) The crosslink density of the cast resin
c) Voids and cracks developed during curing of the resins

Subsequently, the sorbed water molecules cause further chemical and physical changes in the castings which result in more water being sorbed into the polymers.

The mechanism by which the polymers are attacked by water is not immediately obvious, but the following effects may be suspected:

a) Further postcuring
b) Leaching of non-bound materials
c) Ester hydrolysis
d) Development of microdamage

To check these possibilities, a number of tests were carried out. The possibility of ester hydrolysis was discussed in section 4.3.4. In essence, though there is some hydrolysis of esters by water taking place, the extent to which it is carried out is very small. It is because in total immersion tests, the % weight of leachable materials remains constant once equilibrium is reached (fig. 51). With the findings that further cross-linking has little effect on absorption (section 4.3.3) tentatively, it seems therefore that (b) and (d) are the main processes.

iii) Linear Dimensions

The changes in linear dimensions of the films immersed in water at 50°C were measured. The method of measurement was described in section 2.5.

The measurements of the changes in linear dimensions were carried out on films when they were removed from the bath and after drying. The presence of water in cured polyester resins causes swelling. The degree of swelling depends on the weight of uncrosslinked materials leached out and degree of crosslinking.

However, the change in dimension caused by leaching of low molecular weight materials showed little difference between the exposed and unexposed samples (table 22). p. 123 The dimensional changes taking place when samples were immersed in water may be in the direction perpendicular to the plane of the large surfaces. Thus, the changes observed along the planes of the large surfaces show little or no variation.

4.5 EFFECT OF APPLIED STRAIN ON THE PERMEABILITY OF CAST RESIN SHEETS

Studies of the effect of applied strain on the permeabilities of castings were carried out for a single resin (resin 2). The castings, when subjected to an increase of applied strain from zero to 0.4%, showed a gradual increase in permeability (table 36).

Table 36: Effect of Applied Strain on the Permeability of Resin 2 at 50°C

STRAIN %	PERMEABILITY P kg/m^{2}day/cm 10^4
0.0	4.76
0.2	5.44
0.4	8.47

Possible causes of the change in the permeability of castings with increased strain are:

1. The development of crazing or submicroscopic defects, which would probably be permanent, although perhaps capable of limited closing-up after relaxation of stress.
2. Some local molecular orientation, which would be temporary.
3. Scission of a proportion of the network segment, which would be permanent.

4.6 THE PERMEABILITY OF GLASS/RESIN LAMINATES

4.6.1 Consequence of Water in Glass Laminates

Water has severe effects on the mechanical properties of glass reinforced laminates. The transmission of water through laminates may produce certain visual effects. These include resin blistering, surface crazing of variable severity, fibre prominence and fibre "whitening" below the surface (40, 41).

The degradation is a complex phenomenon in that it is a function of both physical and chemical mechanisms. The possible causes of material failure are:

1. Weakening of glass fibres
2. Degradation of resin matrix
3. Debonding of the fibres from the resin matrix

The corrosion of glass by water has not been a subject of investigation in the present work, but the importance of resin deterioration has been discussed in section 4.3. The glass/resin interfacial region is important since the behaviour of this determines the efficiency with which stress is transferred from the glass to resin and vice versa.

4.6.2 Effect of Water on the Glass-Resin Bond

Stress can be transferred efficiently across an interface between the glass and the resin matrix only if the two are in intimate molecular contact, i.e. an adhesive bond exists between the components so that no relative motion is possible between fibre and resin. If this bond is destroyed, either by the action of water or by mechanical means, the maximum interface stress is likely to be less than that when an adhesive bond was present, and hence the ability to transfer load will be reduced. Water at high temperatures is known to break the bond between resin and fibres (41).

Visual and microscopic evidence derived from this present investigation shows that:

a. Some debonding was evident, even before exposure, caused by insufficient wetting and voids running along the length of the fibres
b. No further debonding occurred in the first 72 hours
c. Debonding of fibres was evident after the first 100 hours
d. Microscopic examination revealed that there is some debonding of fibres on the surface (plate 16). The formation of fibre prominence under the gel coat was also observed (plate 17).

PLATE 16
Debonding of Fibres, x 1000

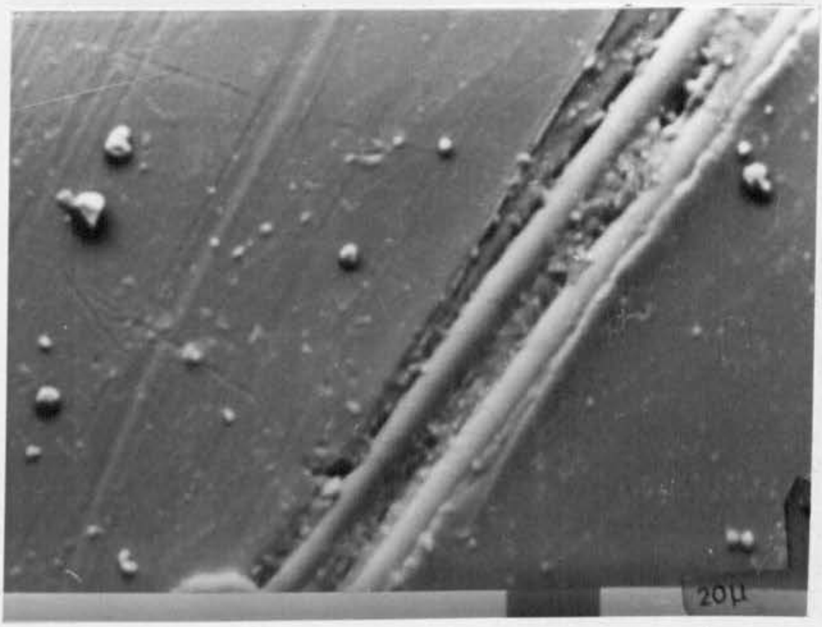
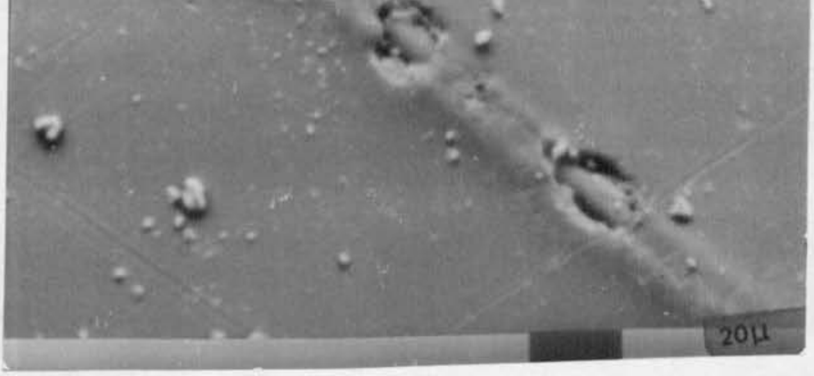


PLATE 17
Fibre Prominence under Gel Coat, x 1000



e. Signs of resin blistering were observed on the surface (plate 18)

f. The most serious debonding was found beneath the surface that was exposed to water. This becomes more prominent when the laminates were dried after exposure. In severe cases, this was accompanied by surface cracking (plate 19).

James et. al. (121) have studied the effect of boiling water on the interfacial region of a glass fibre embedded in a thin film of polyester resin. They showed that the time for maximum swelling of the resin to occur when immersed in water at 100°C coincided with the onset of debonding in a single fibre composite under same condition.

The effect of debonding on permeation was considered by studying a deliberately debonded sheet. In this case, the permeation rate nearly doubled for laminates with debonded fibres (table 37).

PLATE 18
Resin Blister, x 1000

PLATE 19
Surface Cracking

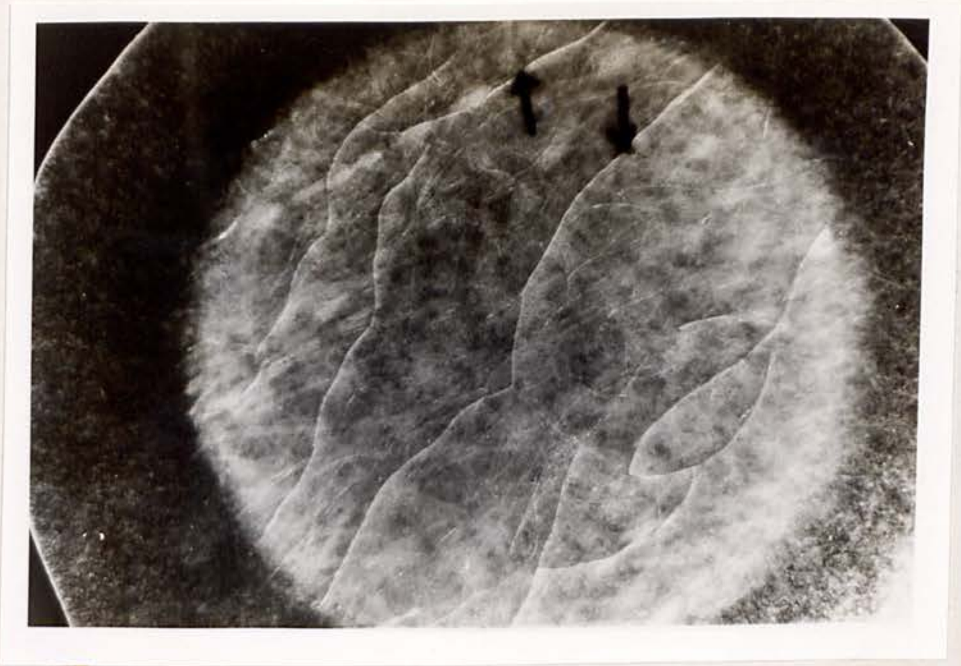


Table 37: Effect of Debonding of Permeability

MATERIAL	GLASS CONTENT	PERMEABILITY kg/m^{2}day/cm 10^4
Casting	0	5.61
Laminate (Resin 3 - woven roving)	46.6	1.76
Laminate (Resin 3 - woven roving with complete debonding)	47.4	2.95

4.6.3 Short and Long Term Transmission Rates

Results obtained for permeabilities of laminates and castings are tabulated in table 38. It is clear that the permeability of a laminate decreases steadily as the volume fraction of the fibres increases. This is found to be true with all laminates, whatever the resin matrix. However, the consistent decrease in permeability of a laminate with increase in glass fibre content, varies somewhat from resin to resin.

It should be noted that the action of water on resins, the thermal expansion of the resins and the changes in properties of the fibre-resin interface, all depend on resin structure. This in turn affects the permeability of laminates to water.

For example, when resin 1 was reinforced with chopped-strand glass mats, the permeability was reduced by 68% (table 38). A further reduction of 68% was observed when resin 1 was reinforced with woven roving mats. Similar behaviour was found with resin 5.

On the other hand, resins 2 and 3 behaved differently, showing only about 20% reduction in permeability when reinforced with chopped-strand mats. The introduction of woven roving reinforcement, however, reduced the permeability by a further 60%.

Table 38: Effect of Glass Content and Orientation on the Permeability

RESIN	TYPE OF SAMPLE	VOL. FRACTION OF GLASS %	PERMEABILITY $kg/m^2day/cm \times 10^4$
1	Casting	0	5.87
	Chopped strand laminate	22.0	1.85
	Woven roving laminate	32.2	0.58
2	Casting	0	4.76
	Chopped strand laminate	17.8	3.77
	Woven roving laminate	21.1	2.29
3	Casting	0	5.61
	Chopped strand laminate	16.8	3.81
	Woven roving laminate	29.3	1.76
4	Casting	0	12.74
	Chopped strand laminate	20.4	11.93
	Woven roving laminate	30.4	4.50
5	Casting	0	8.95
	Chopped strand laminate	17.3	4.07
	Woven roving laminate	31.2	1.80
6	Casting	0	7.39
	Chopped strand laminate	14.9	4.20

4.6.4 Glass Fibre Volume Fraction

The permeability of water through laminates is much more complex than through castings. Water often has appreciable solubility in the polymers so that the polymer becomes swollen. Also, water attacks glass-fibres and the interface.

In addition, the coefficients of thermal expansion of glass and resin differ vastly. The possibility of developing a quantitative theory for the permeability of such systems seems very remote, since there are too many factors that have to be considered. However, some general observations on the permeabilities of cured resins and laminates with varying glass contents could be used to obtain empirical formulae which might fit the conditions applied in the present investigation.

The rigorous mathematics for the steady state diffusion problems for a laminate are not readily derivable. Yet an approximate relationship between the effective permeability constant of the laminate and permeability constants and volume fractions of the individual phases can be derived.

If the fibres are assumed to be impermeable to water molecules, the path for the molecules travelling through a laminate becomes longer, because the diffusing molecules must go around the fibres. In addition to the tortuosity factor, permeability is cut down further, because not all of a given cross-section of a laminate is pure polymer.

Nielsen (89) gives a simple relationship:

$$\frac{P}{Pr} = \frac{Vr}{1 + \left(\frac{L}{2W}\right) Vf}$$

Where P and Pr are the permeabilities of the laminates and resins respectively, Vr and Vf are the volume fractions of resins and fibres in the composite, and L and W are the length and width of the fibres. From the results (table 38), the effect observed suggests that a portion of the matrix is effectively immobilised in the presence of the fibres and made relatively impermeable to water. Such a conclusion is quite consistent with the conclusions of Kumins and Poteman and Kwei that a matrix can undergo some kind of ordering and immobilisation when reinforced, even with low surface area fillers.

If it is assumed for simplicity that the ordered layer is quite impermeable to water and the "effective" volume fraction of fibre corresponding to the observed decrease in permeability is calculated, at least 12% of the resin appears to be immobilised, except in a special case, where there was no resin immobilisation found. These figures differ from those reported by Kwei and Kumins, but the phenomenon of ordering appears to be confirmed. Substituting the results obtained in the present investigation into the expression derived by Nielsen, the observed values are far higher than those predicted.

While the ratio L/2W seems to be satisfactory for fillers with aspect ratio not greater than 100, the results obtained in the present study proved it to be unsatisfactory. Therefore, in choosing a constant for the present system, there are two important considerations to be given to the system. They are:

1. The arrangement of the fibres

2. The nature of the polymer

4.6.5 Reinforcement Type

Results from table 39 show that the permeabilities of chopped strand laminates made from a very highly cross-linked resin (resin 5) show a maximum difference between calculated and observed values. As the degree of cross-linking in the resins decreases, the gap between the calculated and observed values narrows until finally the observed value of the permeability of chopped strand laminates made from resin 4 exceeds the calculated value. It is remarkable that the observed permeabilities of laminates should even be equal to the calculated value (because all laminates made by the hand lay up process always contain voids and dry areas).

Therefore, there must be another factor which contributes to lowering of permeability in laminates besides volume fraction of the fibres. Comparing the results in table 39 obtained for the permeabilities of chopped strand and woven roving laminates respectively, it is reasonable to attribute the lowering of the observed permeabilities in woven roving laminates to fibre orientation and fibre length.

This suggests that fibre orientation not only helps compact packing of the fibres, but reduces permeability considerably.

Table 39: Observed and Calculated Permeabilities

RESIN	TYPE OF MATERIAL	Vf %	$\left(\frac{Pf}{Pu}\right)$ % OBSERVED	$\left(\frac{Pf}{Pu}\right)$ % CALCULATED
1	Casting			
	Chopped strand laminate	22.0	31.5	78.0
	Woven roving laminate	32.2	9.88	67.8
2	Casting			
	Chopped strand laminate	17.8	79.2	82.2
	Woven roving laminate	21.1	48.1	78.9
3	Casting			
	Chopped strand laminate	16.8	67.9	83.2
	Woven roving laminate	29.3	31.4	70.7
	Woven roving laminate (debonded)	29.8	52.6	70.2
4	Casting			
	Chopped strand laminate	20.4	93.6	79.4
	Woven roving laminate	30.4	35.3	69.6
5	Casting			
	Chopped strand laminate	17.3	45.5	82.7
	Woven roving laminate	31.2	20.1	68.8
6	Casting			
	Chopped strand laminate	14.9	56.8	85.1

4.7 EFFECT OF APPLIED STRAIN ON THE PERMEABILITY OF LAMINATES

Transmission of water through laminates is a complex process by itself. When another factor, such as applied strain, is introduced, it becomes very difficult to predict the transport behaviour of the penetrant through the laminates.

Taneja (40) studied the effect of applied strain on casting and laminates made from resin 5. He reported an increase in permeability of chopped strand laminates with strain at various temperatures. He explained that the increase was due to debonding of fibres from the resin and cracks developed in the material.

It was found that the permeability of castings made from resin 2 increases with increasing applied strain. This is probably because of the flaws developing in the resin. Similarly, laminates, when subjected to applied strain, should develop debonding of fibres and cracks in the resin matrix. This in turn results in higher permeability.

However, the permeability of chopped strand laminates made from resin 2 was found to decrease at a very low applied strain of 0.2%. Further increase in the strain increased the permeability. Woven roving laminates on the other hand produced a small increase in permeability at 0.2% applied strain.

The reason for this is not clear, but may lie in a number of factors. With brittle resin laminates, application of external strain may result in debonding of fibres and resin cracking. Laminates made from a more flexible resin may be able to withstand a low level of applied strain before the onset of debonding and resin cracking. Immobilisation of polymer chain segments is evident when resins are reinforced with fibres. This effect becomes pronounced in resins with high degrees of crosslinking (table 39).

Probably, the high degree of immobility of chain segments in brittle resin laminates gives rise to resin cracking and, therefore, increase in permeability. With a moderately crosslinked resin, low level of applied strain probably increases the degree of immobilisation of chain segments, thereby reducing the permeability. However, if the strain level is increased, permeability increases with strain. Higher strains may induce flaws which result in higher permeability.

CONCLUSIONS

The influence of composition of resins and laminates on their permeability to water has been investigated.

Some of the factors which affect the permeability of water through the resins have been studied. They include ratio of saturated to unsaturated acids, molecular weight distribution, changes resulting from the presence of water in the resin and the effect of reinforcement and applied strain.

A minimum value of permeability was measured in a resin which contained saturated acid and unsaturated acid in equal molar ratio. Resins with higher or lower ratios exhibited higher permeabilities.

The presence of a low molecular weight "tail" in the molecular weight distribution causes an increase in permeability. The presence of water in a resin causes resin swelling, hydrolysis, leaching of uncrosslinked materials and crack formation in the resin. This leads to increased water absorption and further damage within the resin.

The relationship between permeability, diffusivity and solubility was found not to obey Henry's Law. As the solubility of a resin increases, the diffusivity decreases.

As the thickness of castings decreases, the permeability rises sharply and therefore cannot be described by the usual inverse law. However, it is proposed that normalisation to standard thickness would be acceptable, if all samples lie within a rather closely defined thickness band and the samples are not too thin.

The permeability of chopped strand laminate is greater than that of woven roving laminate. The observed values of permeability were always less than those calculated for laminates. The effect becomes more pronounced in resins with increasing crosslink density. This supports the hypothesis that there is an immobilisation of a proportion of the polymer chains when reinforced with even fillers with large surface areas.

Permeability of castings increases with increasing applied strain. The gradual increase in permeability with increasing strain appears to have been caused by microvoids and chain scission in the resin. The permeability of chopped strand laminates made from a moderately crosslinked resin was found to decrease at 0.2% strain. Further increase in applied strain increased permeability. Woven roving laminates showed a small increase in peremability at 0.2% strain.

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